

Preparation and Thermal Decomposition of Platinum(II) Metalloacycles¹

Sir:







We wish to report the preparation of several bis(tertiary phosphine)platinum(II) metalloacycles, and kinetic evidence indicating that certain of these substances have much higher thermal stability than analogous acyclic dialkylplatinum(II) compounds. Metalloacycles are of current interest for two reasons. First, members of this class of compounds have been implicated as intermediates in a number of transition metal catalyzed reactions, particularly [2 + 2] cycloadditions of olefins,² olefin metatheses,³ and isomerizations of strained carbocyclic rings.⁴ Second, several lines of evidence suggest that the elimination of a metal hydride is an important, although not necessarily rate-determining,⁵ step in the thermal decomposition of many transition metal alkyls.⁶ Since these eliminations probably occur most readily from conformations of the organometallic compounds in which M-C-C-H dihedral angles are 0°, incorporation of β-CH moieties into a tetramethylene metallocycle, in which M-C-C-H dihedral angles would be greater than 90°, would be predicted to result in a decrease in the rate of thermal decomposition, relative to an acyclic analog, by inhibiting metal hydride elimination.

The potential importance of metalloacyclic intermediates has prompted us to examine the chemistry of representative examples of these substances. The thermal decomposition of di-*n*-alkylbis(triphenylphosphine)platinum(II) had previously proved amenable to detailed mechanistic study;⁵ here, we have extended this investigation to corresponding platinocyclic complexes, and have found that five- and six-membered platinum-containing ring compounds have remarkable thermal stability, with half-lives for thermal decomposition >10⁴ that of acyclic analogs.

Platinocyclic compounds 3-8 were prepared by the reaction of the appropriate di-Grignard reagents with dichloro(1,5-cyclooctadiene)platinum(II) in ether,⁷ followed by displacement of 1,5-cyclooctadiene from the resulting intermediate (1,5-cyclooctadiene)platinum(II) platinocycles by tertiary phosphines without isolation; 3 and 7 have also been prepared by the reaction of *cis*-dichlorobis(triphenylphosphine)platinum(II) with 1,4-dilithiobutane and 1,5-dilithiopentane, respectively.⁸ These compounds have been adequately characterized by elemental analysis, molecular weight determination, and nmr spectroscopy. Their thermal decompositions were carried out in carefully purified, degassed, methylene chloride solutions, using procedures described pre-

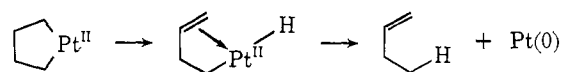
viously.⁵ Rates of decomposition were first order in platinocycle up to 60% decomposition, except where noted. Rates and organic products of decompositions are summarized in Table I.

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

No.	Compd	Rate at		Decomp Products (%)			
		60°	120°	<i>n</i> -Al-	1-Al-	2-Al-	Diene ^b
1	L ₂ PtEt ₂	4.5		50	50	0	0
2	L ₂ Pt(<i>n</i> -Bu) ₂	3.8	9000 ^c	50	49	1	0
3	L ₂ Pt 		0.53	0	78	20	2
4	DiphosPt 		0.17	0	93	7	0
5	L ₂ Pt 		1.0	0	70	25	5
6	L ₂ Pt 		<i>d</i>	10	27	37	26
7	L ₂ Pt 		0.40	0	75	17	8
8	L ₂ Pt 		1.7	0	83	17	0

^a L = PPh₃; the initial concentration of the platinum complex was 0.025 M. Yields are relative; absolute yields were between 95 and 100%. ^b Predominantly α,ω. ^c This value was obtained by extrapolation of kinetic data obtained at 50, 60, and 70°. ^d A mixture of two platinum complexes, epimeric with respect to geometry of the methyl groups, was used. Qualitative kinetics indicated that both decomposed with rates comparable to that of 3 and 5.

Two features of these data are significant. First, the platinocycles 3-7 are markedly more stable thermally than are the acyclic platinum(II) alkyls 1 and 2 or the larger and conformationally more mobile platinocycle 8. It is particularly noteworthy that the presence of one (5) or two (6) secondary C-Pt bonds results in little decrease in this thermal stability; organometallic derivatives of secondary alkyl groups are commonly less stable than those of primary alkyl moieties. Second, the products of the decompositions of 3-7 suggest that the broad outline of the mechanism by which they are produced resembles that established for 2;⁵ *viz.* initial metal hydride elimination, followed by reductive elimination of alkene from an intermediate hydrido-platinum(II) alkyl. In accord with this mechanism,



less than 5% of one deuterium atom is incorporated into the 1-butene formed on decomposition of 3 in methylene-*d*₂ chloride solution, or on decomposition of cyclotetramethylenebis(triphenylphosphine-*d*₁)platinum(II). No carbon-carbon bond cleavage is observed in these decompositions; 3 yields no ethylene or cyclopropane. Despite the similarity in the products of decomposition of 2 and 3, certain differences in the kinetic behavior of these substances indicate that the de-

(1) Supported by the National Science Foundation, Grant GP-28586X. Matthey Bishop, Inc., loaned generous quantities of potassium tetrachloroplatinate.

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

(3) R. H. Grubbs and T. K. Brunck, *ibid.*, **94**, 2538 (1972).

(4) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970).

(5) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *ibid.*, **94**, 5258 (1972).

(6) W. Mowat, *et al.*, *J. Chem. Soc., Dalton Trans.*, 533 (1972); P. S. Braterman and R. J. Cross, *ibid.*, 657 (1972); B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, **94**, 2512 (1972).

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

(8) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

tails of the mechanisms of their thermal decompositions differ to some extent. Thus, addition of triphenylphosphine to solutions of **2** strongly inhibits its thermal decomposition, and analogs of **2** containing bidentate phosphines are more stable than **2**; in contrast, the diphos complex **4** is only moderately more stable than **3**, and addition of triphenylphosphine to solutions of **3** increases the rate of decomposition of this complex.⁹

Although we cannot yet provide detailed mechanisms for the thermal decomposition of the platinumocycles **3–7**, the observation that all of these substances show high thermal stability indicates that resistance to thermal decomposition involving metal hydride elimination is a characteristic of this structural class, and not a peculiarity of one or two isolated platinum complexes. If the same property extends to metallocyclic derivatives of other metals, modes of thermal decomposition other than β -hydride elimination—particularly reductive elimination of two alkyl moieties with carbon–carbon bond formation and fragmentation of carbon skeletons with cleavage of carbon–carbon bonds—should be correspondingly more accessible for these substances than for analogous acyclic derivatives of these metals. Since reactions of these latter types probably form the basis for many of the catalytic reactions in which metallocyclic compounds appear most promising as intermediates,^{2–4} it seems possible that reaction sequences generating metallocyclic rings may offer the opportunity for unusual types of chemical transformations, by the simple expedient of suppressing the metal hydride elimination that dominates much of the chemistry of related acyclic intermediates.

(9) The rate constant for decomposition of **3** in the presence of added triphenylphosphine is given approximately by the expression $k = k_1 + k_2[\text{PPh}_3]$, with $k_2 = 2.8 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$.

(10) John A. Lyons Fellow, 1972–1973.

(11) National Institutes of Health Predoctoral Fellow, 1968–1972.

Joseph X. McDermott,¹⁰ John F. White,¹¹ George M. Whitesides*
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received March 30, 1973

Isolation of a Tetrahedral Intermediate in an Acetyl Transfer Reaction

Sir:

The past 15 years have witnessed the amassing of a large body of experimental data on the mechanism of acyl transfer reactions.¹ Central to these mechanisms is the mode of disposition of tetrahedral addition intermediates of acyl functions.² Tetrahedral intermediates have been established to exist *via* both kinetic and ¹⁸O exchange studies. The most noteworthy example has been found perhaps in the hydrolysis of ethyl trifluorothiolacetate where conclusions based on kinetic results³ were later confirmed by oxygen exchange experiments.⁴ We report herein the first isolation and unequivocal

(1) (a) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. I, W. A. Benjamin, New York, N. Y., 1966; (b) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969; (c) M. L. Bender, "Mechanisms of Homogeneous Catalysis from Proton to Proteins," Wiley-Interscience, New York, N. Y., 1971.

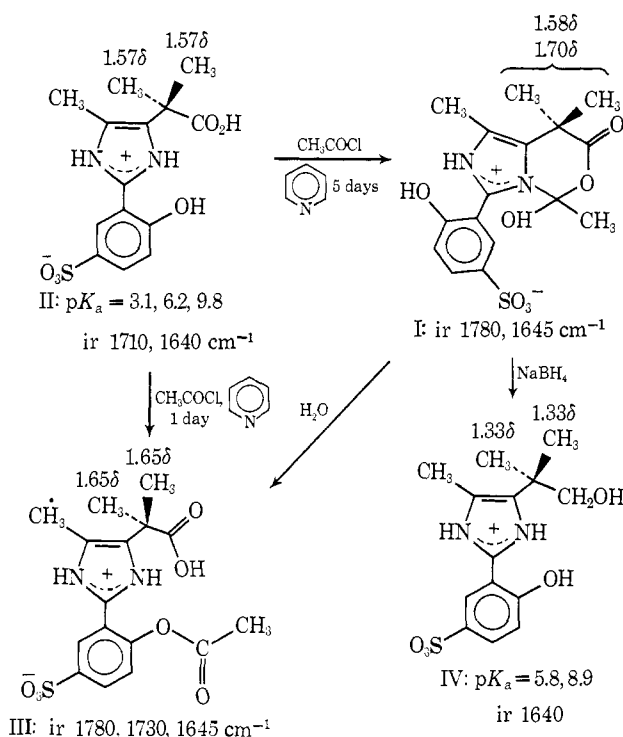
(2) W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972).

(3) L. R. Fedor and T. C. Bruice, *J. Amer. Chem. Soc.*, **87**, 4138 (1965).

(4) M. L. Bender and H. d-A. Heck, *ibid.*, **89**, 1211 (1967).

characterization of a labile acyl tetrahedral intermediate capable of an acyl migration.⁵ The tetrahedral compound I (Scheme I) may be viewed to result from

Scheme I



intramolecular nucleophilic attack either of the imidazole function on a mixed anhydride intermediate or the carboxylate function on an acetylimidazole intermediate.

The tetrahedral compound was prepared by treating II⁶ with 10 equiv of pyridine and 3 equiv of acetyl chloride (distilled) in dry CHCl_3 . After 5 days, the product was collected and washed with CHCl_3 and Et_2O (50–55% (sometimes >80%) yield) (melting point decomposition first detected at 160° turning dark red-brown without melting by 330°; uv (H_2O –1 M KCl, 30° at pH 4) 310, 322 (sh), and 291 nm, reacting with $t_{1/2} = 1.55$ min and isobestic points at 290 and 248 nm to give a compound exhibiting a single peak at 275 nm; ir (KBr) 1780 (CO_2R), 1645 (ImH⁺), 1180 (SO_3^-), and 1035 cm^{-1} (SO_3^-); nmr ($\text{C}_3\text{D}_3\text{N}$) δ 1.58 (s, 3), 1.70 (s, 3), 1.82 (s, 3) (this peak is not present in a sample prepared with CD_3COCl), 2.36 (s, 3), 7.19 (d, 1, $J = 8.4$ Hz), 8.41 (q, 1, $J = 8.4$, $J = 2.2$ Hz), and 9.13 ppm (d, 1, $J = 2.2$ Hz). *Anal.* Calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_7\text{S}$: C, 50.25; H, 4.74; N, 7.33; S, 8.39. Found: C, 50.53; H, 4.60; N, 7.05; S, 8.30). Proof

(5) While the isolation of other tetrahedral compounds has been reported, all are at the juncture of a fused ring system and none are capable of undergoing acyl migration. Furthermore those which are acyl tetrahedral adducts (e.g., R. G. Griot and A. J. Frey, *Tetrahedron*, **19**, 1661 (1963)) are particularly inert ("very stable" in 0.1 N NaOH) and those which are not inert (e.g., a review of Zaugg's work in ref 1a, p 169 ff) are not acyl tetrahedral intermediates.

(6) II was prepared in this laboratory and has the following physical chemical properties: mp >360°; uv (H_2O –1 M KCl, 30° at pH 5) 310 (10.4), 273 (11.5), 285 sh (10.3), and 233 nm (14.9); ir (KBr) 1710 (CO_2H), 1640 (ImH⁺), 1170 (SO_3^-), 1040 (SO_3^-), and 600 cm^{-1} (SO_3^-); nmr of K⁺ salt ($\text{DMSO}-d_6$) δ 1.57 (s, 6), 2.28 (s, 3), 6.89 (d, 1, $J = 8.5$ Hz), 7.59 (q, 1, $J = 8.5$, $J = 2$ Hz), and 8.25 ppm (d, 1, $J = 2$ Hz); pK_a (H_2O –0.1 M KCl) 3.1 (CO_2H), 6.2 (ImH⁺), and 9.8 (PhOH). *Anal.* Calcd for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_6\text{SK} \cdot \text{H}_2\text{O}$: C, 42.40; H, 4.32; N, 7.07; S, 8.09. The same sample submitted to two laboratories gave the following results: C, 42.52; H, 4.21, and C, 41.48; H, 4.20; N, 6.93; S, 7.85.