thereby accounting for 83% of the lead tetraacetate used. The relative yield of the γ-lactone II to the methyl acetate adduct I was found to vary with changes in the acetic acid/olefin ratio as shown in Figure 1. This is consistent with the free-radical chain mechanism[5] shown in Scheme I. The chain propagates *via*

$$\mathrm{Pb^{III}(OAc)_3} \longrightarrow \mathrm{Pb^{II}(OAc)_2} + \cdot\mathrm{CH_3} + \mathrm{CO_2}$$

and terminates *via*

$$\mathrm{Pb^{III}(OAc)_3} + \mathrm{R_1,\ R_2,\ or\ R_3} \longrightarrow (\mathrm{R_1\ R_2,\ or\ R_3})^+ + \mathrm{Pb^{II}(OAc)_2} + \mathrm{AcO^-}$$

In the proposed mechanism of Scheme I it is assumed that $\cdot CH_3$ and $\cdot CH_2COOH$ radicals are not readily oxidized to the corresponding carbonium ions, in contrast to the benzylic radical which should be rapidly oxidized,[6] owing to their relatively high ionization potentials.[7]

The linear dependence of the lactone/methyl acetate adduct ratio on the acetic acid/olefin ratio is consistent with our proposed mechanism, in which a free methyl radical reacts either with the olefin or with the acetic acid.[8]

The allylic acetate IV is formed predominantly *via* hydrogen abstraction by methyl radical and not by the stable $\cdot CH_2COOH$ radical as indicated by the finding that the allylic acetate IV consistently represents approximately one-fifth of the methyl acetate adduct I formed irrespective of the relative ratio of I to II (*i.e.*, $k_1/k_2 \simeq 5$).[9]

Our proposed free-radical mechanism is substantiated by the finding that ultraviolet irradiation (3500 Å) at 25° yielded the same products I and II, while no reaction was observed at this temperature in the absence of light. The ratio of II/I in the photochemical reaction depended on the HOAc/olefin ratio used, just as had been observed in the thermal reaction (Figure 1).

From the slopes in Figure 1, the relative rate constants k_1/k_3 were found to be 130 for the thermal reaction at 138° and 290 for the photochemical reaction at 25°. The activation energy difference for methyl radical abstraction *vs.* addition, $E_3 - E_1$, as determined from these two slopes was equal to 1.7 kcal/mole. An identical value was obtained by comparison of thermal reactions performed at 80 and 138°.

The formation of γ-lactones as well as methyl acetate adducts was observed with all the olefins studied; namely, styrene, *trans*- and *cis*-β-methylstyrene, and octene-1. From the ratio of methyl acetate adduct/lactone obtained with various olefins, when the oxidation with lead tetraacetate was carried out under identical experimental conditions, it was possible to calculate the relative reactivity of these olefins toward the addition of methyl radicals.

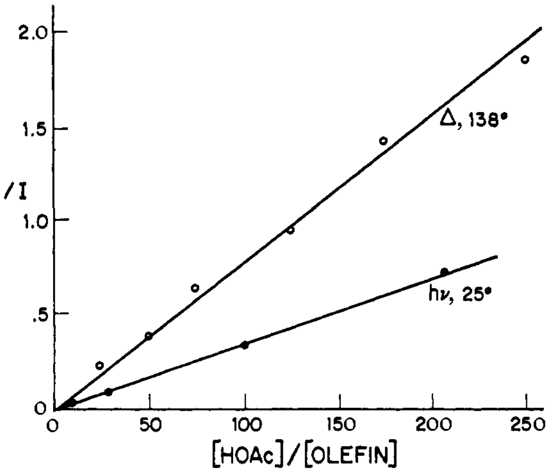

Figure 1. Effect of acetic acid/olefin ratio on the product ratio II/I.

The relative reactivities at 138° so obtained were as follows: styrene (12), *trans*-β-methylstyrene (1), *cis*-β-methylstyrene (0.33), and octene-1 (0.14). The order of reactivity agrees well with that reported for methyl radical generated in other ways.[10]

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[5] The free-radical nature of the reaction is indicated by the fact that the relative yield of I and II is decreased upon the addition of oxygen or radical inhibitors such as 4-*t*-butylcatechol.

[6] J. J. Kochi, J. D. Bacha, and T. W. Bethea, *J. Am. Chem. Soc.*, **89**, 6538 (1967).

[7] The gas-phase IP of $\cdot CH_3$ = 9.83 eV, and the IP of $\cdot CH_2COOH$ is expected to be similar to that of cyanomethyl radical whose IP = 10.87 eV, while that of the benzylic radical is 7.76 eV: R. W. Kaiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 319.

[8] Norman and Thomas[4] proposed that formation of the methyl acetate adduct in the reaction of styrene with $Pb(OAc)_4$ is initiated by molecule-induced homolysis involving no free methyl radicals.

[9] From our studies with toluene[1] we have found that $k_{\text{addition}}/k_{\text{abstraction}}$ for $\cdot CH_2COOH$ is considerably larger than that for methyl radical. Therefore one might expect the ratio of k_1/k_2 for $\cdot CH_2COOH$ to be quite large, so that only addition is observed with β-methylstyrene.[1]

[10] F. Carrock and M. Szwarc, *J. Am. Chem. Soc.*, **81**, 4138 (1959), reported relative reactivities of styrene (9), *trans*-β-methylstyrene (1), *cis*-β-methystyrene (0.43), and propylene (0.25) at 65° using acetyl peroxide and isooctane as a solvent. Considering the temperature difference, our values appear to indicate that methyl radical generated from $Pb(OAc)_4$ in acetic acid containing $Pb(OAc)_4$ is somewhat more selective. This difference in selectivity may be attributed to either a solvent effect or to the possible complexing of methyl radicals with either Pb^{III} or Pb^{II} generated during the course of the reaction.

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Five-Coordinate Complexes of Platinum(II) and Palladium(II)

Sir:

Square-planar complexes of iron group elements are thought to undergo ligand substitution by a mechanism which involves the formation of five-coordinate species either as an activated complex or a metastable intermediate.[1] No direct evidence has appeared to substantiate the formation of the metastable intermediate with platinum or palladium complexes, but numerous examples of crystalline five-coordinate iron group complexes[1-3] are known.

We report here direct nuclear magnetic resonance spectral evidence for five-coordinate complexes formed as intermediates. Adduct formation clearly precedes ligand substitution in reactions of xanthates and dithiocarbamates of palladium(II) and platinum(II) with methyldiphenylphosphine.

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[1] F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 376; L. Cattalini, A. Orio, and M. L. Tobe, *J. Am. Chem. Soc.*, **89**, 3130 (1967).

[2] R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stollberg, *ibid.*, **87**, 658 (1965).

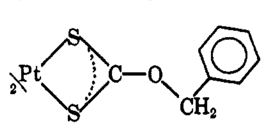
[3] See, for example, E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1967).

Table I. Nmr Spectra of Complexes

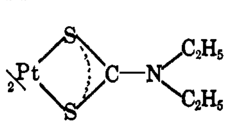
Compound[a]	Position in τ units		
	CH$_3$(Phos)		Other
Pt(S$_2$COCH$_3$Ph)$_2$			C$_6$H$_5$, 2.56 (5);[b] CH$_2$, 4.24 (2)
Pt(S$_2$COCH$_2$Ph)$_2$(Ph$_2$PCH$_3$)	7.80 (3)	$J_{(P-H)}{}^c = 11$ $J_{(Pt-H)} = 40$	C$_6$H$_5$, 2.60 (20); CH$_2$, 4.32 (4)
Pt(S$_2$COEt)$_2$			CH$_3$, 8.45 (3), $J = 7$; CH$_2$, 5.30 (2)
Pt(S$_2$COEt)$_2$(Ph$_2$PCH$_3$)	7.80 (3)	$J_{(P-H)} = 11$ $J_{(Pt-H)} = 41$	CH$_3$, 8.60 (6), $J = 7$; CH$_2$, 5.42 (4)
Pt(S$_2$CNEt$_2$)$_2$			CH$_3$, 8.70 (3), $J = 7$; CH$_2$, 6.40 (2)
Pt(S$_2$CNEt$_2$)$_2$(Ph$_2$PCH$_3$)	7.72 (3)	$J_{(P-H)} = 10$ $J_{(Pt-H)} = 38$	CH$_3$, 8.80 (12), $J = 7$; CH$_2$, 6.26 (8)
Pt(S$_2$COC$_3$H$_5$)$_2$			C$_3$H$_5$, complex multiplet 5.0–3.5
Pt(S$_2$COC$_3$H$_5$)$_2$(Ph$_2$PCH$_3$)	7.77	$J_{(P-H)} = 11$ $J_{(Pt-H)} = 41$	C$_3$H$_5$, complex multiplet 5.0–3.5
Pd(S$_2$COCH$_2$Ph)$_2$			C$_6$H$_5$, 2.54 (5); CH$_2$, 4.36 (2)
Pd(S$_2$COCH$_2$Ph)$_2$(Ph$_2$PCH$_3$)	7.92 (3)	$J_{(P-H)} = 11$	C$_6$H$_5$, 2.58 (20); CH$_2$, 4.43 (4)
Pt(Ph$_2$PCH$_3$)$_2$S$_2$CO	8.17 (3)	Complex triplet $J_{(Pt-H)} = 32$	C$_6$H$_5$, 2.57 (10)
Pd(Ph$_2$PCH$_3$)$_2$S$_2$CO	8.32 (3)	Complex triplet	C$_6$H$_5$, 2.66 (10)

[a] Ph = phenyl, Et = ethyl. [b] Numbers in parentheses indicate normalized integrated intensities. [c] Cycles/second.

When methyldiphenylphosphine, MePh$_2$P, is added to a CDCl$_3$ solution of bis(O-benzylxanthato)platinum(II) (I), the methyl resonance appears as a set of three symmetric doublets, the central one having an intensity approximately four times that of the outer doublet (Figure 1). Since platinum has 33.7% abundance of ^{195}Pt ($I_s = 1/2$), the resonances centered about τ 7.80 are interpreted to give $J_{^{31}P-H} = 11$ cps and $J_{^{195}Pt-H} = 40$ cps, results in close agreement to those obtained by Shaw and Jenkins[4] for some planar dimethylphenylphosphine complexes of platinum(II). *Thus the platinum methyl-hydrogen coupling shows directly that phosphine bonding to the platinum(II) occurs in the complex.*



I



II

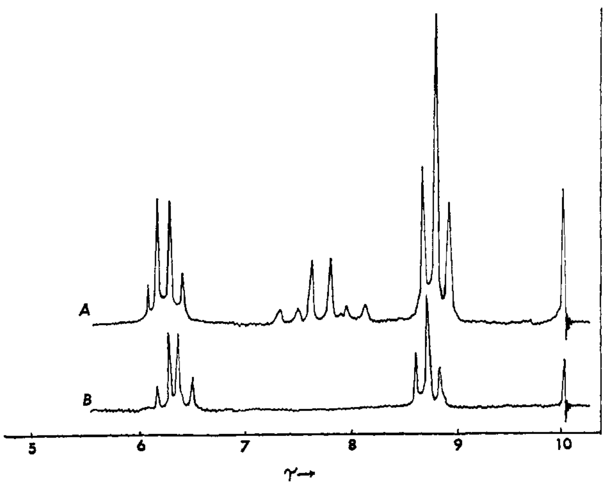


Figure 1. Platinum(II) diethyldithiocarbamate: (A) with Ph$_2$P(CH$_3$), (B) without Ph$_2$P(CH$_3$).

When I is titrated spectrophotometrically in CHCl$_3$ with triphenylphosphine, Ph$_3$P, at ambient temperatures, evidence is obtained for the equilibrium formation of a 1:1 adduct. An isosbestic point is found at 24,500 cm^{-1} with $K_{\text{form}} \sim 1.6 \times 10^4\ M^{-1}$.

An adduct also is obtained when bis(*p*-dithiocumato)platinum(II) reacts with diphenylmethylphosphine. The 1:1 adduct with this base has been isolated and analyzed as a crystalline solid. Its nmr spectrum in CHCl$_3$ at −40° shows a P–CH$_3$ pattern similar to that presented in Figure 1. At room temperature the peaks are considerably broadened and the ^{195}Pt–CH$_3$ coupling is not observed above room temperature. The temperature-dependent spectrum has been analyzed in terms of phosphine exchange. The resulting kinetic activation parameters will be reported elsewhere.

The reaction of at least 2 molar equiv of phosphine with platinum(II) and palladium(II) xanthates leads to the subsequent formation of stable products which appear to contain carbonyl sulfide coordinated to the metal,[5] *e.g.*, (Ph$_2$PCH$_3$)$_2$Pt(COS)$_2$ or (Ph$_3$P)$_2$Pt(S$_2$CO)·CHCl$_3$. The formation of this type of product is complete within a few minutes when excess phosphine is added to the solutions (Table I).

The formulation of the metal-containing reaction product of the phosphines with platinum(II) [or palladium(II)] xanthates as a S$_2$CO^{2-} complex is based on chemical analysis (C, H, and S), molecular weight (in CHCl$_3$), mass spectrum (large *m/e* 60 peak), qualitative glpc of pyrolysis products in which COS is a prominent species, infrared spectrum with CO peaks at 1670 and 1610 cm^{-1}, and identification of the organic reaction products. Since this chemistry is exceedingly complex [as witnessed by the observation that CHCl$_3$ solutions of PtS$_2$CO(PPh$_2$CH$_3$)$_2$ react with benzyl bromide to produce benzyl disulfide quantitatively], we prefer to postpone for the present a complete description of the xanthate product.

Diethyldithiocarbamate complexes of palladium(II) and platinum(II), II, react only slowly (hours) with excess diphenylmethylphosphine to produce what appear to be phosphine-coordinated substitution products.[6] Evi-

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[4] B. L. Shaw and M. M. Jenkins, *J. Chem. Soc., A*, 770 (1966).

[5] J. P. Fackler, Jr., W. C. Seidel, D. Coucouvanis, and J. Mayhew, to be published.

[6] The reactions have not been characterized completely to date.

dence that the phosphine forms an adduct first is observed in the nmr spectrum (Figure 1) where the "triplet" centered near τ 7.8 arises from the previously described pattern arising from Pt–H and P–H coupling.

The geometry of the five-coordinate phosphine adduct of II cannot be unequivocally determined from the nmr data, but certain limitations are placed on this geometry by the observation of sharp, unsplit ethyl resonances. (1) The complex may be square pyramidal with symmetry equivalent ethyl groups and a lifetime long on the nmr time scale. (2) The complex may be either square pyramidal or essentially trigonal bipyramidal with rapid rotation about the $S_2C–N$ bond equilibrating the ethyl groups. (3) The ground-state geometry may be trigonal bipyramidal with a lifetime short on the nmr time scale. Further studies are necessary to distinguish between these possibilities.[7]

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[7] This work was supported in part by the National Science Foundation, GP-7889, and by the Donors of the Petroleum Research Fund, as administered by the American Chemical Society.

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Sulfur Dioxide Insertion. V. A New Mode of Addition of Sulfur Dioxide to a Metal–Carbon Bond[1]

Sir:

The reactions between sulfur dioxide and complexes containing transition metal–carbon σ bonds have invariably afforded addition products with a sulfone ($M–SO_2–C$) type linkage (S-sulfinates).[2,3] In the case of σ-allyl (2-alkenyl) complexes, rearrangement of the hydrocarbon moiety frequently accompanies such insertion.[1,4]

This latter observation prompted us to investigate reactions between sulfur dioxide and 2-alkynylmetal compounds in order to ascertain whether the insertion occurs with rearrangement to the 1,2-alkadienylsulfinato derivatives (1).

$$M—CH_2—C\equiv C—R + SO_2 \longrightarrow M—SO_2—C(R)═C═CH_2 \quad (1)$$

The complex $Mn(CO)_5CH_2C\equiv CH$ (**1**) was synthesized by a slow addition of $NaMn(CO)_5$ (prepared from 2.0 g of $Mn_2(CO)_{10}$ and excess sodium amalgam[5]) to 1.54 g (0.013 mole) of propargyl bromide in tetrahydrofuran at 0° followed by vigorous stirring for 1.5 hr. The solution was then filtered through Zeolite, the solvent was removed *in vacuo* at 0°, and the residue was sublimed at 25° (~0.1 mm) onto a probe cooled to −78°. The yield of a light yellow solid was 2.26 g (90%). *Anal.* Calcd for $C_8H_3O_5Mn$: Mn, 23.5. Found: Mn, 23.4. The product is extremely temperature sensitive, decomposing rapidly at 25°. However, it can be stored indefinitely at −78° and appears to be unaffected by air.

The infrared spectrum of **1** in the carbonyl stretching region consists of the absorption bands assigned as follows: 2118 (w), A_1 (CO); 2099 (vw), $C\equiv C$;[6] 2056 (w), B (CO); 2022 (vs), E (CO); 1990 (s), A_1 (CO); and 1975 cm^{-1} (vw), ^{13}CO (cyclohexane solution). The proton magnetic resonance spectrum exhibits a doublet at τ 8.64 and a 1:2:1 triplet at τ 7.79 ($J \sim 3$ cps), the relative intensities being 2:1, consistent with the presence of the 2-propynylmanganese moiety ($MnCH_2C\equiv CH$). To our knowledge, this compound represents the first authentic 2-alkynyl derivative of a transition metal.[7–9]

The interaction of 2-propynylmanganese pentacarbonyl with SO_2 in pentane at 25° leads to a rapid deposition of a light yellow solid. The reaction is complete within 15 min, affording a nearly quantitative yield of the product. After removal of the solvent, the residue crystallizes from chloroform–pentane. Additional purification may be effected by sublimation at 75° (~0.1 mm) to produce white needles (**2**), mp *ca.* 112° (dec). *Anal.* Calcd for $C_8H_3O_7SMn$: C, 32.25; H, 1.15; S, 10.74; mol wt, 298. Found: C, 32.42; H, 1.18; S, 10.56; mol wt (osmometry in $CHCl_3$), 304, 295, 289. A virtually quantitative yield of the compound has been also obtained from $Mn(CO)_5CH_2C\equiv CH$ and liquid SO_2 at −70°.

The structure of the product may be arrived at with the aid of infrared and proton magnetic resonance spectroscopy. The carbonyl stretching frequency region of the infrared spectrum consists of absorptions at 2128 (m), 2068 (w), 2035 (vs), and 2010 cm^{-1} (s) (CCl_4 solution). The relative positions and intensities of these bands are similar to those found for a number of $Mn(CO)_5(SO_2R)$ complexes[1,2,10,11] and support the presence of a pentacarbonyl moiety in conjunction with an Mn–S bond. In the 1300–800-cm^{-1} region prominent absorptions are present at 1110 (s), 993 (w), 906 (s), and 808 cm^{-1} (m-s) (KBr pellet). The absence of sulfur–oxygen stretching frequencies in the regions 1220–1185 and 1090–1040 cm^{-1} contrasts the spectral behavior of $Mn(CO)_5(SO_2R)$ and militates against an $Mn–S(O)_2–C_3H_3$ structural assignment. However, the absorptions at 1110 and either 906 or 808 cm^{-1} may be attributed to the SO stretching frequencies in an $Mn–S(O)–O–C_3H_3$ linkage.[12,13]

The nmr spectrum of **2** (Figure 1) shows a 1:2:1 triplet at τ 3.52 ($J \sim 2.5$ cps) and a quartet in the region τ 4.28–5.03, each component of which is split into a doublet (separation ~2.5 cps). The intensities of the triplet and the two quartets are in the ratio 1:2. The complete absorption pattern is characteristic of an ABX spectrum with $J_{AX} = J_{BX}$[14] and upon analysis yields τ 4.47 and 4.84 for protons A and B and $J_{AB} \sim 15$ cps.

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[1] For part IV of this series, see F. A. Hartman, P. J. Pollick, R. L. Downs, and A. Wojcicki, *J. Am. Chem. Soc.*, **89**, 2493 (1967).

[2] F. A. Hartman and A. Wojcicki, *ibid.*, **88**, 844 (1966).

[3] J. P. Bibler and A. Wojcicki, *ibid.*, **88**, 4862 (1966).

[4] A. Wojcicki, R. L. Downs, and F. A. Hartman, Abstracts of the 3rd International Symposium on Organometallic Chemistry, Munich, Germany, 1967, p 320.

[5] R. B. King and F. G. A. Stone, *Inorg. Syn.*, 7, 198 (1963).

[6] The band was assigned on the basis of its position and relative intensity; see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 59–61.

[7] The complex $C_5H_5Fe(CO)_2CH_2C\equiv CH$, reported by Ariyaratne and Green,[8] gives the nmr spectrum showing equivalence of the three C_3H_3 protons and most likely should be reformulated as $C_5H_5Fe(CO)_2$-$C\equiv CCH_3$.[9]

[8] J. K. P. Ariyaratne and M. L. H. Green, *J. Organometal. Chem.* (Amsterdam), **1**, 90 (1963).

[9] R. L. Downs, private communication, The Ohio State University, 1967.

[10] F. A. Hartman, Ph.D. Thesis, The Ohio State University, 1966.

[11] E. Lindner and H. Weber, *Angew. Chem.*, **78**, 752 (1966).

[12] S. Detoni and D. Hadži, *J. Chem. Soc.*, 3163 (1955).

[13] S. Braverman and H. Mechoulam, *Israel J. Chem.*, **5**, 71 (1967).

[14] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, pp 89–91.