PLATINUM AND TITANIUM METALLOCYCLES

by

Joseph Xavier McDermott

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Signature of Author.. .....

Certified by.. .....
Thesis Supervisor

Accepted by..... .....
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Professor Jack E. Baldwin.. Chairman

Professor George Whitesides. Thesis Supervisor

Professor Alan Davison.....

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ABSTRACT

Part I

The thermal decomposition of several metallocyclic complexes of the type $L_2Pt(CH_2)_n$, L = phosphine, n = 4, 5, was examined. Those decompositions proved to be more than 10^4 slower than those for acyclic analogs. Product analysis and deuterium labelling studies suggest that the platinocycles decompose by the same metal-hydride elimination found for the acyclic dialkyls. The difference in stability reflects the less conformationally mobile cyclic species' greater difficulty in achieving the configuration for β-hydride elimination. This results in a striking difference in detailed mechanism. Added triphenyl phosphine accelerates the decomposition of the cyclic compounds and decelerates that of the acyclic. For L = n-Bu_3P, a more fundamental change in mechanism occurs. The course of decomposition of the dialkyls continues to be determined by β-hydride elimination. But the corresponding platinocycle (n = 4) releases cyclobutane as its principal thermolysis product.

Part II

Bis(cyclopentadienyl)tetramethylenetitanium (IV) was prepared at low temperature from titanocene dichloride and 1,4-dilithiobutane. In analogy to the platinum complexes, the titanocycle is more stable thermally than di-n-butyltitanocene. This difference is reflected in the chemistry of the metallocycle which thermolyzes to ethylene as well as the expected butene. It reacts with carbon monoxide to yield cyclopentanone, a carbonylation reaction not observed for the di-n-butyl complex. The decomposition of the

metallocycle to ethylene is partially reversible at low temperatures. Titanocene, generated from $(CpTiH)_x$ or by the reduction of Cp_2TiCl_2, reacts with ethylene and then carbon monoxide to give cyclopentanone. The reaction works better with the slightly strained olefin, norbornene. The analogous chemistry of zirconium was examined briefly.

Thesis Supervisor: George M. Whitesides

Title: Professor of Chemistry

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Particular thanks go to Professor Whitesides for guidance in my research efforts, for maintaining a highly varied and interesting research group, and for the valuable reminder that chemistry is a useful, as well as experimental science.

To the people, crazies, and unclassifiables of the GMW labs, I owe an unpayable debt for lightening the burden of spending four years in the MIT machine. Highest honors go to the Kaufman & Co. wrecking crew for explosions, fires, hall hockey, and other amusing diversions; to the members of the chemistry intramural teams for a lot of fun, if not a winning record; and to Harry and Nat for a good year at 181 Harvard Street.

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Table of Contents

	Page
Platinum and Titanium Metallocycles	
Introduction	12
Part I: The Thermal Decomposition of Platinum Metallocycles.	24
Introduction	24
Results and Discussion	28
Synthesis	28
Kinetics	30
Cyclobutane from a Platinocycle	51
Experimental	
General methods	52
Thermolysis reactions and kinetics	55
Thermal decomposition of 5 and 10	57
Thermal decomposition of 6, 7, 8, 11, and 12	57
Ethyllithium	58
Diethylbis(triphenylphosphine)platinum(II)	64
Preparation of platinocycles 6, 7, and 8	65
(Diphos)tetramethyleneplatinum(II), (12)	66
Hexane-2,5-di(magnesium bromide)	67
Bis(triphenylphosphine)-1,4-dimethylthyltetramethyleneplatinum(II), (11)	67
Bis(tri-n-butylphosphine)tetramethyleneplatinum (13)	68

Page

Bis(tri-n-butylphosphine)diethylplatinum(II) (14) 69

Bromobenzene-d_5 70

Phenyllithium-d_5 70

Triphenylphosphine-d_{30} 71

Part II: Synthesis and Reactions of Titanium Metallocycles

Introduction 72

Results 79

Experimental

General Methods 98

Bis(cyclopentadienyl)tetramethylenetitanium(IV) (15) 99

1,4-dilithiobutane and 1,5-dilithiopentane 101

Isolation of 19 in the carbonylation of 15 102

Reaction of 23 with ethylene 103

Reaction of 24 with ethylene 104

Reduction of Cp_2TiCl_2 in the presence of ethylene 104

Reduction of Cp_2TiCl_2 in the presence of ethylene 105
Stoichiometric reaction
Reaction with excess norbornene

Decomposition of 15 and 22 in tetrahydrofuran 107

Reaction of 16 with carbon monoxide 107

Bis(cyclopentadienyl)tetramethylenezirconium(IV) 108

Reductions of zirconocene dichloride 109

Page

Appendix I: The Thermal Decomposition of cis-dimethyl-bis(triphenylphosphine) platinum(II) and related compounds

Introduction 110

Results 113

Experimental

General methods 124

Dimethylbis(tri-n-butylphosphine)platinum (II) (1) 126

Dimethylbis(triphenylphosphine)platinum(II) (2) 127

Dimethylbis(para-t-butylphenyldiphenylphosphine)-platinum(II) (2t) 128

Dibenzylbis(triphenylphosphine)platinum(II) (3) 129

Dineopentylbis(triphenylphosphine)platinum (II) (5) 129

Di-p-methylbenzylbis(triphenylphosphine)-platinum(II) (3a) 131

Thermolysis of 2 in methylene chloride 131
Isolation of trans-chloro(methyl)bis(triphenylphosphine)platinum(II) (6)

Reaction of 2 with $(Ph_3P)_2PtI_2$ by nmr 132

Thermolysis of 2 by nmr 133

Diiodobis(triphenylphosphine)platinum(II) 133

Reaction of 2 with $(Ph_3P)_2PtCl_2$ 133

Methylene trapping by cyclohexene, norbornene, and 1-heptene 134

List of Figures

		Page
Part I:	The Thermal Decomposition of Platinum Metallocycles	
Figure I:	An Arrhenius plot of k for the thermal decomposition of 5 extrapolated to 120°	36
Figure II:	The thermal decomposition of 6 in the presence of $[Ph_3P]$= 0.0 (A), 0.003 (B), 0.007 (C), 0.026 (D), 0.13 (E), 0.26 (F).	38
Figure III:	The rate of decomposition of 6 and 8 vs. added triphenylphosphine	40
Figure IV:	The decomposition of 6: % 2-butene vs. the concentration of PPh_3	42
Figure V:	The thermal decomposition of 5 in methylene chloride at 50°	60

List of Schemes

		Page
Part I:	The Thermal Decomposition of Platinum Metallocycles	
Scheme I.	The Thermal Decomposition of 5.	26
Scheme II.	The proposed Thermolysis Mechanism of 6.	46
Part II:	Synthesis and Reactions of Titanium Metallocycles	
Scheme III.	Potential Reactions of Metallacyclopentanes.	73
Scheme IV.	Quenching of 15.	90
Scheme V.	Reactions of 1,7-octadiene and Titanocene.	94
Appendix I.	The Thermal Decomposition of Dimethylbis(triphenylphosphine)platinum(II) and Related Compounds.	
Scheme VI.	Thermolysis in Methylene Chloride.	115
Scheme VII.	Reaction of 2 with Methylene Chloride.	116
Scheme VIII.	Possible Thermolysis Pathways for 2.	119
Scheme IX.	Methylene Trapping with Olefins	123

List of Tables

Page

Part I: The Thermal Decomposition of Platinum Metallocycles

Table 1. Rates ($k \times 10^{-4}$ sec^{-1}) and Products of Thermal Decomposition of Platinum(II) Metallocycles in Methylene Chloride. 43

Table 2. Thermal Decomposition of 6. Comparison of HCl and Br_2 Quenches. 61

Table 3. Thermal Decomposition of 11. 62

Table 4. Thermal Decomposition of 12. 63

Appendix I: The Thermal Decompositions of Dimethylbis(triphenylphosphine)platinum(II) and Related Compounds.

Table 5. The Exchane Between 2 and L_2PtCl_2 at 120°. 117

Table 6. Thermolysis of 2 in Ch_2Cl_2 at 120°. 118

PLATINUM AND TITANIUM METALLOCYCLES

Introduction

A number of symmetry-forbidden reactions of strained hydrocarbons are catalyzed by transition metal compounds: for example, the valence isomerization of cubane to syntricyclooctadiene and of quadricyclene to norbornadiene can be metal catalyzed[1].

---

(1) H. Hogeveen and H.C. Volger, J. Amer. Chem. Soc., 89, 2486 (1967)

It has been suggested that a one-step transformation is made possible by a relaxation of the Woodward-Hoffman rules[2] within the coordination sphere of the metal[3,4].

---

(2) R.B. Woodward and R. Hoffman, Agnew. Chem. Inter. Ed., 8, 781 (1969)

(3) F.D. Mango, Adv. Catal., 19, 291 (1969); F.D. Mango, and J.H. Schachtschneider, J. Amer. Chem. Soc., 93, 1123 (1971)

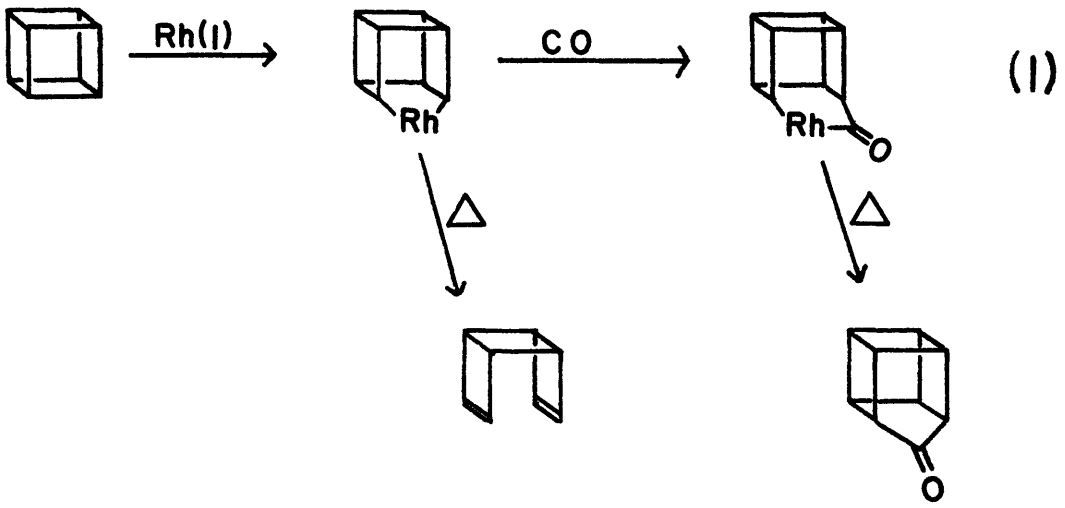
(4) R. Pettit, H. Sugahara, J. Wristers, W. Merk, Discuss. Faraday Soc., 47, 71 (1969)

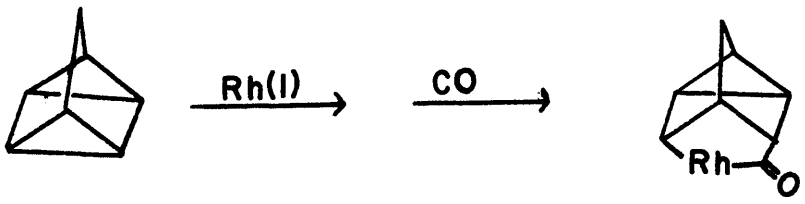
In transition metal catalyzed reactions for which mechanisms have been elucidated, however, bond reorganizations

usually involve a series of discrete intermediates. Thus it comes as no surprise that 1 has been detected[5] by careful experiments on valence isomerizations with $[Rh(diene)Cl]_2$. In particular the intermediate could be trapped with carbon monoxide[5]:

---

(5) L. Cassar, P.E. Eaton, and J. Halpern, J. Amer. Chem. Soc., 92, 3515 (1970)





The key step of these reactions is the oxidative insertion of Rh(I) into a strained carbon-carbon bond to produce a rhodium metallocycle. A reaction that is formally the reverse of the above is the dimerization of norbornadiene. This thermally forbidden [2+2] cycloaddition is facilitated by the presence of a variety of group VIII metal complexes[6].

(6) T.J. Katz and N. Acton, Tet. Let., 2601 (1967)

A detailed study[7] of the dimerization and

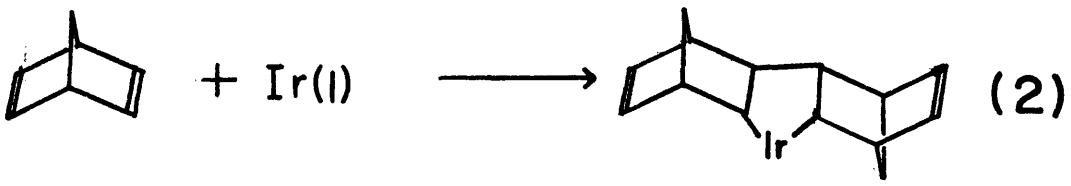
(7) N. Acton, R.J. Roth, T.J. Katz, J.K. Frank, C.A. Maier, and I.C. Paul, J. Amer. Chem. Soc., 94, 5446 (1972)

trimerization of norbornadiene by (diene)Ph_3PRhCl uncovered a complex array of products best rationalized as coming from a common intermediate rather than arising from an uninterrupted electrocyclic reaction. Indeed such an intermediate has been isolated[8] when an iridium catalyst was employed. As in the cycloreversion of cubane, a five-membered metal-

(8) A.R. Fraser, P.H. Bird, S. A. Bezman, J.R. Shapely, R. White, and J.A. Osborn, ibid., 95, 597 (1973)

locycle is involved, thus avoiding the forbidden [2+2]

process by way of an allowed [2+2+2] metallocycloaddition.



(2)

Similar mechanisms have been proposed for cycloadditions of methylenecyclopropane[9,10], and bycyclo[2.1.0] pentane[11] by nickel catalysts and as an initial step in the

---

(9) R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, ibid., 95, 1675 (1973)

(10) P. Binger, Angew. Chem. Inter. Ed., 11, 309 (1972)

(11) R. Noyori, Y. Kumagai, H. Takaya, J. Amer. Chem. Soc., 96, 634 (1974)

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the cyclooligimerization of allene[12].

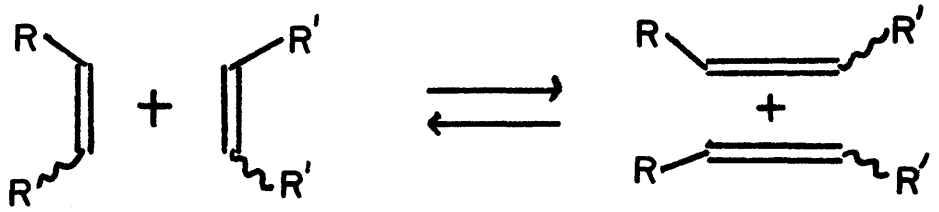
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(12) M. Englert, P.W. Jolly, and G. Wilke, Agnew. Chem. Inter. Ed., 11, 136 (1972)

Olefin metathesis[13] is related to these reactions

(13) N. Calderon, Acc. Chem. Res., 5, 127 (1972)

in that it formally involves a [2+2] process. The mechanism of this reaction is imperfectly understood. A quasi-cyclobutane intermediate



(or activated complex) has been proposed[14] as well as a

(14) C.P.C. Bradshaw, E.J. Howman, and L. Turner, J. Catal., 7, 269 (1967)

rather similar tetracarbenoid species[15]. Although not very

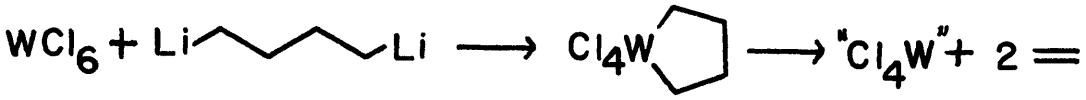
(15) G.S. Lewandos and R. Pettit, J. Amer. Chem. Soc., 93, 7088 (1971)

precisely defined, these proposals seem to involve another "no mechanism" reaction involving a nominally forbidden electrocyclic process.

Alternatively, we can suggest, in analogy to the transformations of strained carbocycles, the intervention of a metallocycle. The recent report of Grubbs and Brunck[16] strongly supports this view. They found a nearly quantita-

(16) R.H. Grubbs and T.K. Brunck, ibid., 94, 2540 (1972)

tive yield of ethylene upon reacting WCl_6 with 1,4-dilithiobutane. This result is particularly significant in view

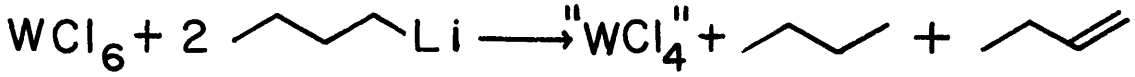


(3)

of the fact that WCl_6 is a well known source of metathesis catalysts and gives an active catalyst upon reaction with two equivalents of n-butyllithium[17] or n-butylmagnesium iodide[18]. Tungsten tetrachloride is itself a catalyst

(17) J.L. Wang and H.R. Menapace, J. Org. Chem., 33, 3794 (1968)

(18) T. Takagai, T. Hamaguchi, K. Fukuzumi, and M. Aayama, J. Chem. Soc. Chem. Comm., 838 (1972)



(4)

in the presence of $AlCl_3$[13].

It still remains to be established how the methylene groups are exchanged within the metallocycle. Metathesis could be effected by reversible conversion into a σ-cyclobutyl complex[19].

---

(19) This proposal by G.M. Whitesides is under investigation in this laboratory. See: P.E. Kendall, Ph.D. Thesis, M.I.T. (1972) and D. Feitler, Progress Report, for details.

Migration of the metal atom to the α-ring position by breaking the α C-C bond to give a metal carbene has been suggested by Grubbs[20]. Thus metathesis would simply involve

---

(20) C.G. Beifield, H.A. Eick, and R.H. Grubbs, Inorg. Chem., 12, 2166 (1973)

---

alternating and reversible fragmentation of the metallocycle

at the α and β C-C bonds. The β fragmentation has already been demonstrated[16].

The exchange of the carbene with the methylene moiety of another olefin is also possible. This exchange has been observed for electron rich olefins[21] and for a

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(21) D.J. Cardin, M.J. Doyle, and M.F. Lappert, J. Chem. Soc. Chem. Comm., 927 (1972)

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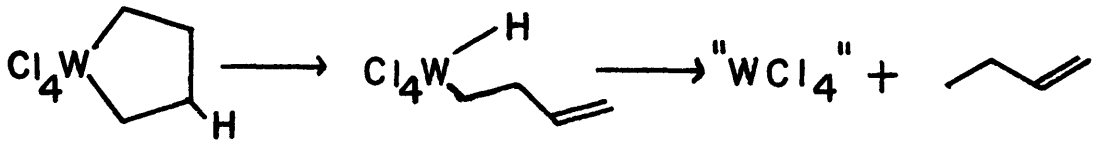
tungsten carbene[22,23].

---

(22) C.P. Casey, private communication.

(23) For a recent discussion of carbenes and metallocycles in metathesis see: D.J. Cardin, B. Catinkaya, M.J. Doyle, and M.F. Lappert, Chem. Soc. Rev., 2, 99 (1973)

Regardless of the details of olefin metathesis, the involvement of a species such as 3 in the process implies that metallocycles are capable of novel transformations. The metal promoted reactions of strained systems are an example of this effect. A particularly interesting feature of eq. 3 is that the fragmentation to ethylene requires that 3 be resistant to metal-hydride elimination (as in eq. 4) which would lead to 1-butene:



A dominant reaction of transition metal alkyls having β-hydrogens is the metal-hydride elimination. Frequently the stability of alkyl complexes is determined by the ease with which this step occurs[24,25]. The rate of elimination can be highly dependent on the structure of

---

(24) P.S. Braterman and R.J. Cross, Chem. Soc. Rev., 2, 271 (1973)

(25) Transition metal alkyls lacking β-hydrogens are usually more stable. For example see: M. Mowat, A. Shortland, G. Yagupsky, N.J. Hill, M. Yagupsky, and G. Wilkinson, J. Chem. Soc. Dalton., 533 (1972)

---

the alkyl group. The great stability of 1-norbornyl metal complexes[26] is not surprising since metal-hydride elimination

---

(26) B.K. Bower and H.G. Tenet, J. Amer. Chem. Soc., 94, 2512 (1972)

---

would lead to a bridgehead double bond. The commonly observed order of decomposition rates[27] - primary<secondary≤ tertiary - is reversed for the t-butyl group in the

crowded complexes tetrakis(t-butyl)chromium[28] and cyclopetadienyl(t-butyl)iron dicarbonyl[29], probably due

(27) J. Kochi and M. Tamura, J. Organomet. Chem., 29, 111 (1971)

(28) W. Kruse, ibid., 42, C39 (1972)

(29) W.P. Giering and M. Rosenblum, ibid., 25, C71 (1970)

to steric restrictions increasing the energy of the preferred transition state for β-hydride elimination.

Both the relative inaccessability of the transtion state and the formation of a high energy double bond account for the stability of σ-cyclopropyl complexes[30,31]. The same appears to be true of cyclobutyl metal complexes[32].

(30) A.Cutler, R.W. Fisk, W.P. Giering, and M. Rosenblum, J. Amer. Chem. Soc., 94, 4355 (1972)

(31) J.F. White, Ph.D. Thesis, MIT, Cambridge, Mass. (1972)

(32) W.P. Giering, private communication.

A small ring metallocycle lacks the conformational mobility of an acyclic alkyl. This limited mobility could lead to enhanced thermal stability and reactions other than metal-hydride elimination, for example eq. 3.

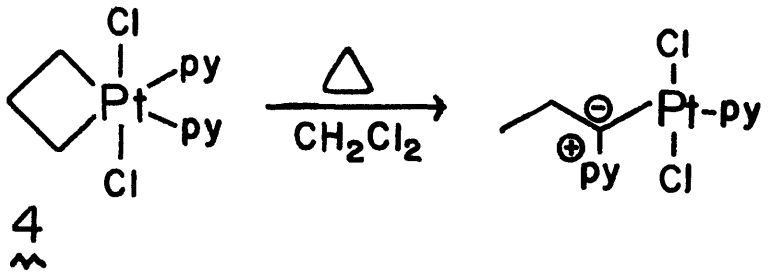
Support for this hypothesis comes from the only known platinocycles before the studies[31] in this laboratory were initiated. Compound 4 was prepared by the oxidative insertion of Pt(II) into cyclopropane[33]. This substance

(33) D.M. Adams, J. Chatt, R.G. Guy, and N. Sheppard, J. Chem. Soc., 738 (1961)

does not eliminate propene when heated[34] but instead under-

(34) R.D. Gillard, M. Keeton, R. Mason, M.F. Pilbrow, and D.R. Russell, J. Organomet. Chem., 33, 247 (1971)

goes an interesting rearrangement (eq. 5). A kinetic study



4

(5)

led the authors to propose a dipolar mechanism[35]. A

(35) R.D. Gillard and M.F. Pilbrow, J. Chem. Soc. Dalton., 102 (1973)

carbene mechanism should probably also be considered. In

any event the inhibition of β-hydride elimination enables an unusual reaction to take place.

In light of the increasing interest in metallocycles, a study was undertaken of five- and six-membered rings containing platinum and titanium[36]. Primary attention

---

(36) The reasons for choosing platinum and titanium will be made apparent in Parts I and II.

---

was focused on the following questions:

I) Do such species in general have greater stability than analogous acyclic dialkyls?

II) Is the stability due to inhibition of metal hydride elimination and does this lead to alternate modes of decomposition?

III) Can the reactions observed for strained carbocycles and olefins (eq. 1,2) be found for unactivated olefins? This could lead to new and useful synthetic reactions, as well as lend weight to the proposed intermediacy of metallocycles in olefin metathesis.

PART I

Thermal Decomposition of Platinum Metallocycles[37]

Introduction.

Until recently there has been virtually no study of saturated metallocycles. Chatt and coworkers first recognized that the reaction of cyclopropane with $PtCl_2$ involved insertion to form a platinocycle[33]. An "ate" complex formed by reaction of $CrCl_2$ with excess 1,4-dilithiobutane was shown by x-ray crystallography[38] to be a chromocycle dimer with a very short Cr-Cr bond.

---

(37) A part of this work has appeared in preliminary form: J.X. McDermott, J.F. White, and G.M. Whitesides, J. Amer. Chem. Soc., 95, 4451 (1973)

(38) J. Krausse and G. Schodl, J. Organomet. Chem., 27, 59 (1971)

Perfluorinated metallocycles have also been known for several years[39] as have polycyano-[40] and other exotic species.

---

(39) P.K. Maples, M. Green, and F.G.A. Stone, J. Chem. Soc. Dalton, 2069 (1973) and references therein.

(40) M. Lenarada, P. Ros, M. Grazani, and U. Belluco, J. Organomet. Chem., 46, C29 (1972)

All of these represent special cases which shed little light on saturated metallocycles as a class. The increasing evidence (see Introduction) of their involvement in catalytic processes and the possibility of synthetic applications, if such metallocyclic intermediates can be diverted to useful products, make them worthy of study in their own right.

The investigation[41] by Gaasch and Whitesides of di-n-butylbis(triphenylphosphine)platinum(II), 5, determined

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(41) G.M. Whitesides, J.F. Gaasch, and E.R. Stedronsky, J. Amer. Chem. Soc., 94, 5258 (1972)

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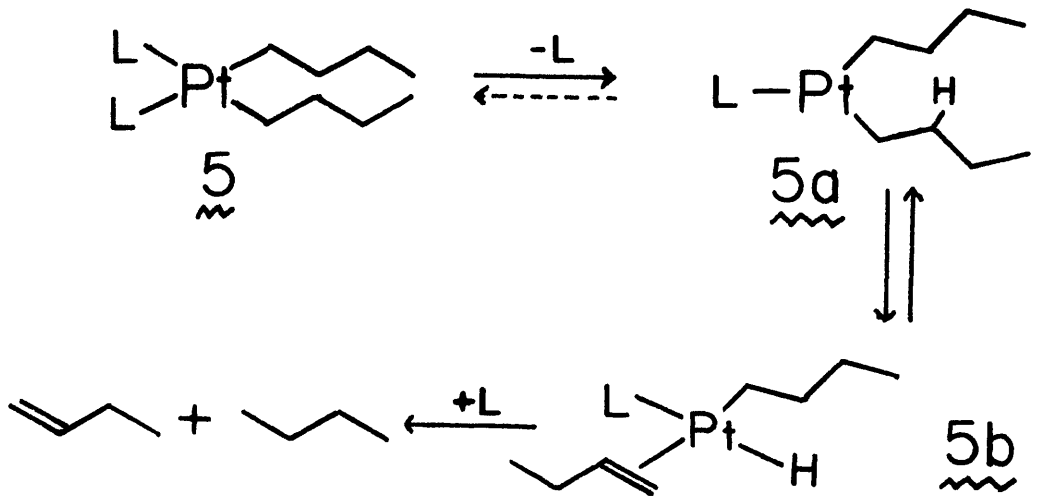
the mechanism of decomposition, Scheme I. Initially 5 loses Ph_3P[42] to give a three coordinate complex 5a which

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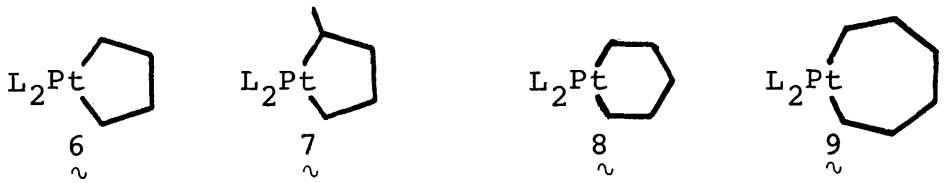
(42) This step appears to be rate determining, but is reversible in the presence of excess phosphine

---

Scheme I



reestablishes the preferred square planar geometry, 5b, by a hydride elimination before the ligand can return. This is followed by an irreversible reductive elimination of n-butane. The thermolysis of 5 became the starting and reference point for the work on platinum metallocycles. White[31] successfully prepared the series of compounds 6, 7, 8, and 9, for L = Ph_3P.



The products of thermal decomposition were the corresponding alkenes, probably indicating a mechanism

involving Pt-H elimination. The striking feature of the results was the stability of 6, 7, and 8 compared to 5 which decomposes at 60° in methylene chloride with a half life of 0.5 hour. The platinocycles did not decompose at a similar rate until a temperature of 120°C was reached. On the other hand, the larger ring, 9, was about as stable as 5. Thus the resistance of 6, 7, and 8 to thermolysis must be attributed to the limited conformational mobility of the five and six membered rings. It was felt that these compounds were worthy of a more detailed investigation.

Results and Discussion

Synthesis. The platinum alkyl complexes employed in this study could all be synthesised by a previously developed[31,43] proceedure. This involved dialkylation of dichloro (cyclooctadiene) platinum (II), $CODPtCl_2$, by a

(43) C.R. Kistner, J.H. Hutchinson, J.R. Doyle, and J.C. Storlie, Inorg. Chem., 2, 1255 (1963)

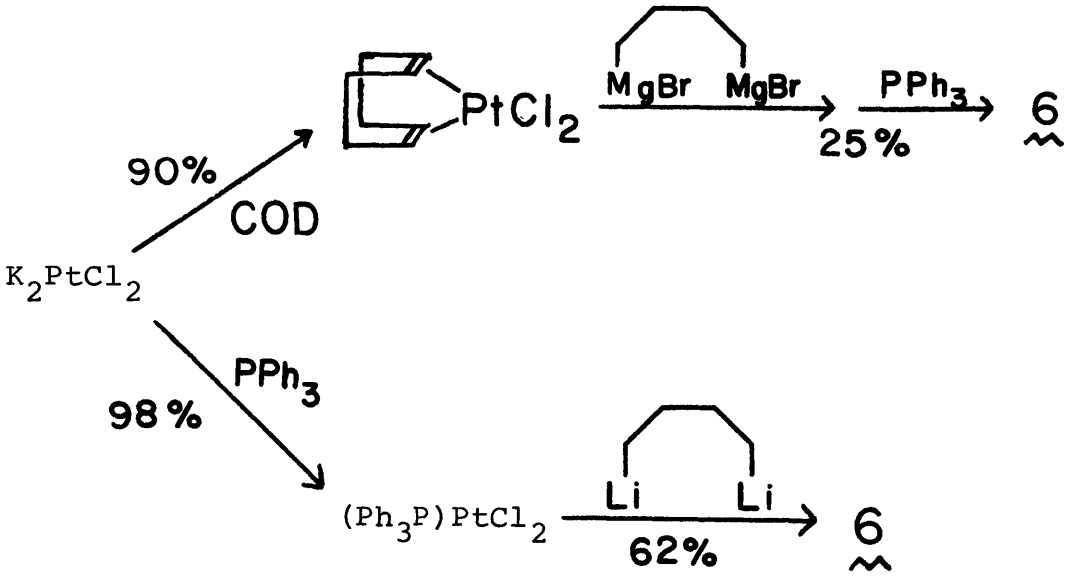
Grignard reagent, followed by displacement of the olefin with phosphine. For the metallocycles this approach suffers from the instability of the intermediate cyclooctadiene complex and the relative insolubility of the di-Grignard reagent in the reaction medium (primarily ethyl ether). Also a column chromatographic purification at 0° is required before reaction with the phosphine[31].

Some bis (phosphine) platinum dialkyls have been prepared[44] by direct reaction of bis (phosphine) platinum

(44) e.g., J. Chatt and B.L. Shaw, J. Chem. Soc., 5075 (1962): J. Chatt and B.L. Shaw, J. Chem. Soc., 1718 (1960)

dichloride with an alkyllithium reagent. Reaction of bis (triphenylphosphine) platinum dichloride with n-butyl-

lithium gives 5 in good yield[41]. The same dichloride was successfully reacted with 1,4-dilithiobutane and 1,5-dilithiopentane to give 6 and 8 in 60-70% yield after recrystallization.



This represents an overall yield of 60% from postassium tetrachloroplatinite compared to 25% for the $(COD)PtCl_2$ proceedure. Further the need for column chromatography is eliminated. The appropriate lithium reagent however is not always readily available. For instance, to prepare 7, one would need 1,4-dilithiopentane which is insoluble in hydrocarbon solvents and unstable in ethyl ether and therefore inconvenient to use.

In practice 6 and 8 were prepared by this method

since 1,4-dilithiobutane and 1,5-dilithiopentane are moderately stable in ethyl ether solution. Compounds 7 and 11 (Table 1) were synthesised from the Grignard reagent and $(COD)PtCl_2$.

Kinetics. White listed[31,45] some preliminary rate data which established the exceptional stability of 6, 7, and 8. But the thermal decomposition proved to be more complex kinetically than was indicated by these early results. Fully reproducible rates depended upon sufficiently purifying the solvent (including a spinning band distillation[46]) and taking extreme care to avoid sample pyrolysis during the sealing of the evacuated tubes.

(45) See White[31] for non-kinetic details of the thermolysis of 6, 7, 8, and 9 including product distributions.

(46) One effect of the spinning band distillation is to rid the methylene chloride of a small amount of chloroform.

When the above precautions had been taken lower initial rates of decomposition were observed for 6 and 8, followed (at approx. 30% decomposition) by a substantial increase in reaction velocity. The thermolysis of 6 at 0.025M is illustrated in Figure II both with and without

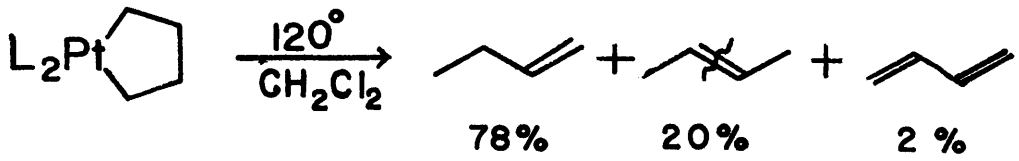
added triphenyl phosphine. The measured initial rate constant was $5.4 \times 10^{-5} sec^{-1}$. When the concentration was lowered to 0.12M a value of 5.1×10^{-5} sec^{-1} was found. As a further check on the meaningfulness of the kinetics, the reaction was followed by bromine quenching rather than the usual quench with concentrated hydrochloric acid.[47] By the bromine analysis, $k = 5.7 \times 10^{-5}$ sec^{-1}. Thus the

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(47) Details of the analytical proceedures are to be found in references 31, 41, and the experimental section of this thesis.

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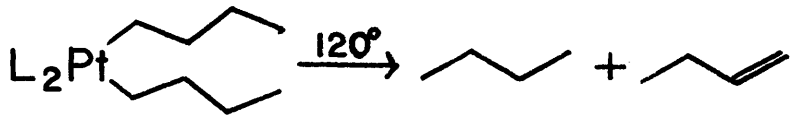
initial rate is reproducible within experimental error (± 6%) and first order for the reaction:



The thermolysis of 5 is strictly first order throughout. The reported[41] rate constant at 60° is 3.6×10^{-4} sec^{-1}. The stability of 6 was compared to that of 5 by determining k for 5 at 120°. This comparison could not be carried out directly, but 5 gave a good Arrhenius plot over the range 50°-70°[48] which could be extrapolated

(48) The value for k determined in this work was 4.1×10^{-4} sec^{-1} at 60°. The difference between this and Gaasch's value probably reflects the use of uncalibrated thermometers. A temperature difference of 0.3°C could cause the discrepancy. The same thermometer was employed throughout the present study to maintain internal consistency.

tc 120°, Figure I. At 120°, 5 decomposes 17,000



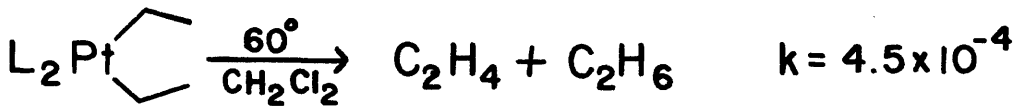
$k_1 = 9.1 \times 10^{-1}\ sec^{-1}$

times faster than 6.

The first order kinetics for 6 hold only during 30% of the reaction. At that point acceleration of the thermolysis is observed. The onset and degree of acceleration were not fully reproducible and no attempt was made at an exact kinetic analysis. An illustration of the effect is found in Figure II, which is a first order plot of % 6 remaining vs. time. Note that added triphenylphosphine increases the rate of decomposition. Above 0.1 M it also largely suppresses the deviation from first order behavior. The effect of added triphenylphosphine on the initial rate can be seen in Figure III. The initial rates have been plotted vs. added phosphine concentration. In the presence

of triphenylphosphine, 6 decomposes by competitive first and second order mechanisms. The overall rate can be expressed as $k = k_1 + k_2[Ph_3P]$, $k_2 = 2.8 \times 10^{-2}\ M^{-1}\ sec^{-1}$. The products of the phosphine assisted mechanism are also butenes. The amount of 2-butene declines with increasing phosphine concentration, Figure IV.

The most striking feature of the effect of triphenylphosphine is that it accelerates the thermolysis of 6 and retards that of 5. Unlike 5, preliminary phosphine dissociation is not important for 6. The steric bulk of the n-butyl groups is appreciably greater than that of tetramethylene. To determine if steric effects were significant the decomposition of diethylbis(triphenylphosphine)platinum (II), 10, was examined. The kinetics were strictly first order with essentially the same rate as 5. The thermolysis of the di-n-octyl complex[41] also occurs at 60° with a half life.

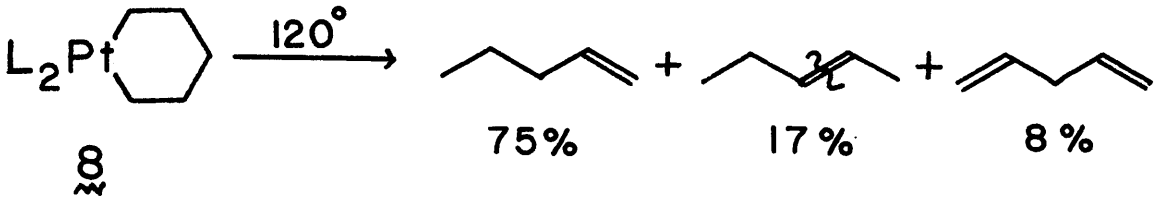


10

similar to 5 and 10. It can be safely concluded that steric interactions between alkyl and phosphine are not an important

factor in determining the stability difference between 5 and 6. The stability of 6 is an inherent property of the platinocylic ring.

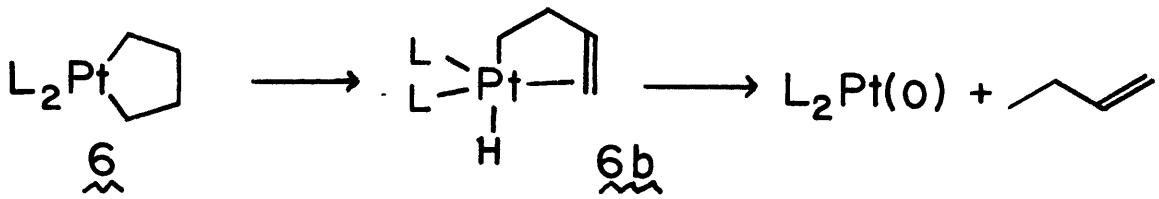
Compound 8 displays the same resistance to thermal decomposition with $k_1 = 4.0 \times 10^{-5}$ sec^{-1} at 120°. Added triphenylphosphine increases the rate of thermolysis but



8

the effect is less marked than for 6.

The products released by 6 and 8 imply a β-hydride elimination mechanism (Table 1),but without preliminary phosphine expulsion.



6 6b

Although five coordinate complexes are not common for Pt(II), there is nothing particularly exceptional about intermediate 6b: 6 is a sixteen electron complex and therefore 6b satisfies the eighteen-electron rule.

Figure I. An Arrhenius plot of K for the thermal decomposition of $\underset{\sim}{5}$ extrapolated to 120°.

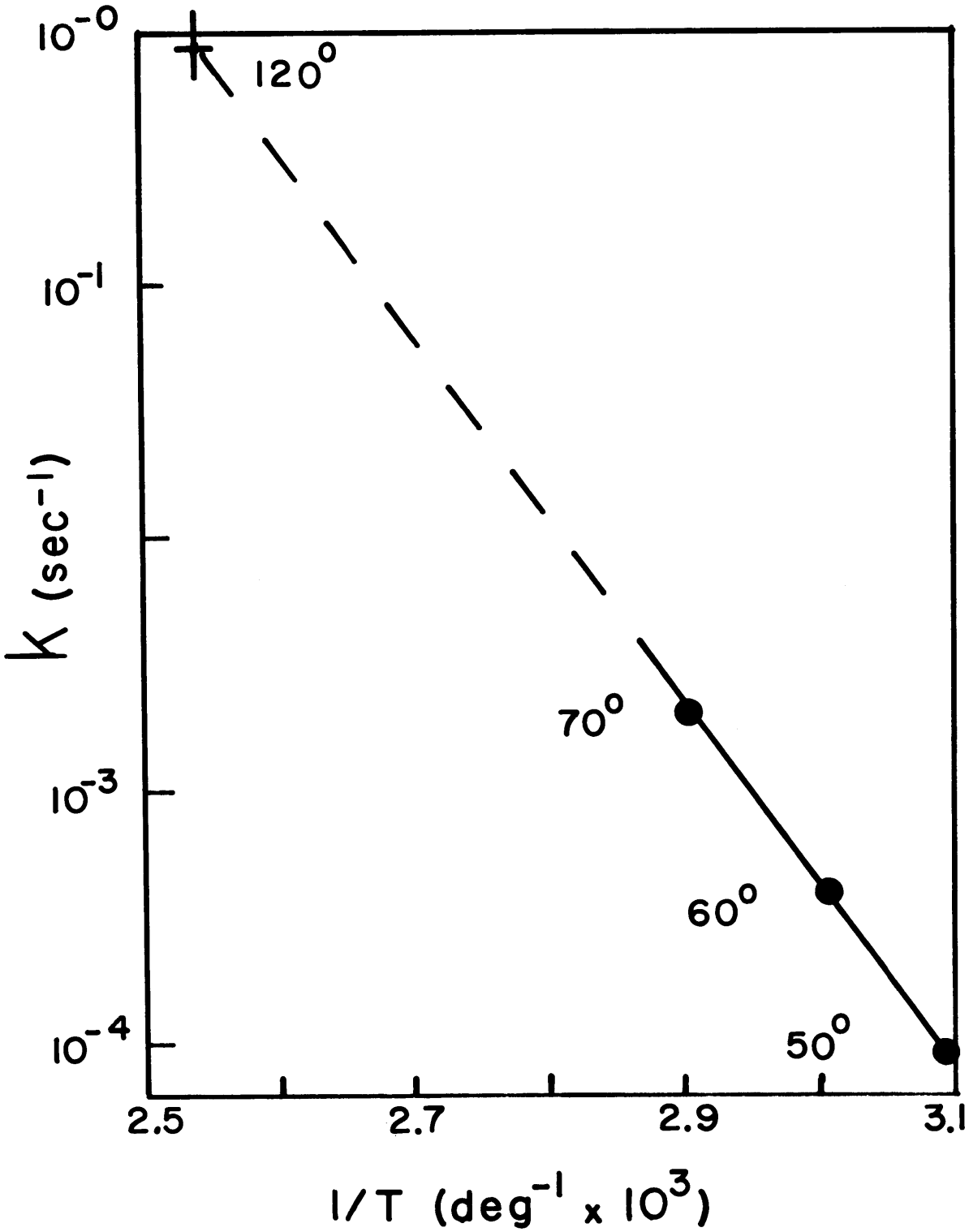

10^{-0}
10^{-1}
10^{-3}
10^{-4}
K (sec^{-1})
120°
70°
60°
50°
2.5
2.7
2.9
3.1
1/T (deg^{-1} x 10^{3})

Figure II. The thermal decomposition of 6 in the presence of Ph_3P. $[Ph_3P]$ = 0.0 (A), 0.003 (B), 0.007 (C), 0.026 (D), 0.13 (E), 0.26 (F). The initial rates are reproducible. The non-linear portions of curves A through D tend to vary slightly in different kinetic runs (see text).

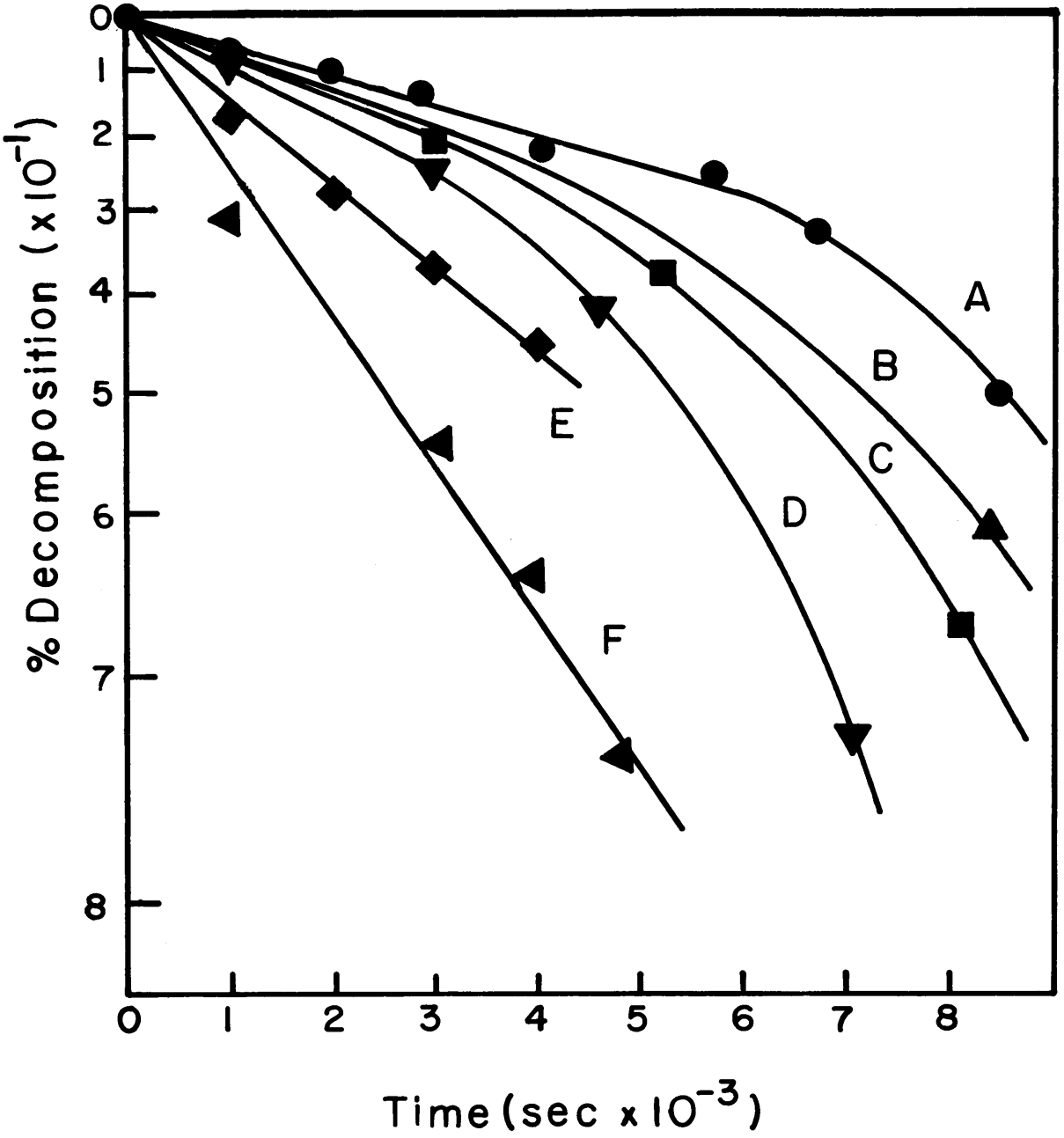

% Decomposition (x10⁻¹)
0
1
2
3
4
5
6
7
8
A
B
C
D
E
F
0
1
2
3
4
5
6
7
8
Time (sec x10⁻³)

Figure III. Rate of decomposition of 6 (●) and 8 (■) vs. the concentration of triphenylphosphine.

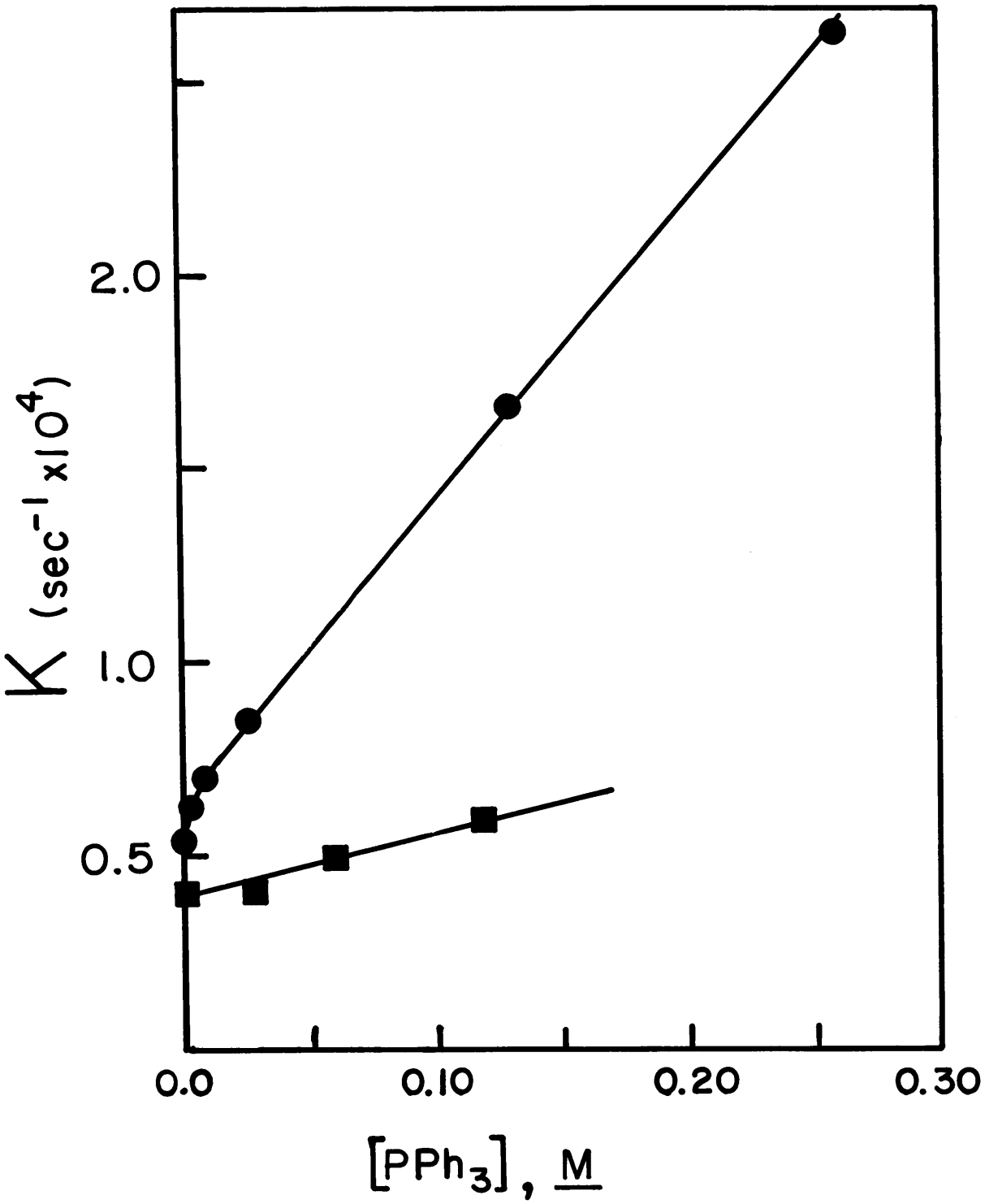

K (sec⁻¹ x10⁴)
2.0
1.0
0.5
0.0
0.10
0.20
0.30
[PPh3], M

Figure IV. The decomposition of $\underset{\sim}{6}$: % 2-butene vs. the concentration of Ph_3P.

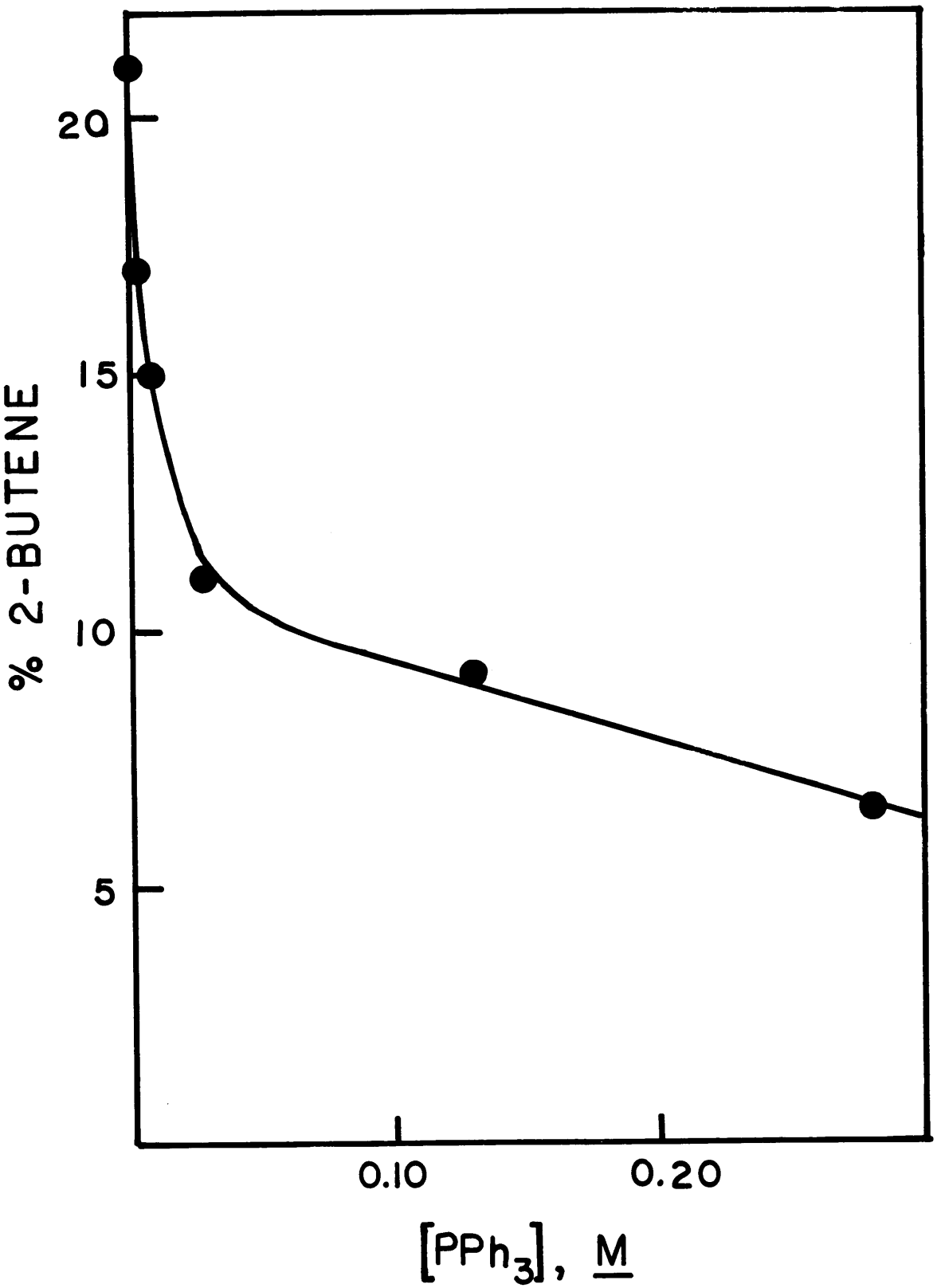

20
15
10
5
% 2-BUTENE
0.10
0.20
[PPh3], M

Table 1. Rates ($k \times 10^{-4}$ sec^{-1}) and Products of Thermal Decomposition of Platinum (II) Metallocycles in Methylene Chloride.[a]

No.	Compd	Rate at 60°	Rate at 120°	n-Al-kene	1-Al-kene	2-Al-kene	Diene[b]
10	L_2PtEt_2	4.5		50	50	--	--
5	$L_2Pt(n\text{-}Bu)_2$	4.1	9100	50	49	1	0
6	L_2Pt 		0.54	0	78	20	2
7	L_2Pt 		1.0	0	70	25	5
8	L_2Pt		0.40	0	75	17	8
9	L_2Pt 	1.7		0	83	17	0
11	L_2Pt 		c	15	28	32	25
12	(diphos)Pt 		0.17	0	83	17	0

(a) L = PPH_3; the initial concentration of the Pt complex was 0.025 M. Yields are relative; absolute yields were between 95 and 100%. Relative yields of olefins and dienes tended to drift during the course of the reaction, particularly for 11 and 12. Relative yields are based on 30% decomposition in order to provide a meaningful comparison.

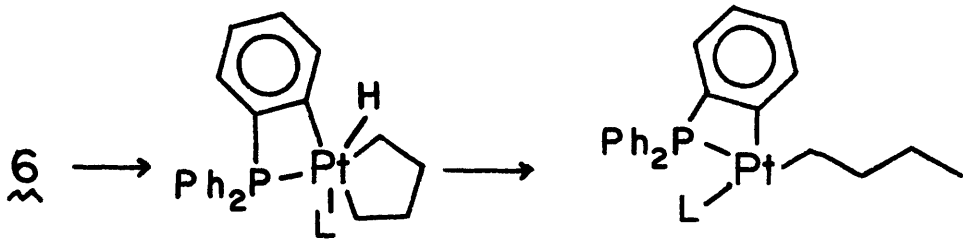
(b) Predominately α,w

(c) Qualitative kinetics indicated that the rate of decomposition was comparable to 7.

Other possible mechanisms would involve oxidative addition of an ortho aromatic C-H bond[49] (eq. 6) or reaction with the solvent.

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(49) A reaction frequently found among VIII metal-aromatic phosphine complexes. G.W. Parshall, Acc. Chem. Res. 3, 137 (1970)

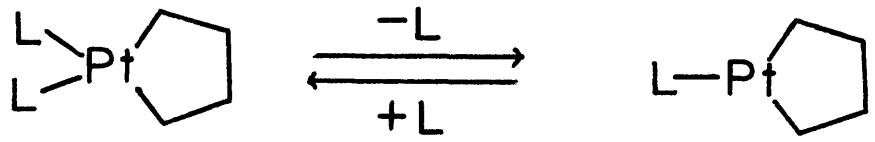


(6)

Upon thermolysis of 6 in CD_2Cl_2 or of 6-d_{30} (prepared from triphenyphosphine-d_{15}) in CH_2Cl_2 5% deuterium was incorporated in to the products in the early stages of the reaction. The metallocycle decomposes at 120° in other solvents, e.g., benzene, toluene, and trichlorotrifluoroethane, at a qualitatively similar rate. There is little reason to doubt that 6b is a key intermediate.

Apparently 5 can decompose by way of a five-coordinate intermediate. As mentioned earlier 5 is stabilized by added phosphine. The lower rate constant, $k = 5.5 \times 10^{-6}$ sec^{-1}, is independent of triphenylphosphine concentration from 0.043 M to 0.20 M[41]. A straightforward explanation

is available: the equilibrium (Scheme I) 5a is sufficiently displaced towards 5 above 0.043 M Ph_3P that direct hydride elimination predominates as in 6. Now a more direct comparison of 5 and 6 is possible. The dialkyl 5 undergoes β-hydride elimination 60 times slower than 5b. The metallocycle 6 is more stable than 5 by a factor of 300 when ligand dissociation is insignificant. One is then forced to the seemingly extraordinary conclusion that 6a is more stable 6 and at least 10^5 more stable than 5a. Since 5



6 6a

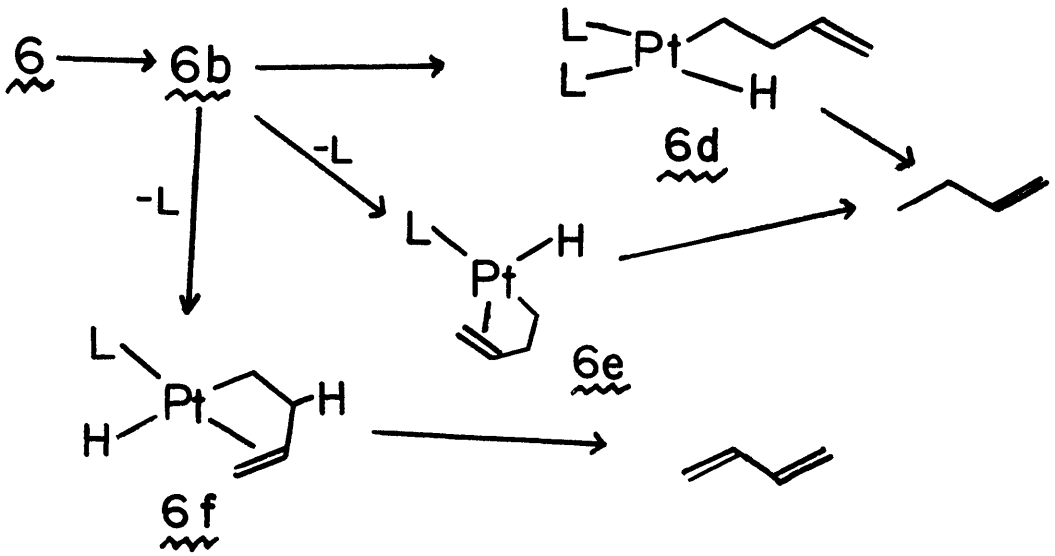
dissociates to 5a at 60° it is reasonable to assume that some 6a is in equilibrium with 6 at 120°. There is evidence for the dissociation in Figure III. The curve has a positive deviation from linearity at low phosphine concentration, precisely the effect expected for displacement of the equilibrium towards 6 by increasing the triphenylphosphine concentration.

The exceptional stability of 6a may be due to the

presence of ring strain. In the three coordinate complex, the C-Pt-C bond angle will try to increase to 120° sharply reducing the already limited conformational mobility of the platinacyclopentane.

A small amount of diene can be detected among the products from 6 and 8. Judging by the product distributions, the dialkyls do not undergo a double hydride elimination of this sort. In Scheme I elimination leads to 5c with the Pt-C and Pt-H bonds cis to one another and set up for reductive elimination of alkane. A more complex situation exists for 6 and 8.

Scheme II.[50] Proposed Thermolysis Mechanism of 6



(50) The letter designations for 6 will apply to analogous structures from other platinocycles. Thus 8a is likewise a three coordinate complex resulting from phosphine dissociation.

Intermediate 6b will stabilize itself by expulsion of a ligand and returning to square planar geometry as in 6d, 6e, and 6f. In 6f the Pt-H and Pt-C bonds are trans, making reductive elimination difficult and enabling a second β-hydride elimination to occur.

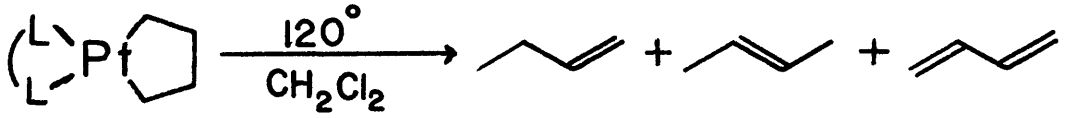
The thermal decompositions of 6 and 8 were studied in solvents other than methylene chloride. The same products and qualitatively similar rates were observed in trichlorotrifluoromethane, 1,2-dichloroethane, and benzene, except that in benzene a 10% yield of n-alkane was produced. The thermolysis of 8 in benzene-d_6 resulted in completely unlabelled n-pentane. The required -H must come from the triphenylphosphine ligands.

The decomposition of 6 and 8 gives a red-brown solution in benzene and a colorless solution in the chlorinated solvents. The red color is characteristic of $(Ph_3P)_2Pt(0)$ thermal degradation products[41,51]. Platinum

(51) F. Glocking, T. McBride, and R.J. Pollok, J. Chem. Soc. Chem. Comm., 650 (1973)

hydrides among these products may be responsible for the n-alkane produced in benzene. Presumably the Pt(0) is re-oxidized in the chlorinated solvents, thus the nearly colorless solutions result.

Compound 12 was readily prepared from 6 by displacement of triphenylphosphine with 1,2-bis(diphenylphosphine) ethane (diphos). The rate of thermolysis (see Table 1 and Table 4) was only three times slower than that of 6 consistent with the proposed mechanism. Unlike 6, no butadiene was present after decomposition.

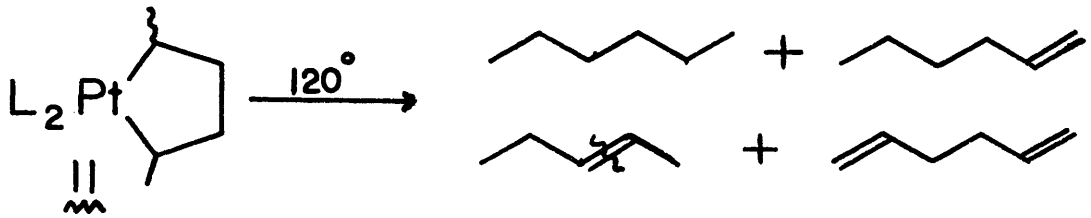


12

No phosphine expulsion 12b→12f is expected in this case due to the bidentate nature of diphos. The seven-membered platinocycle 9, which has about the same stability as 5 (and presumably decomposes by the same mechanism) releases no diene upon thermolysis because no five-coordinate intermediate is involved.

The stability of the platinocycle is only slightly affected by the introduction of a platinum - secondary carbon bond. 7 is only slightly more reactive than 6.

(Table 1). Platinocycle 11 was prepared and the results



of its thermolysis are tabulated in Tables 1 and 3. Even two secondary carbon bonds have little effect on the thermolysis rate of a five-membered platinocycle. However they do promote double hydride elimination with a 20-25% yield of hexadiene. The elimination of hexadiene must generate an interesting platinum dihydride. The dihydride has no apparent effect on the reaction of 6, 7, and 8. But the products from 11 include 15-20% n-hexane which may arise from reduction of hexene or of 11 itself. Bimetallic (not necessarily intermolecular) reductive elimination of alkane has been reported for copper[52] and iridium[53] alkyls.

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(52) G.M. Whitesides, E.R. Stedronsky, C.P. Casey, and J. San Fillipo Jr., J. Amer. Chem. Soc., 92, 1426 (1970)

(53) J. Schwartz and B. Cannon, ibid., 96, 2276 (1974)

A bimetallic process could involve the three-coordinate 14a. This would explain the absence of alkane in the thermolysis of 6, 7, and 8. With both 6a, etc. and the

hydride at lower[54] concentration the bimolecular reaction

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(54) Based on the yields of diene, the hydride must be 3-10 times less concentrated during the decomposition of 6,7, or 8, than during that of 14. Complex 14 will be more highly dissociated due to the steric bulk of the two secondary methyl groups.

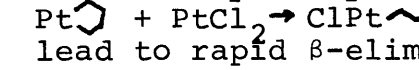
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will be slowed by more than an order of magnitude giving the platinum hydride time to dissipate by other means. (release of molecular hydrogen?).

An important aspect of the kinetics of 6 and 8 remains to be explained, viz., the rate increase after 30% decomposition. Two useful pieces of information are available. One, the rate increase is suppressed at high (> 0.10M) levels of triphenylphosphine or by substituting bidentate diphos for monodentate Ph_3P as ligand. This points to the involvement of three coordinate 6a in the autocatalytic process. Two, deuterium incorporation in the thermolysis products from 6-d_{30} or in CD_2Cl_2 increases during the autocatalytic phase, from 5% early in the reaction to 8% (6-d_{30}) and 15%(6 in CD_2Cl_2) after complete decomposition. Essentially the same percentage of labelling is observed in all three butenes. Platinum hydrides appearing among the decomposition products may be involved. The smooth, clean,

unimolecular decomposition of 5 is probably a typical of transition metal alkyls.[55]

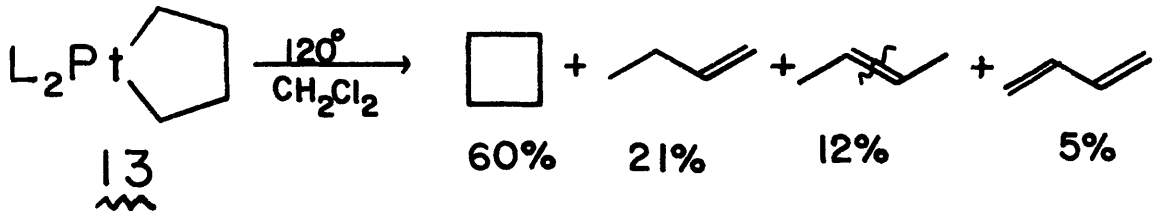
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(55) Another factor in the rate acceleration may be Pt-R exchange with Pt-Cl, a process described in Appendix I. Chloroplatinum complexes could arise from reoxidation of Pt(0) by methylene chloride. The exchange reaction  opens the ring and would lead to rapid β-elimination. For a recent study of other complexities involved in metal-alkyl reactions see: J.K. Kochi, Acc. Chem. Res., 7, 351 (1974)

Cyclobutane from a platinocycle. Regardless of the details of mechanism, the exceptional stability of the 5- and 6- membered platinocycles is an important result. If this is a common feature of metallocycles, then reactions other than β-hydride elimination will be promoted. An example is the thermolysis of 13, bis(tri-n-butylphosphine)tetramethylene-platinum(II). Reductive elimination accompanied by carbon-carbon bond formation has not previously been reported for Pt(II). It is well documented[56] for Pt(IV). However even for Pt(IV)

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(56) J.D. Ruddick and B.L. Shaw, J. Chem. Soc. A., 2969 (1969)



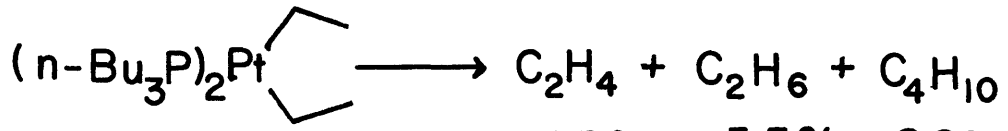
13

complexes with their higher coordination number of six, substitution of an ethyl group for a methyl group redirects the decomposition[57] predominantly through hydride elimination.

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(57) M.P. Brown, R.J. Puddephat, and C.E.E. Upton, J. Chem. Soc. Dalton, 1613 (1974)

The thermolysis of 14 demonstrates that the ring is an important factor in reductive elimination from 13. Absolutely no n-butane was generated from the less stable 14.



14

Experimental.

General Methods. All reactions involving organometallic compounds were carried out under prepurified nitrogen or welding grade argon using standard techniques[58] for

(58) D.F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York (1969)

handling air sensitive compounds. Solvents for use in organometallic reactions were distilled under an inert atmosphere. Ethyl ether was distilled from lithium aluminum hydride. Tetrahydrofuran was distilled from sodium benzophenone dianion. Hexane was stirred over concentrated sulfuric acid for several days, then distilled from the darkened acid and redistilled from a suspension of sodium benzophenone ketyl. Methylene chloride for use in kinetic runs was distilled from BaO under nitrogen, then redistilled through a 60 cm platinum spinning band column. A center cut (approx. 30%) was collected for use. The methylene chloride employed in recrystallizations was reagent grade, as were other solvents unless otherwise noted. Only absolute ethanol was used in synthetic work.

The platinum alkyls in this study are not very sensitive to air or water. Reaction work-ups, recrystallizations, and spectral measurements could be performed in the atmosphere without special precautions. However thermal decompositions were done under anhydrous, oxgen free conditions as discussed below. A number of organo-Pt compounds

were observed to decompose slowly in chloroform at 25° even though they were quite stable in other solvents[59].

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(59) Reactions of chloroalkanes with Pt(0) complexes are known, e.g. W.J. Bland and R.D.W. Kemmit, J. Chem. Soc. (A), 1278 (1968)

Chloroform-d could be satisfactorily employed for spectral measurements provided the solutions were quite fresh. This solvent should be treated with circumpspection in organo-transition metal work.

Melting points were obtained using a Thomas Hoover capillary melting point apparatus and are uncorrected. The observed melting points (actually decomposition points) of the platinum alkyls are usually higher in a sealed evacuated tube, indicating some sensitivity to air above 100°. The melting points previously reported[31] were for open tubes. Both values will be listed below where appropriate. Infrared spectra were taken on a Perkin-Elmer Model 237[60].

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(60) This part of the experimental work was completed before the department paid heed to the anguished pleadings of the peons (graduate students) and purchased a new machine, discarding the venerable, but decrepit, 237.

NMR spectra were run on a Varian T-60 or Perkin Elmer R20B

spectrometer. Chemical shifts are reported in ppm downfield from TMS. Microanalyses were performed by Midwest Microlab, Inc.,Indianapolis, Indiana.

Solutions were analyzed by gas chromatography on a Perkin Elmer Model 990, or a Hewlett-Packard Model 810. Both instruments were equipped with a flame ionization detector. Products were identified by comparison of retention times to those of authentic samples. Identity was considered established by equal retention times on at least two columns with different stationary phases. Product yields were determined by response relative to an internal standard. Response factors were calculated from authentic samples. The following columns were used: column A, 2.5 m Durapak C-8 (Waters Associates) 80-100 mesh; column B, 1.8 m Apiezon N (4%) on alumina (Anasorb F-1, Analabs Inc.) 80-80 mesh; column C, 8 m saturated solution of $AgNO_3$ in tetramethylene glycol (20%) on Chromasorb W, 80-100 mesh; column D, 3 m SE-30 (10%) on Chromasorb W, 80-100 mesh; column E, 3 m SE-30 (15%) on Chromasorb W, 80-100 mesh; column F, 3 m OV-17 (3%) on Chromasorb W, 100-120 mesh. All columns were 1/8" o.d.

Thermolysis reactions and kinetics.

Methods. Thermal decompositions employed 0.025 M

solutions in methylene chloride or other solvent as noted. Internal standards were included in the stock solutions. Pyrex tubes of 6 cm o.d. were cut into 18-cm lengths, sealed at one end, washed with acetone and distilled water, and dried in an oven at 120° for at least 24 hours. The tubes were allowed to cool only under dry nitrogen. About 0.3 ml of the solution to be thermolyzed was added to each tube by syringe. Care was taken to avoid contact of the solution to the upper part of the tube. Otherwise pyrolysis products generated during sealing caused erratic results. The tubes were connected to a vacuum line (<.005 torr) and degassed through three freeze-thaw cycles[61]. The sample was refrozen and the tube sealed with an oxygen-methane flame.

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(61) No loss of internal standard was observed during this proceedure provided the solution was not allowed to warm up to room temperature under vacuum.

The samples were then immersed in a thermostated oil bath constant to $\pm$ 0.2°. The tubes were removed at intervals and quenched by immersion in liquid nitrogen. Chemical quenching was accomplished by opening the tubes and adding 0.3 ml conc. HCl or a five-fold excess of Br_2 (based on Pt) as appropriate, and closing with a no-air

stopper. Samples containing ethane or ethylene were stored at -78° until analyzed. The cold solutions were drawn into a 10 μℓ syringe and injected quickly into the gas chromatograph.

Thermal decomposition of 5 and 10. The kinetics were measured as described previously[31,41] by determining the ratio of alkene to alkane after HCL quench. n-Hexane for 5 and n-pentane for 10 were included as internal standards as a check on the proceedure. The butane and butene from 5 were analyzed on column A or C, ethane and ethylene from 10 on column B. The first order rate constants for 5 were determined at 50°, 60°, and 70°. They were 9.3×10^{-5}, 4.1×10^{-4}, and 2.0×10^{-3} sec^{-1}. Figure V is a plot of the 50° run. Figure I is an Arrehnius plot of the results extrapolated to 120°. The slope is $-1.66 \times 10^{4} = -E_a/R$ which gives an activation energy of 33 Kcal mol^{-1}.

Thermal Decomposition[62] of platinocycles 6, 7, 8, 11, and 12. The same methods of analysis were employed as for 5.

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(62) Product distributions were previously reported[31]. Indistinguishable results were obtained in this work and will not be repeated in detail.

Internal standards (using column C) were n-pentane for 11, n-hexane for 6 and 12, n-heptane for 7 and 8. The peculiarities of the kinetics have been discussed in the Results section. The rate of decomposition of 6 was also measured at 0.012 M. The initial rate of 5.1×10^{-5} sec^{-1} is within experimental error of 5.4×10^{-5} at 0.025 M. Thus the initial rate is indeed first order. As a further check on the results the rate constant was measured by Br_2 quench. The dibromobutanes were analyzed on column D. The products of the two quenches and the measured rate are compared in Table 2. The thermolysis of 11 was followed by HCl quench and is outlined in Table 3 and the thermolysis of 12 in Table 4.

The thermolysis of 13 and 14 was handled as above by HCl quench with n-hexane as an internal standard, on column C. The principal product was not observed in the decomposition of 6. It was identified as cyclobutane by its retention time on Columns A,B, and C. Compound 14 decomposed to a mixture of ethane and ethylene (column B).

Ethyllithium. A 60 ml solution of 30.2 g (0.28 mol) of ethyl bromide in ethyl ether was added dropwise over two hours to 150 ml of ether and 6.5 g (0.95 mol) of Li wire. The first few drops were added at room temp. to initiate the

Figure V. The thermal decomposition of 5 in methylene chloride at 50°.

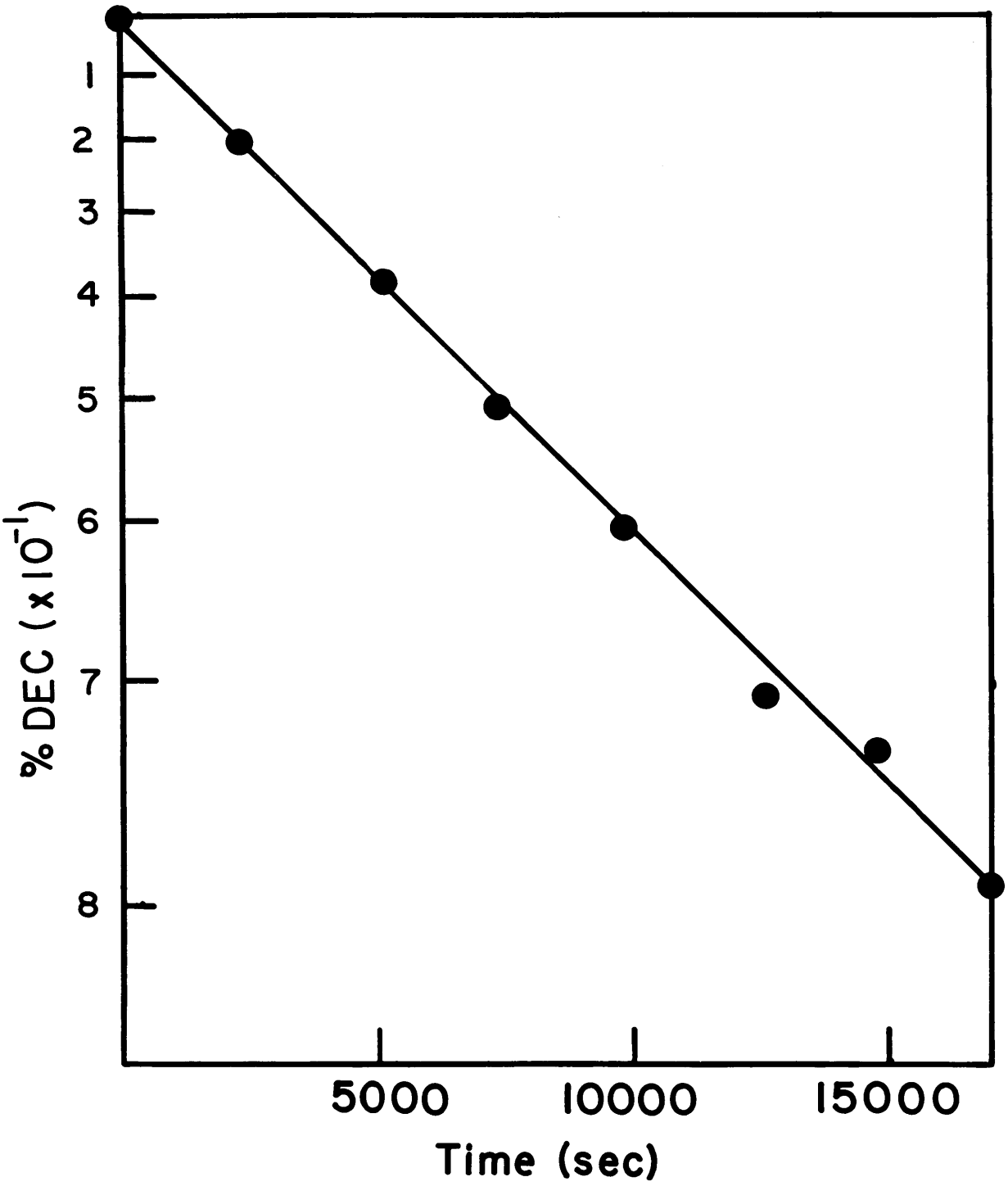

1
2
3
4
5
6
7
8
% DEC (x10⁻¹)
5000
10000
15000
Time (sec)

Table 2

Thermal Decomposition of 6. Comparison of HCl and Br_2 Quenches

	HCl	Yield	Br_2	Yield
6	n-butane	—	1,4-dibromobutane	—
Products	1-butene	78	1,2-dibromobutane	75
"	c-2-butene	13	dl-2,3-dibromobutane	15
"	t-2-butene	7	meso-2,3-dibromobutane	6
Measured Rate	5.4×10^{-5} sec^{-1}		5.7×10^{-5} sec^{-1}	

Table 3

Thermal Decomposition of 11[a]

Time (sec)	Hexane	1-hexene	2-hexene[b]	1,5 hexadiene[c]
50	84.3	5.8	10.0	1.5
160	78.8	6.8	10.5	3.8
650	69.1	9.9	13.3	8.0
1,400	61.8	11.8	15.4	11.0
2,000	56.7	12.3	16.7	14.3
5,000	37.4	17.0	22.6	21.9
10,200	30.0	24.0	24.4	21.6
15,100	25.8	27.0	25.8	21.5
25,900	23.0	—	—	—
120,000[d]	22.0	37	32	10.0

(a) 0.025M in CH_2Cl_2

(b) trans/cis ratio = 0.5 at 50 sec., 1.8 at 5000 sec, and 1.8 at 120,000 sec

(c) other isomers account for less than 10% of the hexadiene

(d) the product distribution near 100% decomposition is highly variable. Some reduction of hexadiene to hexene occurs at long reaction times

Table 4

Thermal Decomposition of 12[a,b]

Time(sec)	butane	1-butene	2-butene[3]	% Decomposed
4,000	90.2	9.3	0.5	9.8
7,960	85.5	13.4	1.1	14.5
12,480	78.5	18.5	3.0	21.5
16,250	73.0	19.0	8.0	27.0
20,200	71.3	19.7	9.0	28.7
24,300	64.4	21.8	13.8	35.6
31,600	60.0	22.4	17.6	40.0

(a) 0.026 M in CH_2Cl_2

(b) Relative yields given. Absolute total yield 98 ± 2%

(c) cis/trans ratio = 0.9 throughout the reaction

reaction. The remainder of the addition was done at 0°. The solution was stirred for an additional hour at 0° then filtered through Celite into a storage tube. Double titration with dibromoethane[63] gave a titer of 1.34 N RLi and 0.02 N residual base. The reagent was stored at -20°. The reagent lost 10% of its titer in two months.

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(63) H. Gilman and F. Cartledge, J. Organomet. Chem., 2, 447 (1964).

Diethylbis(triphenylphosphine)platinum(II), (10), was prepared by the method of Chatt and Shaw[64]. $(Ph_3P)_2PP+Cl_2$[65]

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(64) J. Chatt and B.C. Shaw, J. Chem. Soc., 4020 (1959)

(65) K.A. Jensen, Z. Anorg. Chem., 229, 237 (1936)

(0.9 g, 1.14 mmol) was suspended in 20 ml of ethyl ether. Ethyllithium (2.7 mmol in Et_2O) was added at 0° and the solution stirred for 45 minutes with gradual warming to room temperature. The reaction mixture was quenched with 10 ml of H_2O. The white precipitate was washed thoroughly with water and absolute ethanol, then recrystallized[66] from EtOH-CH_2Cl_2, yielding 0.75g (85%), mp (dec) 153-154° (lit. mp[67] 145-148°), nmr ($CDCl_3$) δ 7.4, 7.2 (m, 30H, P-Ph), 1.7-0.2 (m, 10H $-CH_2CH_3$).

(66) Recrystallizations from CH_2Cl_2-EtOH were carried out in the following manner. A 1 g sample was dissolved in 15 ml of CH_2Cl_2 and placed on a steam bath. As the solvent boiled away it was replaced by EtOH from a dropper to maintain the solution volume. This process was continued until the first sign of crystallization. The sample was allowed to slowly cool to 25° and then stored overnight at 3°.

(67) B.A. Morrow, Can. J. Chem., 48, 2192 (1970)

Anal. Calc. for $C_{40}H_{40}P_2Pt$: C, 61.77; H, 5.10. Found: C 62.05, H 5.20.

The preparation of platinocycles 6, 7, and 8 was carried out as previously described.[31] The nmr and infrared spectra were identical to those reported[31]. The melting points in sealed tubes differ from those reported for samples exposed to the atmosphere and are listed here; 6, 235°-237° (198°) 7, 190° - 191° (176°); 8, 218°-220° (189°). The open tube values[31] are given in parenthesis.

Platinocycles 6 and 8 were also prepared by an alternate method[68] which gives a much better yield (based on

(68) This synthesis has apparently been independently employed by Grubbs[20] but no details were given.

K_2PtCl_4) and eliminates the need for column chromatography.

$(Ph_3P)_2PtCl_2$ (0.802 g, 1.01 mmol) was stirred in 40 ml of ethyl ether at 0°. An ether solution of 1,4-dilithiobutane (1.5 mmol) was added by syringe and the solution stirred for 10 minutes at 0°, then allowed to warm to room temp. over an additional 20 minutes. The reaction was quenched with water and the white ppt collected. The ppt was washed with water and ethanol. Recrystallization[66] from EtOH-CH_2Cl_2 gave white crystals, 0.48 g (62%) of 6, mp (dec in vacuo) 235-237°.

Metallocycle 8 was prepared in an analogous manner in 70% yield.

(Diphos)tetramethyleneplatinum(II), 12, was prepared from 6 by displacement of Ph_3P by diphos. A 0.13 mmol sample of 6 was dissolved in 10 ml CH_2Cl_2 along with 0.064 g (0.16 mmol) of diphos. The reaction was monitored by nmr. Free PPh_3 could be detected after 15 minutes. The one unobscured peak due to complexed PPh_3 at 7.22δ had disappeared after 24 hours. No further change in the spectrum was observed after 40 hours. The solvent was removed at reduced pressure leaving a clear oil. Addition of absolute ethanol caused the oil to solidify. The solid was collected and washed thoroughly with ethanol. Recrystallization from EtOH-CH_2Cl_2 yielded 0.043 g (53%) of product having mp 242-247° and nmr

($CDCl_3$) δ 7.4,7.3 (m, 20H, P-Ph), 2.0-0.5 (m, 12H)

Anal. Calc. for $C_{30}H_{32}P_2Pt$: C, 55.47; H, 4.96. Found: C, 55.23; H, 5.11.

Hexane-2,5-di(magnesium bromide). A portion of a 50 ml ether solution of 2,5-dibromohexane (6.6 g, 27 mmol) was added to a flamed out flask containing 3.6 g of Mg turnings. After the reaction had initiated the remaining solution was added. The solution was stirred for 30 minutes until spontaneous refluxing had ceased, then refluxed an additional hour to ensure completion of the reaction. Two layers formed. The upper layer was reduced in volume by a stream of N_2 until the total volume was 20 ml. The solution was diluted with 130 ml of tetrahydrofuran. The Grignard reagent was filtered through a plug of Celite into an air-tight storage tube. Titration of a water quenched aliquot gave a total base concentration of 0.186 N, about a 50% yield.

Bis(triphenylphosphine)-1,4-dimethyltetramethylene-platinum(II), 11. (Cyclooctadiene) platinum dichloride[31] (0.28 g, 0.75 mmol) was suspended in 25 ml of ethyl ether at -50° by rapid stirring. Hexane-2,5-di(magnesium bromide), 0.8 mmol in 9 ml of tetrahydrofuran, was introduced by syringe and the solution stirred for one hour at -20°. The solution was passed through a short silica gel column[69] at

(69) This technique is discussed in detail by White[31] in the preparation of 6 and 7.

-10° and the column washed with an additional 25 ml of Et_2O. The solution was decolorized with a small amount of charcoal, then filtered onto 0.40 g (1.55 mmol) of triphenylphosphine. After 30 minutes the solvent was removed at reduced pressure leaving a yellow solid which was washed with ethanol and pentane. The weight of crude product was 0.27 g. Recrystallization[66] from EtOH-CH_2Cl_2 gave 0.20 g (33%) of colorless crystals having mp (dec in vacuo) 189-194°, nmr ($CDCl_3$) δ 7.47, 7.26[70] (m, 30H, P-Ph), 2.3-1.0 (m, 6H, $PtCHCH_2$), 0.80 (m, 6H, $CH-CH_3$). The multiplet at 0.80 has

(70) The pmr of triphenylphosphine bonded to Pt(II) appears as two unresolved and often overlapping multiplets separated by ~0.2δ

roughly the appearance of a triplet, but is in fact two overlapping doublets (J = 7 HZ) due to the presence of two isomers, epimeric with respect to the methyl groups. J_{PtH} = 64 HZ is also observed for the methyl groups.

Bis(tri-n-butylphosphine)tetramethyleneplatinum(II), 13. A 0.201 g (0.54 mmol) sample of (COD)$PtCl_2$ was stirred

in 35 ml of ethyl ether and 10 ml of tetrahydrofuran.

Seven ml of 0.095 M butane-1,4-di(magnesium bromide) was added at -50°. The solution was stirred for 40 min while warming to -15°. The reaction was quenched through a silica gel column[69] at 0°. The column was washed with an additional of ether. Tri-n-butylphosphine, 0.25 ml (1.1 mmol), was added by syringe and the solution was allowed to stand at 25° for one hour. After decolorization with activated charcoal, the solvent was removed at reduced pressure leaving a light yellow oil. The oil was taken up in 10 ml of methanol. Water was added until a slight cloudiness persisted. Cooling overnight to -25° yielded 0.06 g (17%) of white needles, having mp 79-80°, and nmr ($CDCl_3$) δ 2.4-1.0 (m, ~42H, a broad unresolved signal with a maximum at 1.57), 1.1-0.7 (m, ~20H, sharp signal at 0.98 due to PC_3H_6-$\underline{CH_3}$).

Anal. Calc. for $C_{28}H_{62}P_2Pt$: C 51.20, H 9.51. Found: C 51.38, H 9.76.

Bis(tri-n-butylphosphine)diethylplatinum(II), 14. A 0.375 g (1.0 mmol) sample of (COD)$PtCl_2$ was suspended in 25 ml of ethyl ether at -20° by rapid stirring. At ether solution of EtMgBr (2.5 mmol) was added and the reaction mixture stirred for 45 minutes until a clear homogeneous solution of (COD)$PtEt_2$[43] was obtained. Tri-n-butylphosphine (0.5 ml, 2.2 mmol) was added and the solution was

stirred an additional hour at 0° and the reaction quenched with water. The organic phase was dried and the solvent removed at reduced pressure leaving a yellow oil. The oil was dissolved in 10 ml of hot methanol which was quickly cooled to -70°, precipitating a white semi-solid material after 30 minutes. The methanol was discarded. 15 ml of fresh methanol was added to the solidified oil. Cooling to -25° with vigorous scratching caused crystallization to commence. The crystals grew at the expense of the oil during 24 hours. The white needles were washed with pentane at -25°, and dried by pumping at 0.02 torr. The compound is an oil at 25°C, having mp 5°.

Bromobenzene-d_5. Into 150 ml of trifluorotrichloroethane at 0° was introduced 20g(0.24 mmole) benzene-d_6 and 0.3g of aluminum trichloride. A solution of 40g Br_2(0.25 mmole) in 40 ml of the same solvent was added dropwise over 5 hours. A large amount of DBr is given off during the course of the reaction. The solution was warmed to 25° and poured into 8% aqueous NaOH. The organic layer was washed with water, dried and distilled giving 23.4g (61%) of bromobenzene-d_5.

Phenyllithium-d_5. Bromobenzene-d_5, 23.4 g in 40 ml of ethyl ether, was added dropwise over two hours to 4 g of

cut up lithium wire in 120 ml of ether at 0° under argon. The solution was stirred for an additional 30 minutes at 25° and centrifuged to remove suspended solids. The lithium reagent was used immediately in the next reaction.

Triphenylphosphine-d_{30}. A solution of 2.8 ml of phosphorous trichloride (32 mmol) in 40 ml of ethyl ether was added to the PhLi-d_5 at 0°. The addition took 20 minutes. The solution was stirred an additional 30 minutes while warming to room temperature and poured carefully into an ice-water mixture. The organic layer was washed once more with water, dried, and the solvent removed at reduced pressure. Recrystallization from ethanol-heptane yielded 4.3g (49%) m.p. 76-78°. Mass spectral analysis: 97% d_{30} and 3% d_{29}. The ionization voltage was 50 ev.

PART II

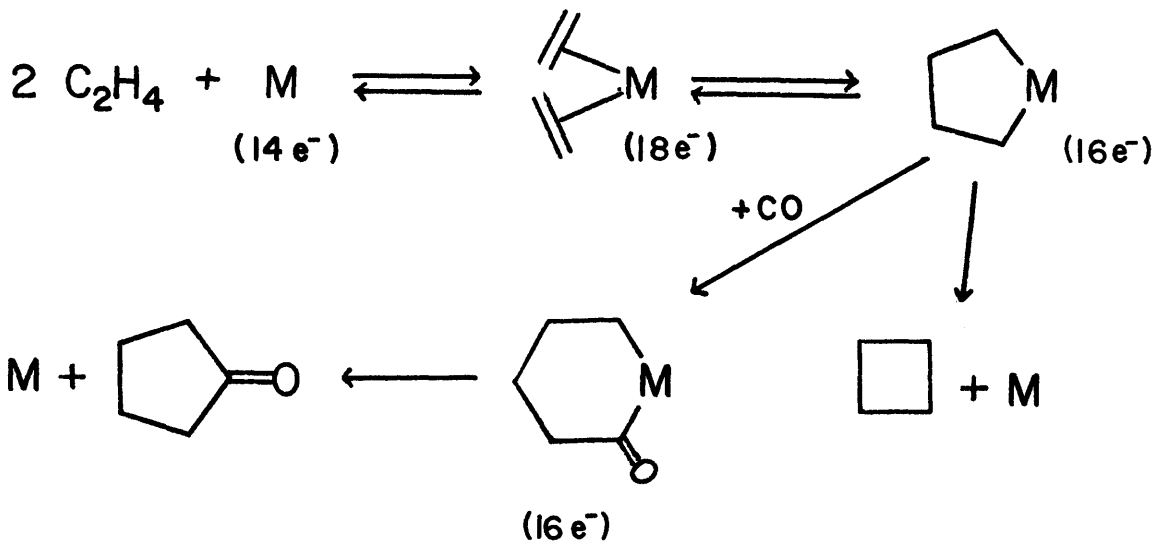
Synthesis and Reactions of Titanocene Metallocycles

Introduction.

In Part I it was found that bis(tri-n-butylphosphine)platinacyclopentane releases cyclobutane upon thermolysis, a novel reductive elimination for Pt(II). In contrast, the analogous but acyclic, diethyl complex displays no tendency towards a similar C-C bond forming reaction. It was the initial premise of this study that the comparatively high thermal stability of metallocycles, due to their resistance to β-hydride elimination, would promote unusual metal-alkyl transformations. A set of such reactions is outlined in Scheme III.

In the scheme the various reactions the metallocycle must compete with M-H elimination and the formation of butene (or substituted butenes). This elimination frequently dominates the chemistry of transition metal alkyls. In the cycloreversion of cubane[5] or the dimerization of norbornadiene, successful competition is scarcely surprising since hydride elimination is largely precluded

Scheme III



by the stereochemical requirements of the rigid carbon skeleton[26].

It is of considerable interest to determine to what extent the reactions of Scheme III can be extended to molecules lacking the severe restrictions of rigid, strained hydrocarbons. Aside from any mechanistic implications, the novel carbon-carbon bond forming steps could be of use to organic synthesis, i.e., the direct formation from unactivated olefins, of cyclobutanes, or of cyclopentanones with the addition of carbon monoxide.

The cyclopentanone synthesis has been reported recently for highly strained olefins such as benzonorbornadiene reacting with $Fe(CO)$[71]. This reaction has also been observed for methyl acrylate[72]. Photolysis with iron carbonyl gives the diolefin complex which reacts further,

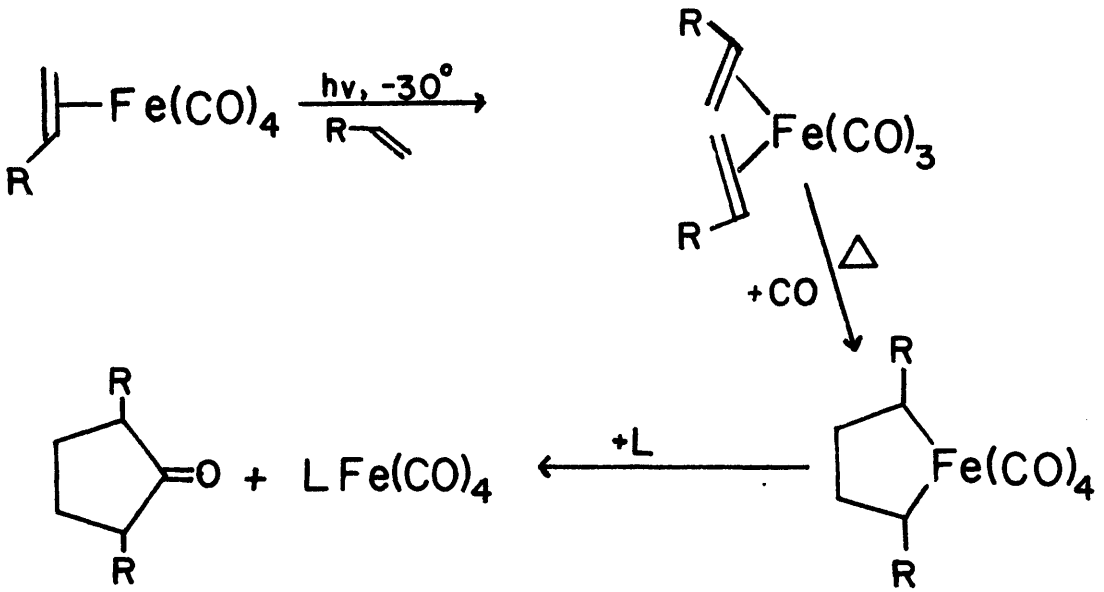
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(71) J. Mantzaris and E. Weissberger, J.Am. Chem. Soc., 96, 1873 (1974)

(72) F.W. Grevels, D. Shulz, and E.K. von Gustorff, Agnew. Chem. Inter. Ed., 13, 534 (1974)

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photochemically or thermally, to the ferrocycle in moderate yield. Treatment with triphenylphosphine induces reductive elimination of 2,3-dicarbomethoxcyclopentanone. The same

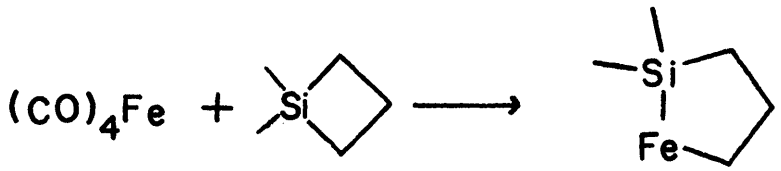


reaction works very poorly for norbornene and not at all for cyclohexene and olefins lacking activation by strain or other special features.

Reductive elimination of cyclobutane from a platinocycle was demonstrated in Part I. A fairly general synthesis of cyclobutanes from olefins is an intriguing possibility. Platinum itself does not appear particularly promising in this regard. The reverse reaction, oxidative addition of cyclobutane, is unknown, although an analogous insertion has been found for a silacyclobutane[73]. In any

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(73) C.S. Lundy and M.F. Lappert, J. Chem. Soc. Chem. Comm., 445 (1972)



case a reaction that produced cyclobutane or derivatives would be of greater interest than their destruction.

The remaining process of Scheme III the bis(olefin)→ metallocycle equilibrium, has been discussed in relation to olefin metathesis but could be more widespread among metal catalysts. Ethylene dimerization to butene results

if H-elimination competes with breaking of the β C-C bond. Dimerization has been frequently observed[74] with both homogeneous and heterogeneous catalysts.

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(74) E.L. Muetterties and J.C. Sauer, J. Am. Chem. Soc., 96, 3411 (1974)

Particularly suggestive of the intermediacy of metallocycles is the fact that ethylene butene is a commonly observed side reaction of metathesis catalysts[75].

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(75) R.L. Banks and G.C. Bailey, J. Catal. 14, 276 (1969)

In Scheme III species have been labelled with the number of valence electrons surrounding the metal, in accordance with the usual conventions[76]. The eighteen electron rule[76] is a useful guide through the maze of

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(76) C.A. Tolman, Chem. Soc. Rev., 1,337 (1972)

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organometallic chemistry. Thus it is not surprising that molybdocene forms only a monoethylene adduct even under 150 atmospheres[77]. Further reaction to a metallocycle

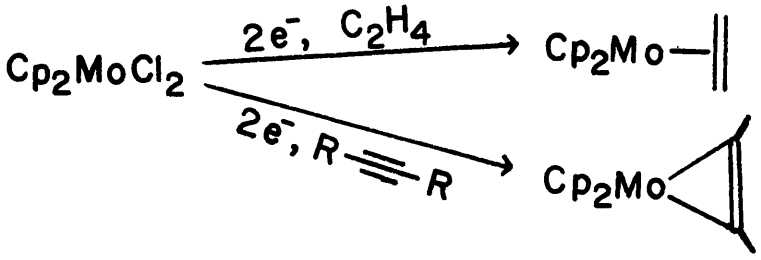
(77) J.L. Thomas, J.Am. Chem. Soc., 95, 1838 (1973)

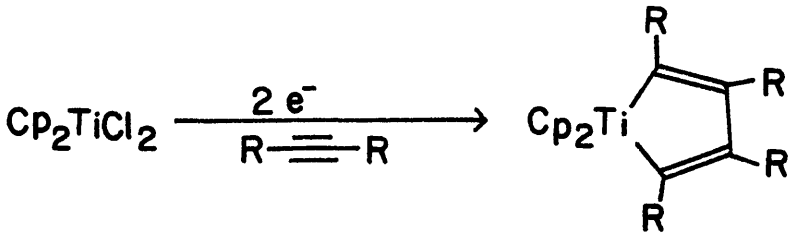
would require a high energy 20e- intermediate. Similarly only a monoacetylene complex[77] is formed while titanocene continues on to the metallocyclopentadiene[78,79]. The

(78) K. Sonagashira and N. Hagira, Bull. Chem. Soc. Jap., 39, 1178 (1966)

(79) G. Fachinetti and C. Florianni, J. Chem. Soc. Chem. Comm., 66 (1974)

decisive difference is the presence of two fewer valence electrons in titanocene.





Of course the correct number of valence electrons

may be a necessary but certainly not a sufficient condition for Scheme III to take place. The 16e- platinocycles of Part I did not give a trace of ethylene. Many diethylene or other olefin complexes of group VIII metals are known, e.g., bis(ethylene)cyclopentadienylrhodium(I)[80], without a report of one turning itself into a metallocycle. It

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(80) R. Cramer, J. Amer. Chem. Soc., 94, 5681 (1972). This and related complexes have been subjected to nmr and kinetic investigations.

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would appear that the group VIII metals are not a fruitful place to search.

After the number of valence electrons the most important general property of a complex is the number of d electrons held by the metal in its formal (but not unimportant) oxidation state. Grubbs obtained ethylene from a tungsten (VI), d° species[16]. All metathesis catalysts are low d metals, including several of titanium and zirconium[81].

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(81) D.H. Kubicek and E.A. Zuech, U.S. Patent 3,670,043. (Chem. Abstr. 77:P100716w)

The chemistry of titanocene has been well studied

(though not always well illuminated) and seemed a good candidate for study of metallocyclic complexes. Titanocene dichloride is a suitable synthetic precursor to a titanocycle which is a 16e-, d° complex.

Results.

When titanocene dichloride is treated with $BrMg(CH_2)_4MgBr$ in THF at -60°, ethylene as well as butene is produced upon warming to room temperature. Cp_2TiCl_2 reacts with 1,4-dilithiobutane in Et_2O at -78° to yield an orange compound, 15, which decomposes slowly above -20° to a similar mixture of ethylene and butene.

Methyllithium and n-butyllithium react with Cp_2TiCl_2 in an analogous manner. In contrast to 15, orange Cp_2TiMe_2[82]

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(82) K. Claus and G. Bestian, Ann. Chem., 654, 8 (1962)

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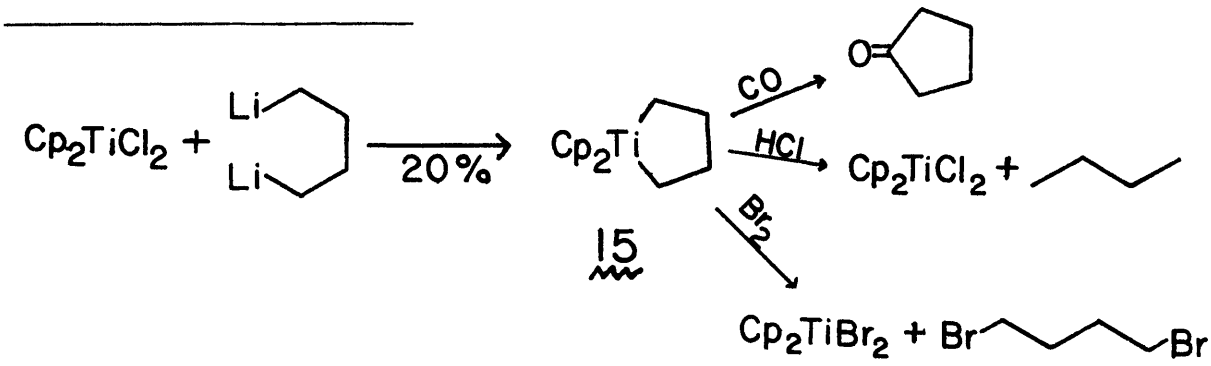
(16) is moderately stable at room temperature and can easily be isolated. The presumed product of the reaction with n-butyllithium, $Cp_2Ti(n\text{-}Bu)_2$ (17), decomposes readily above -50° and has not been isolated. This is a common result since the presence or absence of β-hydrogens is often the major factor in determining the stability of transition metal alkyls.

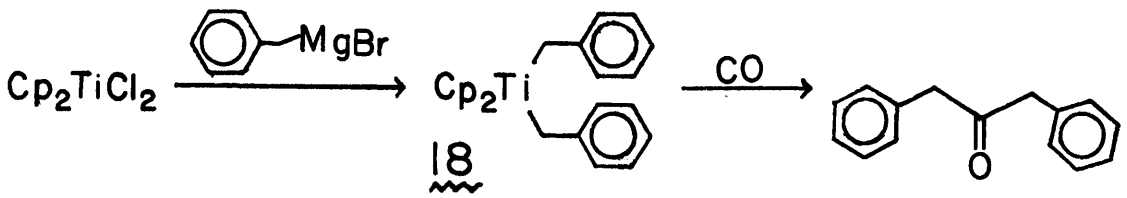
The orange compound, 15, is undoubtably tetramethylene titanocene. It reacts with carbon monoxide to yield cyclopentanone. A reaction analogous to that reported[83]

(83) G. Fachinetti and C. Floriani, J. Chem. Soc. Chem. Comm., 654 (1972)

for dibenzyltitanocene (18). Cyclic 15 is markedly more stable than acyclic 17, losing no more than half of its concentration in one hour at 0°.[84]

(84) A similar contrast in stability between metallocycles and their acyclic analogues was found for 6 vs. 5 and 13 vs. 14 in Part I





Purification and isolation of 15 were possible

provided that all operations were carried out well below ambient temperature. Removal of the solvent under vacuum followed by column chromatography of the residue in pentane gave a bright orange fraction. The optimum temperature range for this proceedure is -40° to -30° within which the desired compound is stable. Any polymeric alkyls resulting from the reactions of Cp_2TiCl_2 with the dilithium reagent would have stability comparable to 17. The conditions for work up of 15 destroy the less stable 17.

Crystals of 15 were obtained from pentane below -80°. They are quite unstable, turning black upon warming. Efforts to sublime 15 yielded only a violet colored substance, possibly the known[85] Ti(III) hydride, $(Cp_2TiH)_2$. The orange

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(85) J.E. Bercaw and H.H. Brintzinger, J. Amer. Chem. Soc., 91, 7301 (1969)

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crystals redissolve in pentane to give a solution identical to the chromatographic fraction which was therefore used in all subsequent work.

The titanocycle reacts with HCl and Br_2 in the expected fashion. The titanocene is recovered as the dihalide. In ethyl ether and polar solvents the reactions are nearly quantitative and can serve as an assay for the complex. In

pentane the yields are lower, particularly for bromination. This problem was solved by addition of ether to the pentane solution before the bromine quench.

The yield of 15 measured by these methods is consistently about 20% based on Cp_2TiCl_2. Although some losses are incurred in the workup proceedure, direct analysis of the reaction solution (by carbonylation, see below) shows that they are not severe. The titanocene dichloride dissolves almost entirely before excess lithium reagent is quenched, therefore the low yield cannot be due to incomplete reaction. The intermediate monoalkyl is not likely to be a source of trouble, because the monoalkyls have been found to be more stable than the dialkyls[86].

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(86) J.A. Waters and G.A. Mortimer, J. Organomet. Chem., 22, 417 (1970)

Alkylation with methyllithium gives a bright orange solution and dimethyltitanocene in up to 90% yield. Both 1,4-dilithiobutane[87] and n-butyllithium give much darker

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(87) The same reagent gives 60-70% metallocycle with $(Ph_3P)_2PtCl_2$ See Part I.

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solutions and poorer yields of titanocene alkyls. Possibly they act as reducing agents[88] as well as alkylating agents

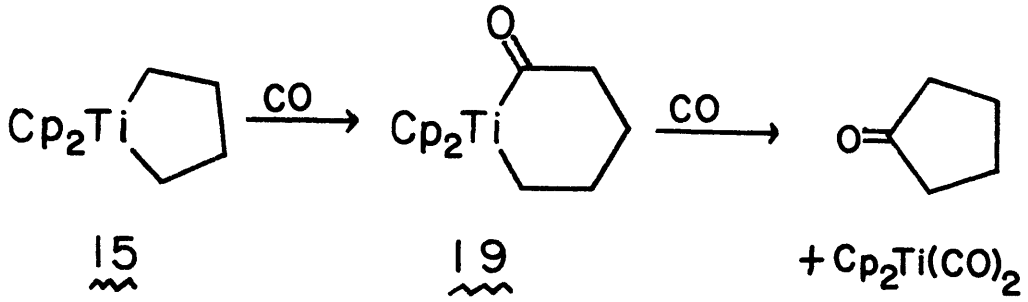
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(88) n-Butyllithium has been shown to be a strong one electron reducing agent under some conditions.

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towards titanocene dichloride.

Carbonylation of 15 under 10 atm of CO while gradually warming to 25° gives cyclopentanone in 80-90% yield based on the assay of 15. Under one atm of CO, a yellow brown solution results which also produces cyclopentanone upon heating. However exposure to air before the thermolysis substantially reduced the yield suggesting the presence of an oxygen sensitive intermediate. A solution of 15 in pentane at -55° under one atm of CO precipitates a yellow solid in 70-80% yield. The nmr (CD_2Cl_2) δ 6.25 (s, 10H), 2.5-1.0 (m, 8H) and the ir (CD_2Cl_2) 1720 cm^{-1} (s) are consistent with the identification of the solid as 19.

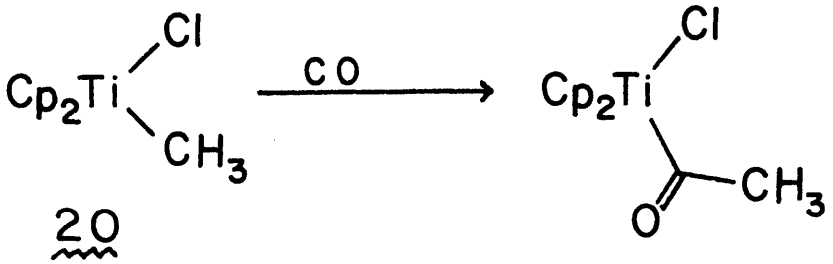


The acyl complex 19 releases cyclopentanone when heated in solution. The yield is improved under an atmosphere of carbon monoxide. The titanocene is converted, at least in part, to $Cp_2Ti(CO)_2$ as identified by its ir spectrum. Spectra of 19 could be taken at ambient temperature, but slow decomposition resulted. The half life of the acyl complex is approximately one hour at 25° in the absence of carbon monoxide.

It is of interest to compare this result to the reactions of 16, 17, and 18 with carbon monoxide. The stable alkyl, 18, gives[83] dibenzyl ketone and $Cp_2Ti(CO)_2$ (eq. 7b). An acyl intermediate was not detected. The same authors[89] an acyl complex by employing 20, removing the

(89) G. Fachinetti and C. Floriani, J. Organomet. Chem., 71, C5 (1974)

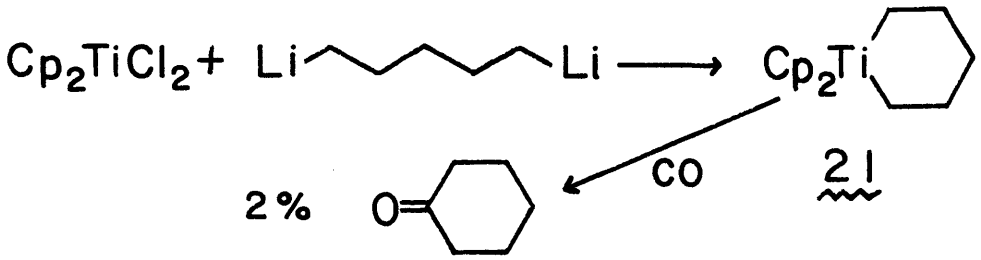
possibility of reductive elimination.



20

In our hands $Cp_2Ti(CH_3)_2$, 16, is converted slowly to $Cp_2Ti(CO)_2$ under CO. The acyl intermediate could not be detected at 25°, by nmr. The reaction rate becomes vanishingly slow if the temperature is reduced. Carbon monoxide reacts much more readily with 15 than with 16 and 18. At 0°, 15 is consumed within minutes, and 19 precipitates in good yield at -55° in less than two hours. A difference of at least 10^2 in reactivity between 15 and 16 must exist and evidently accounts for our ability to isolate the acyl complex, 19. This difference in reactivity may be due to ring strain in 15.

The six-membered titanocycle, 21, was prepared similarly to 15. A very poor yield of cyclohexanone was obtained after treatment with CO, even though 21 appears



to be only slightly less stable than 15. The larger ring probably inserts CO more slowly (similar to 16 and 18). The difference between 15 and 21 is consistent with the

ring strain hypothesis.

A mixture of butane and butene is produced by solutions of $Cp_2Ti(\underline{n}\text{-Bu})_2$, 17, upon gradual warming whether or not CO is present. No 5-nonanone could be found even under 10 atm of carbon monoxide. The thermal instability of 17 prevents it from undergoing acylation[90].

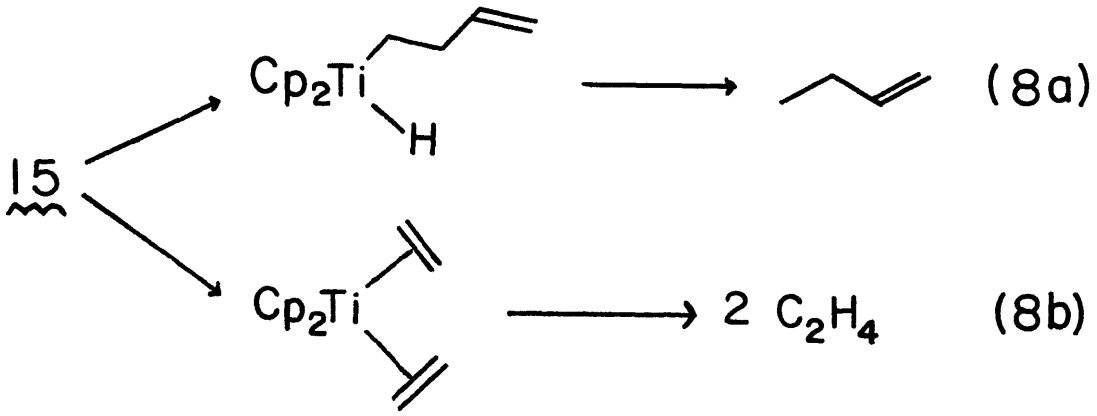
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(90) Curiously, the decomposition of 17 does not generate the reactive form of titanocene efficiently. The yield of $Cp_2Ti(CO)_2$ is poor even under high CO pressure: J.G. Murray, J. Amer. Chem. Soc., 83, 1287 (1961)

Thus the chemistry of 15 is significantly different than that of the acyclic dialkyls particularly those with β-hydrogens. The results of thermal decomposition strengthen this conclusion. The mechanism by which 17 yields butane and butene is no doubt similar to that found[41] for dialkyl platinum complexes.

There is no evidence of any C-C bond breaking. In particular no ethylene or ethane are found among the products. In contrast 15 decomposes to a mixture of butene and ethylene. Ethylene is favored by higher temperature, 10% at -20° 90% at 200°. Small amounts of butane and ethane are also found, probably due to the titanium hydrides that inevitably

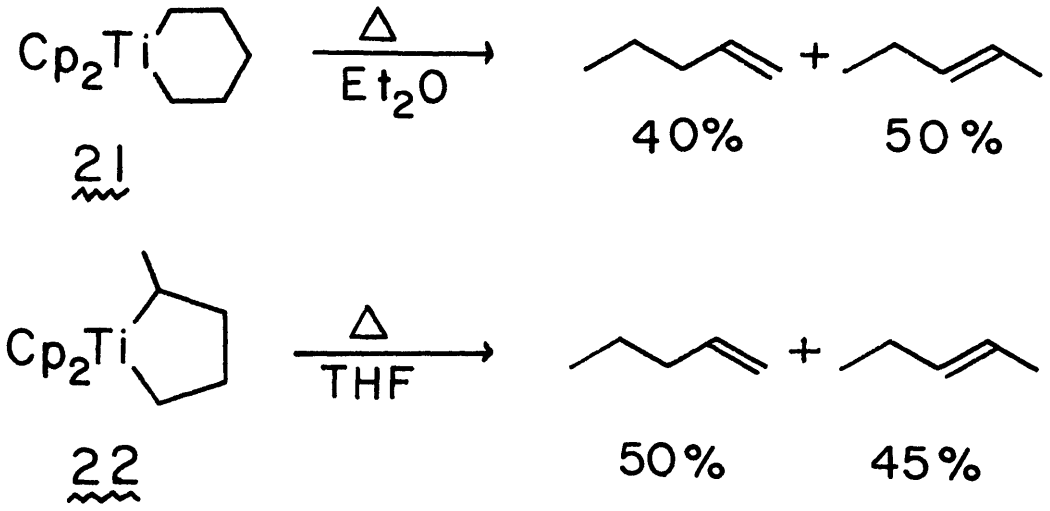
appear during the reaction.



We have not investigated the mechanism of ethylene formation in detail. It seems likely to involve a direct transformation of the metallocycle into a diethylene complex. This conclusion is strengthened by the behavior of 21, which thermolyzes to a mixture of pentene isomers. Ethylene and propylene were not present among the decomposition products. Although of similar thermal stability to 15, 21 lacks the simple one step rearrangement available to 15. The ring strain, evidenced by its rapid reaction with CO, may encourage the fragmentation.

The thermolysis of 22 was also briefly examined. No more than a trace of ethylene and propylene were observed when 22 decomposed slowly at -10°. Titanocycle 22 is significantly less stable than 15 with respect to Ti-H elimination (although still more stable than acyclic 17).

The competing decomposition pathways (eq. 8) are delicately balanced in the titanocene system.



The decomposition of 15 to butene (eq. 8a) is presumably irreversible, because it involves formation of an alkyl C-H bond. However eq. 8b could be reversible. As pointed out above, similar reactions have been observed with highly strained olefins such as norbornadiene (eq. 3). It is also well documented for tetrafluoroethylene and group VIII metals[39]. A possible [2+2] cycloaddition has been reported[91] for a titanium-based catalyst.

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(91) L. G. Cannel, J. Amer. Chem. Soc., 94, 6867 (1972)

The above considerations prompted us to test the reversibility of eq. 4b. Titanocene is not an isolable compound but is an important intermediate in several reactions[92,93]

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(92) J.E. Bercaw, R. H. Marvich, L.G. Bell, and H.H. Brintzinger, ibid., 94, 1219 (1972)

(93) E.E. van Tamelen, W. Cretney, N. Klaentschi, and J.S. Miller, J. Chem. Soc. Chem. Comm., 481 (1972)

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involving the reduction of Cp_2TiCl_2. The dimer $(Cp_2Ti)_2$ acts as a source of the reactive monomer in solution[92].

$$(Cp_2Ti)_2 \xrightarrow{CO} Cp_2Ti(CO)_2$$

23

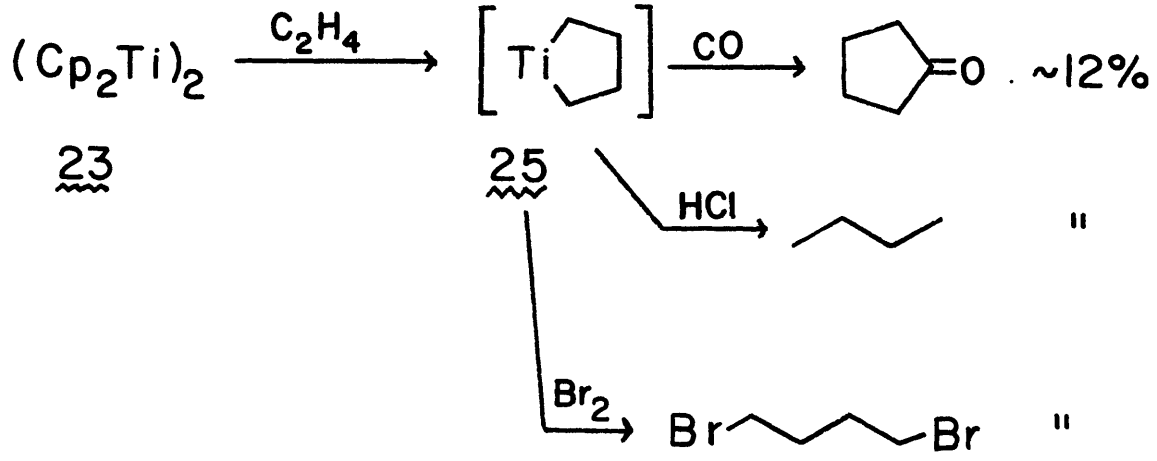
$$(Cp_2Ti)_2 \overset{N_2}{\rightleftharpoons} Cp_2Ti(N_2)TiCp_2$$

24

Titanocenes 23 and 24 both react with ethylene at -30°. Since 24 loses N_2 fairly readily at this temperature, both reactions may well involve 23. If aliquots of the resulting solution are treated with HCl, Br_2, and CO under the same as 15, the results strongly suggest the presence of a titanocycle, 25. The yields in Scheme IV are based on the amount of 23 used in the reaction. The thermal stability of 25

is low. The yields of quench products (Scheme IV) are diminished if the sample is first allowed to warm to 25°. It is probable that 15 and 25 are identical, but efforts to isolate 15 from the crude reaction mixture were unsuccessful.

Scheme IV



Since titanocene is also produced upon the reduction of Cp_2TiCl_2[93], it should be possible to generate 25 (or 15?) from titanocene dichloride, ethylene, and a

source of $2e^-$. The choice of reducing agent is restricted by the requirement for a reasonably fast reaction below -30°. The alkali metals, their amalgams, and Na-K allloy proved unsatisfactory. They reduce titanocene dichloride slowly even at room temperature. For example, 1% Na amalgam requires several hours to reduce Cp_2TiCl_2 to Cp_2TiCl in toluene. Further reduction to Ti(II) takes several days.

Aromatic anions[94] such as those of naphthalene are

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(94) N.L. Holy, Chem. Rev., 74, 273 (1974) A review of aromatic radical anions and dianions.

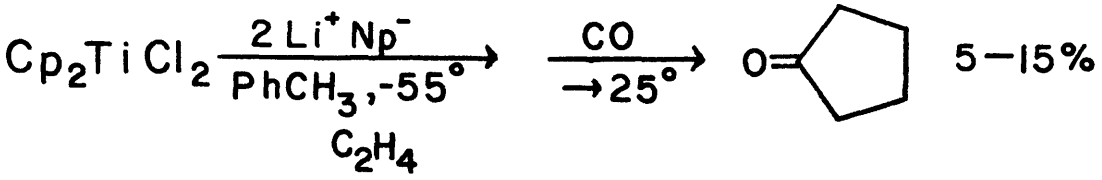
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efficient reducing agents at low temperature but must be prepared in coordinating solvents, e.g. THF, DME, which could compete with the olefin for titanocene. This problem was minimized by the use of a highly concentrated solution.

A 0.1 M solution of Cp_2TiCl_2 was reduced in toluene with lithium naphthalide (1.7 M in THF) in the presence of ethylene. Carbonylation in the usual fashion gave cyclopentanone. Based on titanium, a 5% yield was obtained with a stoichiometric amount of ethylene and 17% with a solution saturated with ethylene at one atm pressure.

The yield for the stoichiometric reaction is lower

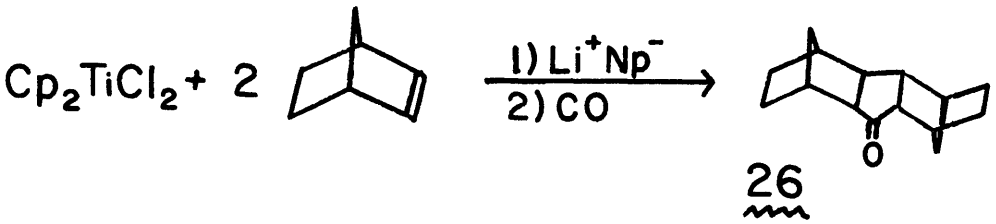
than that for 23 in Scheme IV. This result may be due to the presence of tetrahydrofuran. The reduction does give a good yield of available titanocene. When norbornene is



substituted for ethylene in eq. 5 a 24% yield of the ketone dimer (exo-exo isomer) 26 is obtained[95]. The yield could be increased to 75% (based on Ti) by using a 10-fold excess of norbornene.

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(95) The same product was obtained[71] in 5% yield by heating $Fe(CO)_5$ with neat norbornene for 40 hours.

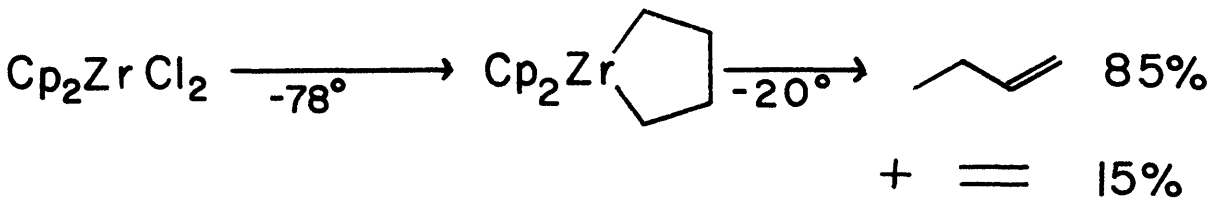


26

Thus it is possible to trap most of the reduced Cp_2TiCl_2 as a titanocene metallocycle. The low yields, except for an excess of reactive olefin, suggest that titanocene forms a bis olefin complex only with difficulty.

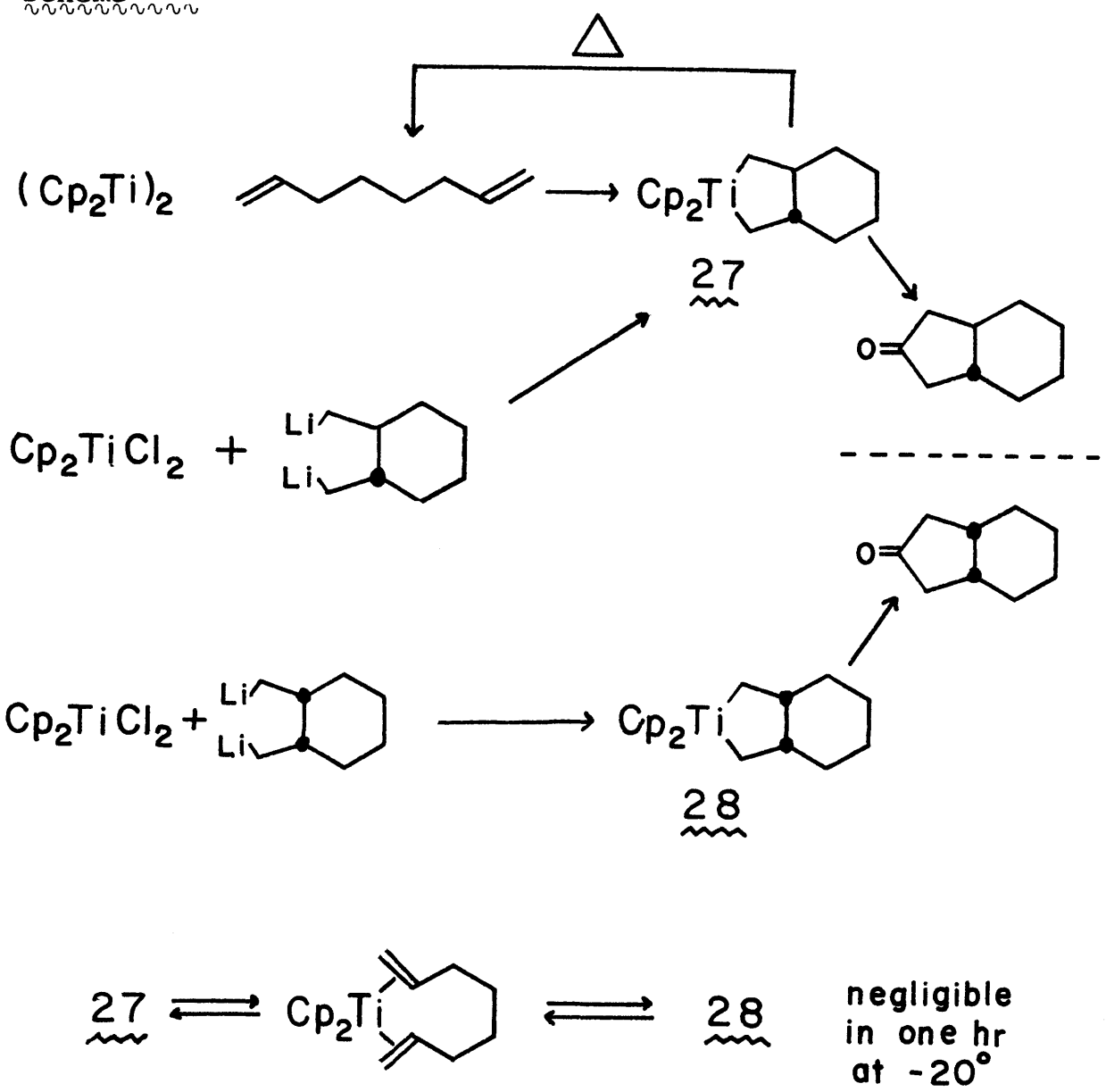
The titanocene dimer, 23, reacts with 1,7-octadiene to give trans-hexahydroindanone but in very low yield (Scheme V). The order of reactivity norbornene>ethylene> 1,7-octadiene probably reflects the relative affinity of the metal for the olefins as ligands. Nevertheless the yields are not simply the result of an unfavorable equilibrium. In the case of 1,7-octadiene, the titanocycle is not in equilibrium with the olefin at low temperature. Isomers 27 and 28 (Scheme V) do not epimerize in one hour at -20°, as demonstrated by the isomeric purity of the carbonylation products.

Eq. 8b represents the first reported release of ethylene from a well characterized metallocycle. The same reaction was observed for the zirconium analogue of 15 and may be common for low d e- transition metal complexes.



The result lends support to Grubbs interpretation[16] of the reaction between tungsten hexachloride and 1,4-dilithiobutane. Tungsten metallocycles may be intermediates in

Scheme V [93]



(96) Based on the work of M.E. Wilson. See M.E. Wilson, Progress Reports

olefin metathesis but 15 and its analogues apparently are not. There was no evidence of metathesis[97] when 23 was

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(97) Reduction of py_2TiCl_4 in toluene with two equivalents of lithium naphthalide gave a solution which displayed low metathesis activity towards propene. After 24 hours at 25°, 2% of the propene had been converted to a mixture of ethylene and 2-butene, in equimolar amounts. The absence of 1-butene, pentenes, and hexenes suggests that authentic metathesis had been observed. The same titanium complex has been reported[81] to be a metathesis catalyst when treated with aluminum alkyls.

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was stirred in toluene with propene or 2-pentene at 25° for 24 hours. Some reduction of the olefins to n-pentane was noted.

The transformation of a titanocene-diolefin complex into a saturated metallocycle is potentially a powerful synthetic reaction. Unfortunately the yields of cyclopentanones obtained by carbonylation are fair to poor. The 80% or better yield of cyclopentanone from 15 indicates that the difficulty lies in the metallocycle formation step. A number of problems can be identified at this time.

The polymeric hydride precursor of 23 is poorly characterized. In practice both compounds are of uncertain and no doubt highly variable purity, judging by the difficulty of reproducing reactions with 23. The direct

reduction of titanocene dichloride would seem the more attractive approach. But suitable reducing agents, e.g., lithium naphthalide, must be prepared in ethereal solvents which compete for the titanocene.

In any case titanocene is capable of undersirable side reactions. Reduction of titanocene dichloride at 25° leads to a stable inert green dimer[98,99]. This, and other more obscure oligimerizations, may be competing reactions even at lower temperatures, particularly in the presence of weakly coordinating ligands such as ethylene. The hydrogenation activity of reduced titanocene dichloride

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(98) G.W. Watt, L.J. Baye, and F.O. Drummond, J. Amer. Chem. Soc., 88, 1138 (1966)

(99) The compound was originally believed to be true titanocene, but the error was later recognized. H.H. Brintzinger and J.E. Bercaw, ibid., 92, 6182 (1970)

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of reduced titanocene dichloride was found to be substantially higher when it was immobilized[100] on a support to

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(100) R.H. Grubbs, C. Gibbons, L.C. Kroll, W.D. Bonds Jr., and C.H. Brubaker, ibid., 95 2373 (1973)

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prevent oligimerization. In our hands the same system,

titanocene immobilized on polystyrene, showed no activity for producing cyclopentanone from ethylene and carbon monoxide.

The green dimer mentioned above is a fulvalene complex and attack by titanium on the cyclopentadienyl C-H

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(101) A. Davison and S.S. Wreford, ibid., 96, 3017 (1974)

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bond appears to be a major source of titanocene instability. The use of pentamethylcyclopentadiene[102] leads to more tractable metallocenes for both titanium[103,92] and molybdenum[77]

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(102) R.B. King and M.B. Bisnette, J. Organomet. Chem., 8, 287 (1967)

(103) J.E. Bercaw, E. Rosenberg, and J.D. Roberts, J. Amer. Chem. Soc., 96, 612 (1974)

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and would be worth trying in the cyclopentanone synthesis. Peralkylated cyclopentadienes may no longer be difficult to prepare in reasonable quantities[104].

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(104) D. Feitler, private communication

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under welding grade argon. In particular 23 and its hydride precursor must be handled under rigorously 0_2-free conditions for the reactions to succeed. As previously reported[92], the hydride is pyrophoric. One sample ignited in a flask due to a small air leak. No problems were encountered with the residues of the reactions reported here, but caution is recommended with all reactions involving organo-titanocene species.

Diethyl ether was distilled from lithium aluminum hydride. Toluene was distilled from calcium hydride after refluxing for 12 hours. Pentane and hexane were washed free of olefins with concentrated sulfuric acid and distilled from a suspension of sodium benzophenone ketyl. Tetrahydrofuran was distilled from a solution of sodium benzophenone dianion. All distillations were run under argon. $CF_2ClCFCl_2$ was purged with argon or degassed under high vacuum before use. Nmr spectra were run on a Varian T-60 or Hitachi Perkin-Elmer R20B (60MHz) and a R22 (90MHz). Infrared spectra were measured with a Perkin-Elmer Model 567. Standard tightly stoppened NaCl solution

cells proved satisfactory for air sensitive compounds if the spectra were taken promptly.

Glc analyses were performed on a Perkin-Elmer Model 990, equipped with a flame ionization detector and using the following columns, all 1/8" o.d.: (A) 3 m, 5% carbowax 20M on Chromasorb P, 80-100 mesh; (B) 3 m, 10% SE-30 on Chromasorb 80-100 mesh; (C) 8 m, 20% of a saturated solution of $AgNO_3$ in tetramethylene glycol on Chromasorb W, 80-100 mesh; (D) 1.8 m 4% Apiezon N on Alumina (Anasorb F-1, Analabs Inc.) 80-90 mesh; (E) 3 m, 3% OV-17 on Chromasorb W, 100-120 mesh. Columns A and B were used for analysis of the carbonylation and bromination reactions of 15 and the reactions of titanocene with ethylene, and 1,7-octadiene. Low molecular weight hydrocarbons were analyzed on C. D was employed to resolve ethane and ethylene which overlap on C.

Titanocene dichloride was obtained from Alpha Inorganics and used without further purification. The ethylene was Matheson C.P. grade. Other chemicals were reagent grade and used without further purification. Liquid reagents to be added to air sensitive solutions were first purged with argon.

Bis(cyclopentadienyl)tetramethlenetitanium(IV), 15.

Titanocene dichloride (1.0 g, 4.0 mmol) was stirred rapidly as a suspension in 35ml of ether at -78°. A solution of 1,4-dilithiobutane (4.5 mmol) in ethyl ether was added by syringe dropwise over a 10 min interval. Vigorous stirring was continued until nearly all the dichloride had dissolved (1-2 hours). Excess lithium alkyl was destroyed by the addition of 100 μl of methanol. Removal of the solvent at -40° and 0.1 torr left a brown residue. The residue was extracted with 15 ml of pentane at -30° giving an orange brown solution. The suspended solids were removed by centrifugation. The pentane solution was the transferred to a dry, 10-cm long column of alumina (Woelm, grade #1) which had been thoroughly flushed with argon and provided with a cooling jacket at -35°. More cold pentane was passed through the column until a bright orange band eluted. Concentration of the solution and cooling below -80° gave orange crystals which discolor above -30°. The compound has a sharp singlet in the nmr spectrum (60 MHz, 0°) at δ 6.20 when dissolved in $CF_2ClCFCl_2$. The methylene region was obscured by residual traces of ether or pentane. The same solution in $CF_2ClCFCl_2$ can be prepared by substituting the halocarbon (mp -37°) for pentane above. If the sample is allowed to stand at 0°, light brown solids

settle out of solution and the NMR singlet decreases to half its original value in 0.5 hr. Treatment of the solution with Br_2 typically gives 0.8 mmol of 1,4-dibromobutane. Carbonylation with one atm of CO at -30° and slowly warming to 25° over several hours yielded 0.6-0.7 mmol of cyclopentanone as measured by glc (n-dodecane as internal standard). Addition of conc. HCl to a solution of 15 in $CF_2ClCFCl_2$ precipitates an orange-red solid, identified as Cp_2TiCl_2 by mp (dec) 275-280° and nmr ($CDCl_3$) δ 6.55 (s, Cp). n-Butane was the only volatile product.

1,4-Dilithiobutane and 1,5-dilithiopentane. A solution of 1,4-dichlorobutane (11.0 ml, 0.10 mol) in 50 ml of ethyl ether was added dropwise over a period of two hrs to 100 ml of ether containing 2.8 g of lithium (1% Na) wire at 0°. The reaction was stirred at 0° for 24 hrs. The solution was freed of suspended solids by centrifugation and stored in a Schlenk tube at -20°. If kept at this temperature, the reagent has a useful life of three to four weeks. The titer of RLi was 1.2 N (90% yield) with 0.02 N residual base by dibromoethane quench[105].

(105) G.M. Whitesides, C.P. Casey, and J.K. Krieger, J. Amer. Chem. Soc., 93, 1379 (1971)

Analysis of the dibromoethane quench for alkyl bromides showed that most of the RLi titer was the desired dilithium reagent. Cyclobutane is the principle by product of the reaction along with smaller amounts of butane and butene. No ethylene was observed. Much less satisfactory results were obtained using either unalloyed lithium or 1,4-dibromobutane. 1,5-dilithiopentane was prepared in an analogous manner in 85% yield.

Isolation of 19 in the carbonylation of 15. A pentane solution of 15 (0.8 mmol by Br_2 quench) was stirred for two hours under one atm of carbon monoxide at -55°. A yellow-brown solid separates from solution. The solid was washed once with cold pentane, then dissolved in a minimum amount of toluene at 0°. Pentane was added slowly until a slight cloudiness persisted. A yellow solid crystallized when the solution was slowly cooled to -60°. After two hours the solution was discarded and the solid washed with pentane and dried under a stream of argon at 0°, yielding 0.16 g (75%). Nmr(CD_2Cl_2) δ 6.25

(s, 10H, Cp), 2.5-1.0 (m, 8H, $(CH_2)_4$). An ir spectrum of the same solution had a strong band at 1720 cm^{-1} which gradually disappeared at 35° to be replaced by a broad band centered at 1740 cm^{-1}. The carbonyl band of cyclopentanone is at 1745 cm^{-1}. The Cp resonance at 6.25 disappeared at a similar rate and a half life of 15 min at 35° can be estimated. Analysis of the resultant solution by glc showed cyclopentanone to be present. Solid 19 decomposed completely when left at 25° for 24 hrs. In solution 19 is extremely sensitive to oxygen.

Reaction of 23 with ethylene. The grey-green hydride $(Cp_2TiH)_x$[92] (107 mg, 0.60 mmol) was stirred in toluene at -78°. Ethylene (35 ml, 1.2 mmol) was added by syringe and the solution was warmed to -35° dissolving the solid. The reaction was stirred, for three hrs at this temperature. The argon atmosphere was replaced by one of carbon monoxide and the reaction mixture was allowed to warm to room temperature over several hours. After 12 hrs a 12% yield (based on $(Cp_2TiH)_x$ of cyclopentanone was measured by glc. If an HCl quench was substituted for the carbon monoxide, a similar yield of butane was obtained.

Reaction of 24 with ethylene. A dark blue solution of 24 was prepared[92] from 1 mmol of $(Cp_2TiH)_x$ and 15 ml of toluene or ethyl ether. Ethylene (50 ml, 2 mmol) was introduced at -78° after the nitrogen atmosphere had been replaced by argon. The reaction mixture was allowed to warm to -30° whereupon it changed to a green-brown color. After one hr aliquots were reacted with HCl, CO, and Br_2 for glc analysis. Butane, cyclopentanone, and 1,4-dibromobutane were obtained in 10-15% yield based on $(Cp_2TiH)_x$. The bromine quench was not used in toluene because of the similar retention times of 1,4-dibromobutane and benzyl bromide.

Reduction of Cp_2TiCl_2 in the presence of ethylene. A solution of lithium naphthalide was prepared by stirring a 2 M solution of naphthalene in tetrahydrofuran with a slight excess of lithium wire. During the first hour the exothermic reaction was cooled occasionally with an ice bath to maintain the temperature at 25° or below. After five additional hrs, the titer, typically 1.7 M, was determined[106] by quenching an aliquot with deoxygenated water and titrating with standard HCl.

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(106) S. Bank and B. Bockrath, J. Am. Chem. Soc., 93, 430 (1971); S. Bank and B. Bochrath, ibid., 94, 6076 (1972)

Titanocene dichloride (0.25 g, 1.0 mmol) was suspended in 15 ml of toluene at -50° by rapid stirring under an ethylene atmosphere. Lithium naphthalide (2.1 mmol) was added dropwise over 15 min. Most of the Cp_2TiCl_2 dissolved during this period. The remainder dissolved with an additional 30 min stirring at -40°. The ethylene atmosphere was replaced by carbon monoxide and the reaction mixture was allowed to warm to room temperature in 4 to 5 hrs. After 6 hrs at 25°, 0.17 mmol of cyclopentanone was present by glc using n-dodecane as an internal standard. A more prolonged reaction at 50° did not increase the yield.

Reduction of Cp_2TiCl_2 in the presence of norbornene. Stoichiometric reaction. Titanocene dichloride (0.25 g, 1.0 mmol) was stirred in 10 ml of toluene at -50°. Lithium naphthalide (1.2 ml of a 1.7 M solution) was added dropwise over 15 min and the reaction was warmed to -30°. After 30 min of additional stirring the solution was carbonylated by allowing to slowly warm to 25° under one atm of CO. Only one product was detected by glc (column E) with the same retention time as the ketone dimer produced in the reaction with $Fe(CO)_5$[71]. A 24% yield was measured using octadecane as an internal standard. 30 ml of pentane was

added and the reaction mixture shaken in air with 1 M HCl until the red color had discharged and no more solids precipitated. After filtration, the solution was dried over Na_2SO_4. Removing the solvent at reduced pressure left a yellow oil which solidified. The ketone dimer was isolated by preparative tlc on silica gel eluted with hexane-10% ethyl acetate. The pure compound was 26[107],

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(107) The ir and nmr spectra of related compounds have been reported[71].

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the exo-trans-exo-ketone dimer, nmr($CDCl_3$) δ 2.35 and 2.16 (m, 4H, bridgehead), 1.93 and 1.70 (d, 4H, J = 7.5 Hz, cyclopentanone), 1.5-1.1 (m, 8H, $-CH_2CH_2-$), 1.04 (m, 4H, bridge). Mass spectral analysis gave a parent ion at m/e 216.

Reaction with excess norbornene. A tenfold excess of norbornene (2.1 g, 21 mmol) was used in the above reaction. The yield of ketone dimer was 75% based on titanocene dichloride. The reaction solution was heated to 75° for 15 hrs under carbon monoxide but no increase in the yield of ketone was observed.

Decomposition of 15 and 22 in tetrahydrofuran. Titanocene dichloride (0.13 g, 0.5 mmol) was dissolved in 20 ml of THF. Butane-1,4-di(magnesium bromide) was added at -78° with rapid stirring which was continued for two hours at -60° giving a dark orange solution. A solution of 22 was prepared in the same manner by using pentane-1,4-di(magnesium bromide). At this point an HCl quench gave only n-butane and n-pentane respectively.

When the unquenched solutions were allowed to warm above -20°, they gradually changed from orange to purple. An HCl quench and glc analysis showed that the color change was associated with decomposition of 15 and 22. 22 was estimated to decompose approximately 3x faster than 15, judging by the rate of color change. The solution of 15 yielded butene and ethylene in 4:1 ratio. An isomeric mixture of pentenes with only a trace of ethylene and propene were found after the thermolysis of 22 at -20 to 0°C.

Reaction of 16 with carbon monoxide. A 0.1 M solution of 16 in $CF_2ClCFCl_2$ was stirred at 25° under 10 atm of CO. At intervals the solution was examined by nmr. The spectrum of 16 ($CF_2ClCFCl_2$) δ 6.10(s, 10H), 0.02(s, 6H), was observed to decline only slightly after several hours. No evidence for an acyl complex could be found at any time.

The simplicity and sharpness of the spectrum would make even a small amount visible. Losses of 16 were accounted for by $Cp_2Ti(CO)_2$ plus unidentified insoluble material, probably thermal decomposition products since 16 is not stable in solution at 25° for more than a few hours. At lower temperatures no reaction was apparent.

Bis(cyclopentadienyl)tetramethylenezirconium(IV)

was prepared in site by adding a solution of 1.7 mmoles of 1,4-dilithiobutane to 0.52 g (1.7 mmoles) of zirconocene dichloride in 20 ml of ethyl ether at - 78°. The reaction mixture was stirred until all the dichloride[108] had dissolved. Carbonylation of the solution gives 1-2% cyclopentanone. If the pale yellow solution is allowed to warm up to 25° it becomes dark yellow-brown. Both ethylene and butene are produced, 15% ethylene and 85% of a mixture of butenes. No ethylene and very little butene were found when the solution was quenched with HCl at -50°.

(108) Bis(cyclopentadienyl)dimethylzirconium has been prepared by the reaction of Cp_2ZrCl_2 and methyl lithium. E. Samuel and M.D. Rausch, J. Amer. Chem. Soc., 95, 6263 (1973)

Reductions of zirconocene dichloride in the presence of ethylene and norbornene were conducted in an identical fashion to those of titanocene dichloride. Ethylene gave only 1% cyclopentanone. The yield of the ketone dimer was 5% with a stoichiometric amount of norbornene and 8% when a tenfold excess was used. The yields are based on Cp_2ZrCl_2.

Appendix I

The Thermal Decomposition of Dimethylbis(triphenylphosphine)-platinum(II) and Related Compounds.

Introduction.

Complexes of the type, $(phosphine)_2PtR_2$, decompose[1] by β-hydride elimination if R = $-CH_2CH_2R'$. When β-hydrogens are lacking, the dialkyl is much more resistant to thermolysis. The greater kinetic stability of so-called "elimination stabilized" metal alkyls[2,3] is found throughout the transition series.

(1) G.M. Whitesides, J.F. Gaasch, and E.R. Stedronsky, J. Amer. Chem. Soc., 94, 5258 (1972)

(2) M. Mowat, A. Shortland, G. Yagupsky, N.J. Hill, M. Yagupsky, and G. Wilkinson, J. Chem. Soc. Dalton., 533 (1972)

(3) P.J. Davidson, M.F. Lappert, and R. Pierce, Acc. Chem. Res., 7, 209 (1974)

Several general pathways are open for the decomposition of these complexes: (1) direct homolysis, M-R → M+R·,

which does not appear to be common and for which unambiguous examples cannot be found in the literature[4]; (2) reductive elimination, R-M-R → M + R_2, which has been established for Pt(IV)[5] and Au(III)[6] and is common as a bi-

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(4) A homolytic mechanism has been proposed for trimethyl (cyclopentadienyl)platinum(IV) but firm proof is lacking: K.W. Eggar, J. Organomet. Chem., 24, 501 (1970)

(5) M.P. Brown, R.J. Puddephat, and C.E. E. Upton, J. Organomet. Chem., 49, C61 (1973)

(6) A. Tamaki, S.A. Magenis, J.K. Kochi, J. Amer. Chem. Soc., 95, 6487 (1973)

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metallic process[7], 2 M-R → 2M + R_2, for Cu(I), Ag(I), and

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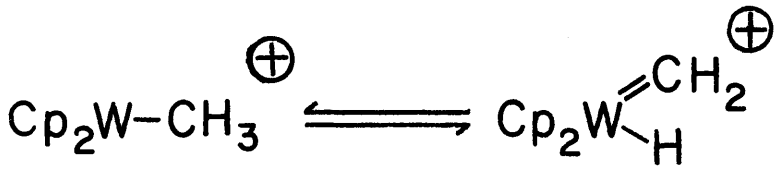
(7) J.K. Kochi, Acc. Chem. Res., 7, 351 (1974)

Au(I); (3) α-elimination, leading to a coordinated carbene, M-CH_2R → H-M=CHR, which may occur more often than has been recognized[8].

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(8) Labelling studies have implicated α-elimination in the themolysis of $Ti(CH_3)_4$: A.S. Khachaturov, L.S. Breslov, and I. Yu Paddubnyi, J. Organomet. Chem., 42, C18 (1972)

The transition metal-carbon bond is not as weak as was once thought, and activation energies of 50-60 Kcal mol^{-1} are likely for the direct explusion of a primary radical from a complex. α-Elimination of a hydride, although less favorable than β-elimination, would seem to be a more likely process than homolysis. A recent study of tungstocene complexes found evidence from deuterium labelling for the following fast equilibrium[9]:



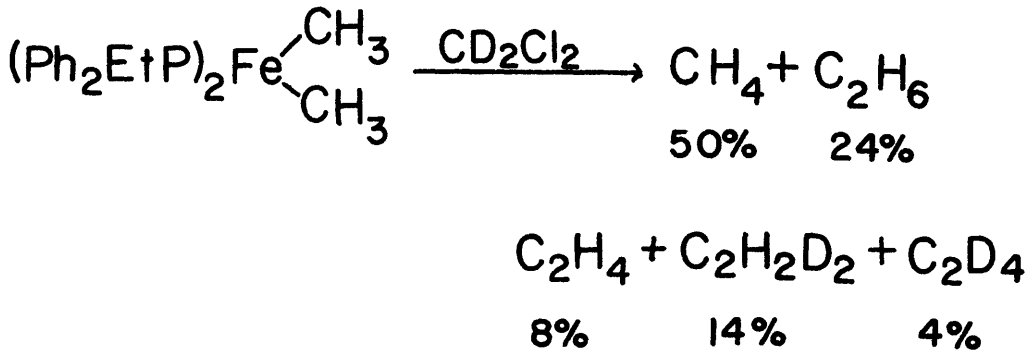
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(9) N.J. Cooper and M.L.H. Green, J. Chem. Soc. Chem. Comm., 761 (1974)

Coordinated methylene may have also been involved in the thermolysis of a dimethyliron(II) species in methylene chloride[10].

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(10) T. Ikariya, and Akio Yamamoto, ibid., 720 (1974)

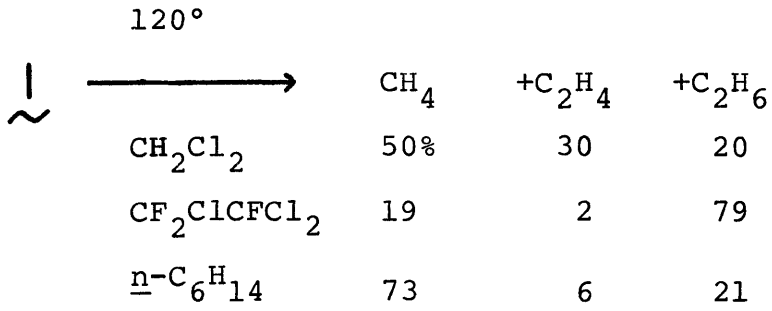


During the kinetic study of the platinocycles (see Part I) it was noted that the kinetic stability was comparable to that of several elimination stabilized platinum dialkyls. The metallocycles are effectively stabilized since their β-hydrogens are relatively inaccessible to the metal. The possibility existed that the two types of complexes have common features to their modes of decomposition. Therefore a brief study of the thermolysis of several platinum(II) dialkyls without β-hydrogens was undertaken.

Results.

The thermolysis of the metallocycle, bis(tri-n-butylphosphine)tetramethyleneplatinum(II), yielded cyclobutane as the major product (Part I). Butenes were also

formed, presumably by β-hydride elimination. Thus it was anticipated that dimethylbis(tri-n-butylphosphine)platinum (II), 1, would release ethane almost exclusively when heated to 120° for 30 hr. Unexpectedly methane and ethylene were produced in significant yields[11].



(11) The yields listed are relative. Absolute yields were 80-90%.

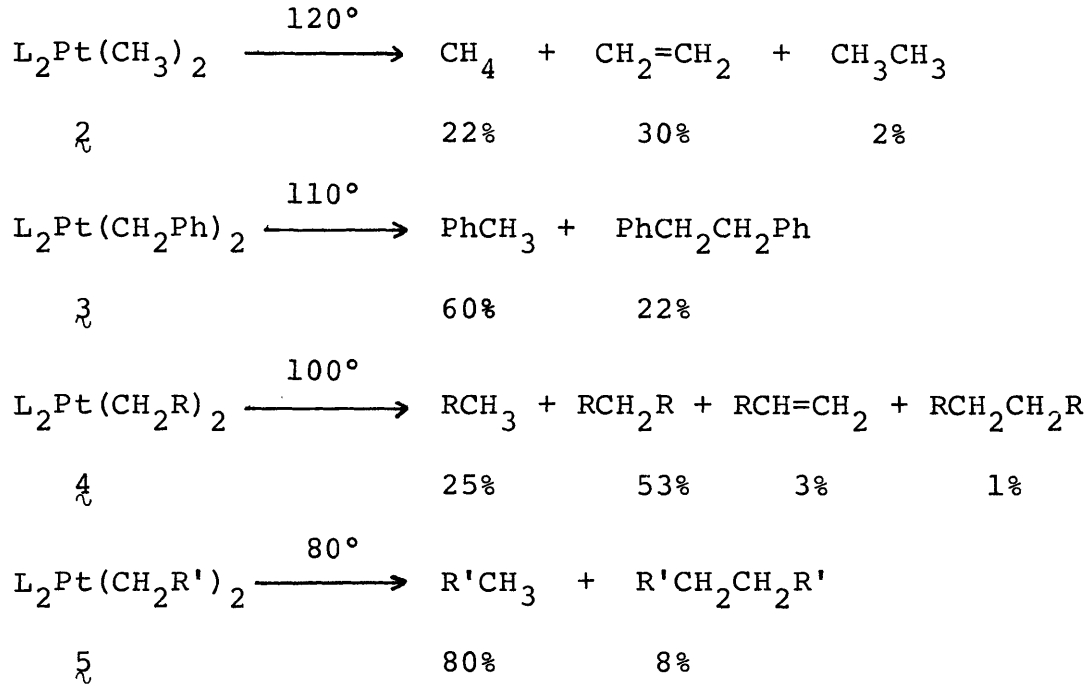
The ethane could be the result of a reductive elimination, but the formation of methane and ethylene suggest to involvement of an α-elimination.

The thermolysis in methylene chloride of a series of triphenylphosphine complexes 2, 3, 4, and 5 was also studied. The results (with absolute yields listed) are shown in Scheme VI.

The rates of decomposition could be determined qualitatively by quenching samples with bromine and analy-

zing for RBr, which is a measure of the undecomposed compound. The order of decreasing kinetic stability was

Scheme VI[12]



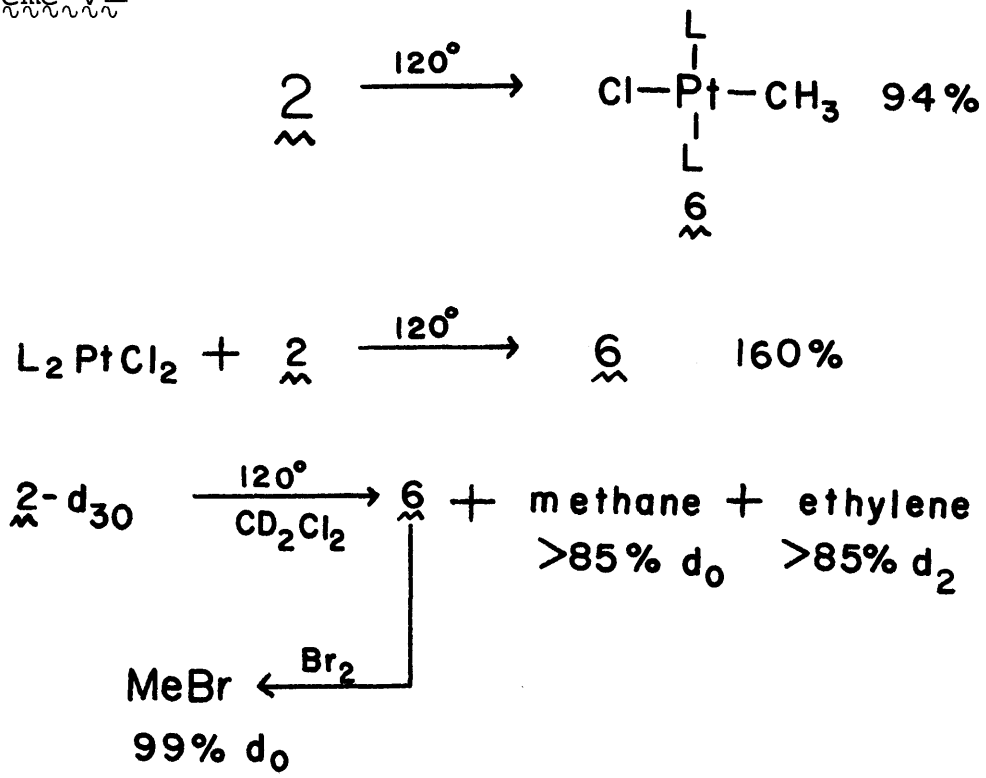
(12) In Scheme VI, L = Ph_3P, R = $-SiMe_3$, R' = $-CMe_3$. The temperatures listed are those at which the compounds decompose at equal rates. Pt compounds have the cis configuration. Reactions were run for 48 hr in methylene chloride.

found to be $2 \gtrsim 3 > 4 > 5$. Increasing the bulk of the alkyl group decreases the stability of the molecule. This result can easily be explained as a steric effect if the initial step of the reaction is phosphine dissociation.

Added triphenylphosphine was found to inhibit the decomposition of 2 and 5.

The dimethyl complex, 2, was subjected to a more detailed investigation. If a 0.1 M solution of 2 is held at 120° for 40 hr, slow cooling to -20° causes trans-chloro(methyl)bis(triphenylphosphine)platinum(II), 6, to crystallize in high yield (90-95%). Clearly a complex mechanism is required to produce 6 as well as the volatile products of Scheme VI. Considerable light is shed on this problem by the results outlined in Scheme VII.

Scheme VII[13]



(13) In Scheme VII, L = Ph_3P. Labelled 2 was prepared with Ph_3P-d_{15}. The methyl groups are unlabelled. All reactions were run in methylene chloride.

Product 6 is the result of an exchange reaction between 2 and $(Ph_3P)_2PtCl_2$. The exchange is relatively slow (50% complete in 40 min at 120° for 0.1 M solutions), but still faster than the decomposition of 2 (50% complete in 10 hr). Both reactions were monitored by nmr and the results are listed in Tables 5 and 6. The exchange reaction is authentic and not simply a catalyzed decomposition of 2 by the dichloro complex, because a 160% yield of 6 (based on 2) was isolated. Cis-diiodobis(triphenylphosphine)platinum(II) exchanges more rapidly with 2, the reaction going to completion in one hour.

Table 5. The exchange between 2 and L_2PtCl_2 at 120°.

Time (min)	Ratio, 2 : 6
45	42:58
90	32:69
200	16:84

Table 6. Thermolysis of 2 in CH_2Cl_2 at 120°.

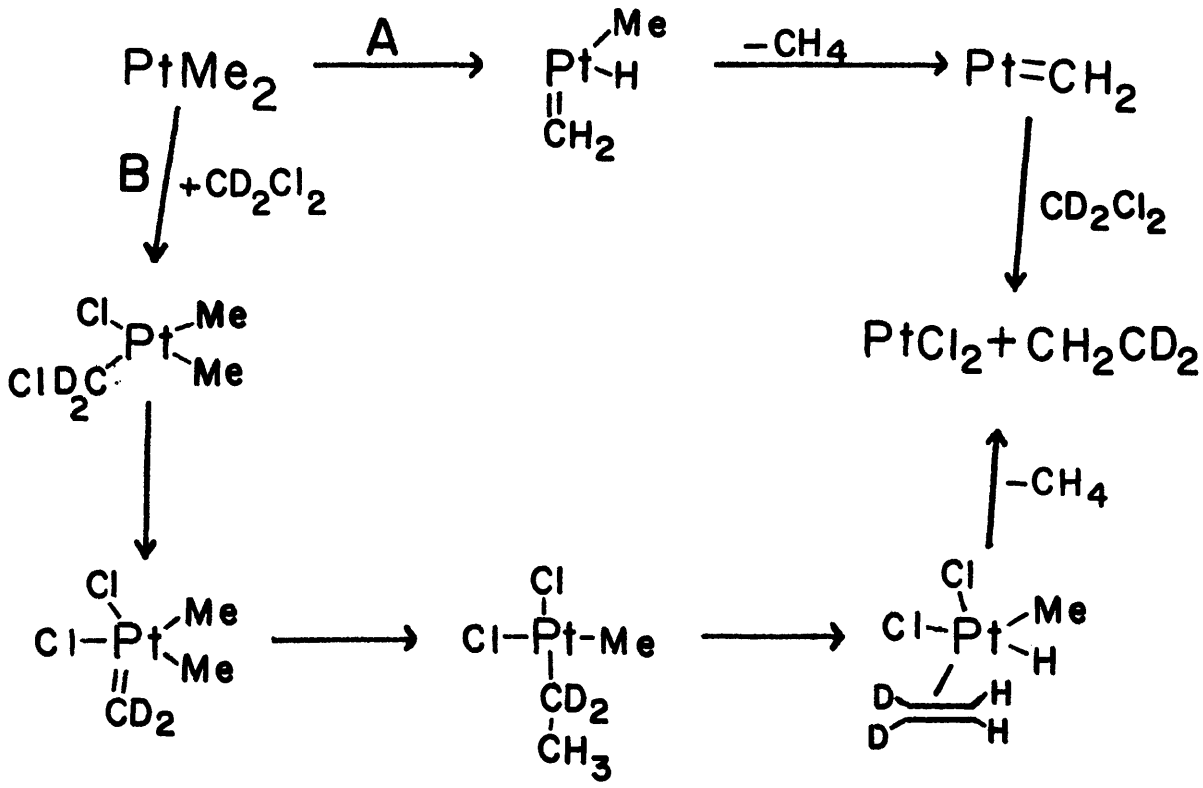
Time (min)	Ratio, 2 : 6
45	no 6 detectable
160	88:12
300	72:28
600	50:50

The decomposition of 2 must involve a reaction of the following sort: $2 + CH_2Cl_2 \rightarrow (Ph_3P)_2PtCl_2 + CH_4 + C_2H_4$. The dichloro complex then exchanges with another molecule of 2 yielding the final product 6^{14}. Deuterium labelling (Scheme VII) shows that the elimination of methane is

(14) Note that only ~50% of 2 actually decomposes to yield methane and ethylene. The remainder undergoes exchange to the more stable 6. Thus the low yields of volatile products for 2 in Scheme IV are nicely explained. When multiplied by two the yields are in the same range as for 3, 4, and 5.

primarily the result of a transfer of a hydrogen from one methyl group to the other. The ethylene is mostly d_2 when the reaction is done in CD_2Cl_2. Two plausible mechanisms can be proposed (Scheme VIII), both involving platinum carbenes.

Scheme VIII[15]



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(15) In Scheme VIII the phosphines have been omitted to simplify the diagram. In CD_2Cl_2 a small amount (~10% each) of CH_3D and C_2H_3D are formed. This evidence for H-D exchange is most readily fit into Pathway B.

The decompositions of 3, 4, and 5 are probably even more complex than that of 2. Only 3 gives a substan-

tial yield of coupling product. The bibenzyl, however, is not the result of a unimolecular reductive elimination. If 3 and 3a are thermolyzed together an approximately statistical distribution of coupling products are found[16].

$$L_2PtR_2 \quad + \quad L_2PtR'_2 \xrightarrow[CH_2Cl_2]{120^\circ} R\text{-}R + R\text{-}R' + R'\text{-}R'$$

3 3a 1.5 : 3.0 : 2.0

(16) In 3a, the benzyl group has been replaced by a p-methybenzyl group. Alkyl-alkyl group exchange should be slower than alkyl-halogen exchange and thus too slow to explain this result.

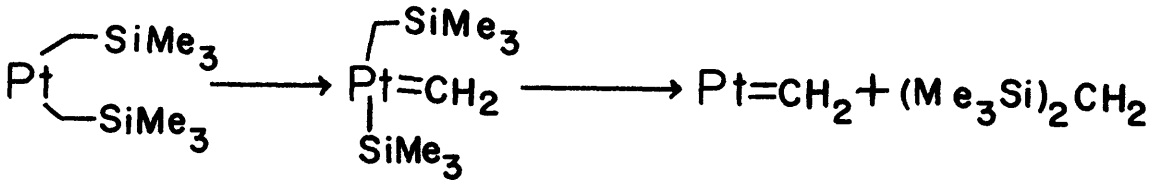
The two main products from 4 cannot come from the same molecule, indicating competing pathways for thermolysis. A mechanism similar to that of Scheme VIII can account for the tetramethysilane. A low yield of trimethysilylethylene was found, which is another product expected for a Scheme VIII type of reaction.On the other hand, bis-(trimethylsilyl)methane requires a different process, the α-elimination of a silyl group[17,18]. The analogous product,

(17) The fate of the remaining methylene group is not known. Some ethylene is formed during the reaction, but only enough to account for 20% of the methylene.

(18) Intermolecular cleavage of C-Si bonds by transition metals has been reported: M.P. Collier, B.M. Kingston,

and M.F. Lappert, J. Chem. Soc. Chem. Comm., 1498 (1970); C.S. Lundy and M.F. Lappert, ibid., 445 (1972)

2,2,4,4-tetramethylpentane, was not detected in the decomposition of 5, indicating a substantial difference in the liability of the C-C and C-Si bonds.



4

The exchange reaction observed for 2 does not appear to be important for 3, 4, and 5. No products analogous to 6 were found. Alkyl-halogen exchange would be expected to be slower for the bulkier alkyl groups. Furthermore 3, 4, and 5 decompose faster than 2. Thus exchange is too slow to play a significant role in the decomposition of these compounds.

The thermolysis of 2t[19] in toluene, benzene, and $CF_2ClCFCl_2$ also yields methane as a major product. In these solvents only traces of ethylene are produced. If carbene intermediates are involved it should be possible

to trap the methylene with olefins. Methylene transfer from chloromethyiridium[20] and chloromethyliron[21] complexes have been reported to give cyclopropanes.

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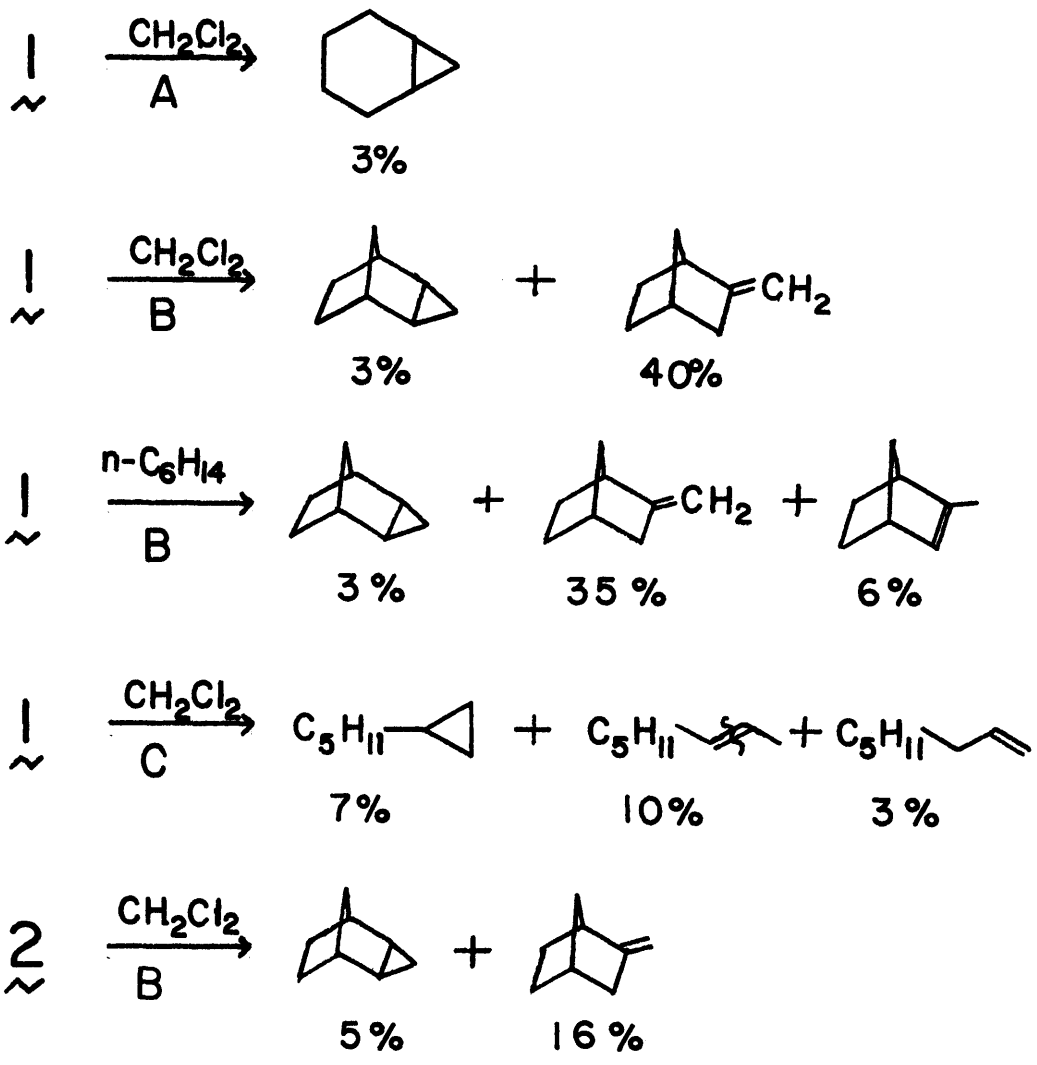
(19) Compound 2 is quite insoluble in most solvents other than chloroform and methylene chloride. This problem was solved by using 2t in which the triphenyl phosphine was replaced by para-t-butylphenyldiphenylphosphine.

(20) F.D. Mango and I. Dvoretsky, J. Amer. Chem. Soc., 88, 1654 (1966)

(21) P.W. Jolly and R. Pettit, ibid., 88, 5044 (1966)

The trapping experiments outlined in Scheme IX are highly suggestive of platinum-methylene intermediates. The yields of cyclopropanes are low, but acyclic isomers are produced in larger amounts. This may indicate the intermediacy of a platinacylobutane which can eliminate the hydrocarbon moiety by several routes. An alternative explanation of acyclic methylene adducts involves the insertion of the olefin into a Pt-CH_3 bond, followed by β-hydride elimination. It is rather difficult to explain by this route methylenenorbornene, 1-octene, or the absence of branched octenes.

Scheme IX[22]



(22) All reactions were run at 120° CO for 48 hr with the the following trapping reagents: (A) cyclohexenes; (B) norbornene; (C) 1-heptene. The yields are based on 1 or 2. The olefin is present in excess. The initial concentrations were 0.1 M in 1 or 2 and 1 M in olefin.

Experimental

General methods. Experimental techniques, solvent purification, and instrumental methods are the same as those of Part I and Part II and will not be repeated here. All syntheses of platinum alkyls involved the same general strategy[23] of dialkylating (cyclooctadiene)platinum dichloride with the appropriate Grignard reagent and displacing the diene with two equivalents of a phosphine. Both

(23) C.K. Kistner, J.H. Hutchinson, J.R. Doyle, and J.C. Storlie, Inorg. Chem., 2, 1255 (1963)

reactions proceed smoothly at 25°. Compound 4 was a sample obtained from White[24] and was not synthesised. The

(24) J.F. White, Ph.D. Thesis, M.I.T., Cambridge, Mass. (1972)

platinum alkyls used in this study are not sensitive to air or moisture at 25° and could be recrystallized and handled without special precautions.

Gas chromatograms were run on the following 1/8" o.d. columns: (A) 1.8 m 4% Apiezon N on alumina (Anasorb F-1, Analabs Inc.): (B) 8 m 20% of a saturated solution

of $AgNO_3$ in tetramethylene gycol on Chromasorb W, 80-100 mesh; (C) 3 m 10% SE-30 on Chromasorb W, 80-100 mesh; (D) 3 m 15% SE-30 on Chromasorb W 80-100 mesh; (E) 3 m 3%-OV-17 on Chromasorb W 100-120 mesh.

Deuterated solvents were obtained from Stohler Isotope Chemicals, Rutherford, N.J. Triphenylphosphine-d_{15} was prepared in Part I. Isotope analyses were performed by glc-ms techniques by Prof. Biemann's group. Ionizing voltages of 40-50 ev were used. Although lower ionizing voltages are to be preferred for deuterium analysis, the correspondingly lower sensitivity was not compatible with the small quantities of sample to be analyzed. The small uncertainty in the isotope distribution has no material effect on interpretation of the results.

The rate of thermolysis of $\underset{\sim}{2}$, $\underset{\sim}{3}$, $\underset{\sim}{4}$, and $\underset{\sim}{5}$ in methylene chloride was followed by quenching samples with bromine (a five-fold excess based on the initial concentration of the complex). The alkyl bromides thus formed represent undecomposed platinum alkyl and were analyzed by glc as follows:

Compound	Quench Product	Internal Standard	Column
$\underset{\sim}{2}$	CH_3Br	n-octane	D
$\underset{\sim}{3}$	$PhCH_2Br$	n-nonane	E
$\underset{\sim}{4}$	$(CH_3)_3SiCH_2Br$	n-nonane	C
$\underset{\sim}{5}$	$(CH_3)_3CCH_2Br$	n-octane	C

All reactions at elevated temperatures were run in Pyrex tubes of 6 mm (<1 ml) or 8 mm (>1 ml) o.d. The tubes were prepared from 15 cm lengths cut from tubing of standard thickness. The sample was added to the tube and degassed by three freeze-thaw cycles under vacuum. Then the tube was sealed with the sample frozen under vacuum. For analysis, the tubes were allowed to cool to 25° (-78° if methane and ethylene are present),opened carefully, a quenching reagent added if appropriate, and the tubes capped with a no-air stopper. At least 200 tubes of this size have been heated to 120° without one exploding.

cis-Dimethylbis(tri-n-butylphosphine)platinum(II). 1,5-(Cyclooctadiene)platinum dichloride[24] (0.40 g, 1.1 mmol) was stirred in 20 ml of ether at 0°. Methylmagnesium bromide (3.7 mmol in 1.5 ml of ether) was added and the solution stirred for 20 min at 0° and 20 min while warming to 25°. The reaction is quenched with water at 0°. The organic phase (containing (COD)$PtMe_2$[23]) was washed with water, dried, and filtered onto 0.5 ml (2.2 mmol) of tri-n-butylphosphine. The solution was allowed to stand for 12 hr, then the solvent was removed at reduced pressure. The oily residue was taken up in a minimum of methanol at 40° and water was added dropwise until cloudiness persisted.

A few drops of methanol were added to clarify the solution. It was then cooled to -20° for 24 hr with a few seed crystals, yielding 0.38 g (55%), mp 49-50°, nmr(CD_2Cl_2) δ 1.6(m, 36H, P-$CH_2CH_2CH_2$-), 1.0(m, 18H, an approximate triplet for P-C_3H_6-CH_3), 0.41(m, 6H, Pt-CH_3, an AXY pseudo-quartet due to two magnetically non-equivalent phophorous nuclei, J_{PH} = 5 and 6, with satellites due to Pt^{197} (s = 1/2), J_{PtH} = 68).

Anal. Calc. for $C_{26}H_{60}P_2Pt$: C, 49.58; H, 9.60. Found: C, 50.03; H, 9.95.

cis-Dimethylbis(triphenylphosphine)platinum(II), 2. (Cyclooctadiene)platinum dichloride (1.13 g, 3.02 mmol) was suspended in 40 ml of ethyl ether by rapid stirring at 0°. An ether solution of methylmagnesium bromide (10 mmol in 4 ml) was added by syringe. The reaction mixture was stirred for 20 min at 0° and 20 min while warming to 25°. The solution was recooled to 0° and carefully quenched with 20 ml of water. The organic phase was washed with water, dried, and filtered onto 1.6 g (6.1 mmol) of triphenyphosphine. The solution was briefly purged with argon, then let stand for two hours. A copious white precipitate of 2 soon forms. The solvent was removed at reduced pressure

and the solid recrystallized from ethanol-methylene chloride[25],

(25) Recrystallizations from CH_2Cl_2-EtOH were carried out in the following manner. A 1 g sample was dissolved in 15 ml of CH_2Cl_2 and placed on a steam bath. As the solvent boiled away it was replaced by EtOH from a dropper to maintain the solution volume. This process was continued until the first sign of crystallization. The sample was allowed to slowly cool to 25° and then stored overnight at 3°.

yielding 1.78 g (79%), mp (dec) 235°. The nmr spectrum was identical to that reported previously[26]: nmr($CDCl_3$) δ 7.40, 7.20 (m, 30H, P-Ph, two broad, overlapping multiplets),

(26) E.O. Greaves, R. Bruce, and P.M. Maitlis, J. Chem. Soc., Chem. Comm., 860 (1967). For Pt-CH_3, they give δ 0.37, J_{PtH} = 69.

0.38(m, 3H, Pt-CH_3, an AXY "pseudo-quartet" with J_{PH} = 6 and 8 and satellites due to J_{PtH} = 70)

cis-Dimethylbis(para-t-butylphenyldiphenylphosphine) platinum(II), 2t, was prepared in the same manner as 2 from 0.45 g (1.25 mmol) of (COD)$PtCl_2$, 2 ml of CH_3MgBr (5 mmol), and 0.80 g (2.5 mmol) of para-t-butylphenyldiphenylphosphine[24]. A 0.68 g yield (63%) was obtained, mp (dec) 232-234°, nmr($CDCl_3$) δ 7.35, 7.20(m, 28H, P-Ph), 1.28(s, 18H,

$-C(CH_3)_3$), 0.45(AXY, 6H, J_{PH} = 8.5, 6.5, J_{PtH} = 70)

cis-Dibenzylbis(triphenylphosphine)platinum(II), 3, was prepared in a similar manner to that reported[24] previously but without isolation of the intermediate. (COD)$PtCl_2$ (0.37 g, 1.0 mmol) was stirred in 30 ml of ethyl ether at 0°. Benzylmagnesium chloride (3 mmol in 2 ml of ether) was added. After 30 min at 0° and 30 min while warming to 25°, 2 ml of absolute ethanol was added to destroy excess Grignard reagent and the solution filtered onto 0.55 g (2.1 mmol) of triphenylphosphine. After one hour the solvent was removed at reduced pressure and the solid recrystallized from CH_2Cl_2-EtOH[25], yielding 0.684 g (76%) of light yellow crystals, mp (dec) 150-152° (lit[24] 148°). The nmr spectrum was identical to that reported by White[24].

cis-Dineopentylbis(triphenylphosphine)platinum(II), 5.[29]

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(29) Prepared previously[24] in situ but not isolated in pure form. The decomposition of 5 at room temperature in chloroform[24] appears to be due to reaction with the solvent since solutions are stable for several days in methylene chloride.

(COD)$PtCl_2$ (0.19 g, 0.5 mmol) was stirred in 25 ml of ethyl

ether at -20°. Neopentyllithium[30] (1.2 mmol in 2 ml of

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(30) D.E. Applequist and D.F. O'Brien, J. Amer. Chem. Soc., 88, 743 (1963)

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hexane) was introduced by syringe and the reaction mixture stirred for 0.5 hr. until a clear solution was obtained. The solution was allowed to warm to 0° and the excess lithium reagent destroyed with water. The organic layer was dried and the solvent removed at reduced pressure. The solid residue was dissolved in 6 ml of methylene chloride containing 0.26 g (1.0 mmol) of triphenylphosphine. The displacement reaction could be monitored by nmr. The t-butyl resonance at δ 1.0 in the cyclooctadiene complex is replaced by a δ 0.82 resonance in the triphenylphosphine complex. The reaction was complete after two hours and the volume reduced to 2 ml in a stream of argon. The solution was then diluted to 12 ml with absolute ethanol and stored at -16° for 18 hr, yielding 0.217 g (52%) of pale yellow crystals, mp(dec) 130-135°, nmr(CD_2Cl_2) δ 7.4, 7.2(m, 30H, P-Ph), 1.81(m, 4H, AXY pattern for Pt-CH_2-, J_{PH} = 21,7 and J_{PtH} = 78, 0.82 (s, 18H, -$C(CH_3)_3$).

Anal. Calc. for $C_{46}H_{52}P_2Pt$: C, 64.10; H, 6.08. Found: C, 64.24; H, 6.44.

cis-Di-p-methylbenzylbis(triphenylphosphine)platinum(II), 3a. p-Methylbenzylmagnesium chloride (2.4 mmol in ether) was added to a suspension of $(CODPt)Cl_2$ (0.375 g, 1.0 mmol) in 25 ml of ethyl ether at 0°. The reaction mixture was stirred for 45 min at 0° and 45 min at 25°. Excess Grignard reagent was destroyed with 1 ml of ethanol. The solution was filtered, then stirred with 0.55 g(2.2 mmol) of triphenylphosphine for one hour. The solvent was removed at reduced pressure and the crude product was washed with water and ethanol. Recrystallization from ethanol-methylene chloride[25] yielded 0.644 g (70%) of light yellow crystals, mp (dec) 200°, nmr($CDCl_3$) δ 7.35, 7.25(m, 30H, P-Ph), 6.93(m, 8H, $PtCH_2C_6H_4$-), 2.77(m, 4H, AXY pattern for Pt-CH_2-, J_{PH} = 11, 8, with satellites due to J_{PtH} = 90).

Anal. Calc. for $C_{52}H_{48}P_2Pt$: C, 67.17; H, 5.20. Found: C, 67.07; H, 5.49.

Thermolysis of 2 in methylene chloride. Isolation of trans-chloro(methyl)bis(triphenylphosphine)platinum(II), 6. Compound 2 (0.202 g, 0.27 mmol) was placed in an 8- mm Pyrex tube with three ml of methylene chloride. The sample was degassed by three freeze-thaw cycles at 0.02 torr and the tube sealed under vacuum. The tube was immersed in an oil bath at 120° with brief agitation to dissolve the

solid. After 40 hours the sample was removed from the bath and allowed to slowly cool to room temperature. In 12 hours the tube was filled with white, needle-shaped crystals. The solution was cooled to -20° for two hours, then the tube was opened and the crystals collected, washed with absolute ethanol and air dried. The yield was 0.195g, 94%, mp (dec) 291-293°. The compound precipitates silver chloride when treated with Ag(I) in solution, and therefore is a chloro complex. It was identified by its nmr spectrum[27] and elemental analysis as trans-chloro

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(27) C.D. Cook, and K. Y. Wan, J. Amer. Chem Soc., 92, 2595 (1970) The authors report Pt-CH_3 at 0.01 ($CDCl_3$), J_{PH} = 6.5, J_{PtH} = 79.4.

(methyl)bis(triphenylphosphine platinum(II), nmr ($CDCl_3$) δ 7.41, 7.20 (m, 30H, P-Ph), 0.02(t, 3H, J_{PH} = 6.4 with satellites due to J_{PtH} = 79)

Anal. Calc for $C_{37}H_{33}P_2PtCl$: C, 57.70; H, 4.32. Found: C, 57.29; H, 4.33.

Reaction of 2 and $(Ph_3P)_2PtCl_2$ by nmr. Compound 2 (0.032 g, 0.043 mmol) and $(Ph_3P)_2PtCl_2$ (0.036 g, 0.045 mmol) were placed in a medium wall nmr tube with 0.5 ml of methylene chloride. The solution was degassed by three freeze-

thaw cycles and the tube was sealed under vacuum. The tube was heated to 120° and nmr spectra were taken at intervals. The ratio of 2 to 6 was determined by measuring the area of the methyl signals at δ 0.38 (2) and δ 0.02 (6). Since 6 has only one methyl group its signal was multiplied by two giving the results in Table 5.

Thermolysis of 2 by nmr. A 0.032 g sample (0.043 mmol) of 2 was sealed in a medium wall nmr tube with 0.5 ml of methylene chloride as above. The tube was heated to 120° and the nmr spectrum taken at intervals. The results are in Table 6.

cis-Diiodobis(triphenylphosphine)platinum(II)[28]. Bis(triphenylphosphine)platinum dichloride (2.0 g, 2.5 mmol) was heated on a steam bath with 20 g of potassium iodide in 40 ml each of acetone, chloroform, ethanol, and water.

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(28) S.H. Mastin, Ph.D. Thesis, UCLA, Los Angeles, Cal. (1968), p. 60.

When the chloroform layer had boiled off, the reaction mixture was allowed to cool and the bright yellow solid collected and washed with water, ethanol, and ethyl ether. The compound was recrystallized from methylene chloride

yielding 1.96 g (80%), mp (dec) 302-304° (lit[28] 303-304°).

Reaction of 2 with $(Ph_3P)_2PtI_2$. Compound 2 (0.038 g, 0.05 mmol) and $(Ph_3P)_2PtI_2$ (0.049 g, 0.05 mmol) were heated to 120° in 0.6 ml of methylene chloride in a sealed nmr tube. After one hour the nmr spectrum was taken. Only trans-iodo(methyl)bis(triphenylphosphine)platinum(II) could be detected. The spectrum[27] is very similar to that of 6 except that the methyl triplet is at δ 0.10.

Methylene-carbene trapping by cyclohexene, norbornene, and 1-heptene. The reactions were run in the usual fashion in sealed tubes at 120° for 40 hr with the olefin in 10-fold excess. The solutions were 0.1 M in platinum complex and 1.0 M in olefin. Authentic samples of the cyclopropanes were prepared by reaction of the olefin with a modified[31] Simmons-Smith reagent. 2-Methylenenorbornane was prepared by a Wittig reaction on norcamphor. Glc analysis were performed on column D with the olefin serving as an internal standard.

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(31) R.J. Rawson and I.T. Harrison, J. Org. Chem., 35, 2057 (1970)

Biographical Sketch

The author was born on March 23, 1947 in Boston, Massachusetts. After attending local schools, he entered Boston College and graduated magna cum laude with a B.S. in chemistry. He entered the Massachusetts Institute of Technology in September, 1967, but attended for only one year. (General Hershey made him an offer he could not refuse.) After an all-expenses-paid tour of the Far East, Oklahoma, and other scenic locations, the author returned to M.I.T. to work for Professor George M. Whitesides in organometallic chemistry. He has accepted a position with American Cyanamid Company of Stanford, Connecticut.