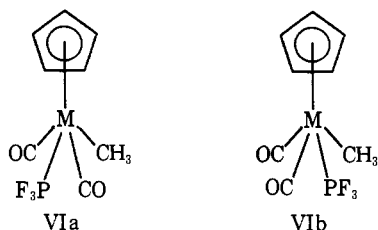


in boiling toluene thus resulted in the replacement of one carbonyl group with a trifluorophosphine ligand without any migration of the methyl group³³ from tungsten to either phosphorus or carbon.



The analogous reactions of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ with $\text{Ni}(\text{PF}_3)_4$ were also investigated. The reaction between $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{Ni}(\text{PF}_3)_4$ in boiling toluene gave a yellow crystalline solid of composition $\text{CH}_3\text{Mo}(\text{CO})_2(\text{PF}_3)(\text{C}_5\text{H}_5)$. Its infrared spectrum was similar to that of the tungsten analog $\text{CH}_3\text{W}(\text{CO})_2(\text{PF}_3)(\text{C}_5\text{H}_5)$ (VI, $\text{M} = \text{W}$), suggesting analogous structures (VI, $\text{M} = \text{Mo}$). The reaction between $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ and $\text{Ni}(\text{PF}_3)_4$ in boiling toluene gave after chromatography on Florisil an unstable liquid. The infrared spectrum of this liquid in the $\nu(\text{CO})$ region exhibited $\nu(\text{CO})$ frequencies at 2018 and 1960 cm^{-1} ,

corresponding to unreacted $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ (lit.³⁴ $\nu(\text{CO})$ for $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$, 2010 and 1955 cm^{-1}) and an additional stronger $\nu(\text{CO})$ frequency at 1982 cm^{-1} , consistent with the presence of a monocarbonyl derivative $\text{CH}_3\text{Fe}(\text{CO})(\text{PF}_3)(\text{C}_5\text{H}_5)$. The instability of this product precluded attempts to purify it further.

The work described in this paper shows that tetrakis(trifluorophosphine)nickel can serve as a source of trifluorophosphine in the synthesis of metal-trifluorophosphine complexes. In some cases the tetrakis(trifluorophosphine)nickel also acts as a dehalogenating agent. The reactions of metal carbonyls with tetrakis(trifluorophosphine)nickel proceed similarly to their reactions with phosphorus trifluoride⁸⁻¹³ in that a wide range of closely related and difficultly separable mixed metal carbonyl trifluorophosphine derivatives can be formed. Tetrakis(trifluorophosphine)nickel appears to be unsuited for the insertion of a PF_3 group into an alkyl-metal bond.

Acknowledgment. We are indebted to the National Institute of General Medical Sciences for partial support of this work under Grant No. GM-14664-03.

(34) A. Davison, J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

Pentamethylcyclopentadienyl Derivatives of Transition Metals. II. Synthesis of Pentamethylcyclopentadienyl Metal Carbonyls from 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene¹⁻³

R. B. King* and A. Efraty⁴

*Contribution from the Department of Chemistry, University of Georgia,
Athens, Georgia 30601. Received October 28, 1971*

Abstract: Reactions of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene, $(\text{CH}_3)_5\text{C}_5\text{COCH}_3$, with metal carbonyls provide a convenient route to various pentamethylcyclopentadienyl metal carbonyl derivatives. Thus the reaction of $\text{Cr}(\text{CO})_6$ with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane gives green $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$. The reaction of $\text{Mo}(\text{CO})_6$ with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane gives a mixture of yellow $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ and red $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$. Reaction of $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$ with acetylpentamethylcyclopentadiene in boiling methylcyclohexane gives yellow $\text{CH}_3\text{W}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$. Reaction of $\text{Mn}_2(\text{CO})_{10}$ with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane gives pale yellow $(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$. Reaction of $\text{Fe}(\text{CO})_5$ with acetylpentamethylcyclopentadiene in boiling 2,2,5-trimethylhexane gives red-violet $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]_2$. However, the reaction of $\text{Fe}_2(\text{CO})_9$ with acetylpentamethylcyclopentadiene in pentane at room temperature gives a mixture of the yellow waxy diene complex $[(\text{CH}_3)_5\text{C}_5\text{COCH}_3]\text{Fe}(\text{CO})_3$ and the pale yellow crystalline σ -acetyl derivative $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$. Reaction of $\text{Co}_2(\text{CO})_8$ with acetylpentamethylcyclopentadiene in boiling cyclohexane gives red crystalline $(\text{CH}_3)_5\text{C}_5\text{Co}(\text{CO})_2$. The infrared, proton nmr, and mass spectra of the new pentamethylcyclopentadienyl metal carbonyl derivatives are described.

Several years ago¹ we reported the preparations of several pentamethylcyclopentadienyl metal carbonyls by reactions of pentamethylcyclopentadiene (I)

(1) The paper, R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **8**, 287 (1967), should be considered as part I of this series since it serves as an introduction to our work with pentamethylcyclopentadienyl derivatives of transition metals.

(2) For a preliminary communication of this work, see R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **93**, 4950 (1971).

(3) Portions of this work were presented at the Fifth International Conference on Organometallic Chemistry, Moscow, U. S. S. R., August 1971, paper 235, abstracts, Vol. II, p 14.

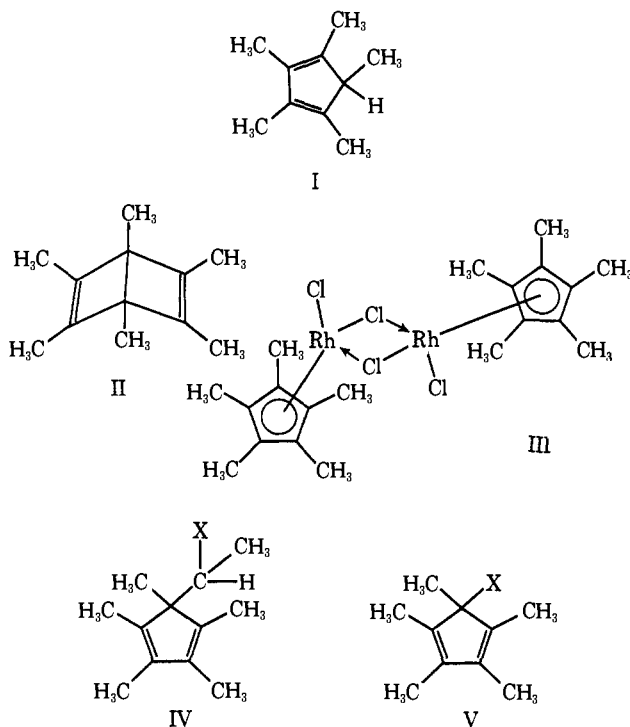
(4) Postdoctoral research associate, 1968-1971.

with various metal carbonyls. Of particular interest was the reaction of pentamethylcyclopentadiene with hexacarbonylmolybdenum which gave a red compound $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$ with a different type of stoichiometry than that of the molybdenum carbonyl derivative $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ obtained in an analogous reaction of unsubstituted cyclopentadiene with hexacarbonylmolybdenum.

This relatively early observation on pentamethylcyclopentadienylmolybdenum carbonyl chemistry demonstrated that the chemistry of the pentamethylcyclo-

pentadienyl metal carbonyls was not completely analogous to that of the unsubstituted cyclopentadienyl metal carbonyls. More detailed investigations into the chemistry of the pentamethylcyclopentadienyl metal carbonyls, therefore, became of interest. However, such investigations have been hampered by the need to employ a five-step synthesis to obtain the necessary pentamethylcyclopentadiene⁵ from commercially available starting materials. Before the chemistry of pentamethylcyclopentadienyl metal carbonyl derivatives could be investigated in sufficient detail to provide a complete comparison with known⁶ chemistry of the unsubstituted cyclopentadienyl metal carbonyl derivatives, either a more convenient and efficient synthesis of pentamethylcyclopentadiene from commercially available starting materials or a method for preparing pentamethylcyclopentadienyl metal carbonyls using a more readily available organic starting material than pentamethylcyclopentadiene was required.

The first indication that pentamethylcyclopentadienyl derivatives of transition metals might be preparable without using pentamethylcyclopentadiene itself as a starting material was the observation by Kang and Maitlis⁷ that hexamethylbicyclo[2.2.0]hexadiene ("hexamethyl-Dewar-benzene") (II) reacted with hydrated



rhodium trichloride in boiling methanol to give the pentamethylcyclopentadienyl derivative $[(\text{CH}_3)_5\text{C}_5\text{RhCl}_2]_2$ (III) in nearly quantitative yield. Further investigation into the course of this unusual reaction⁸ showed that acid was required for this rearrangement and that 5-(1-substituted ethyl) pentamethylcyclopentadienes (IV) formed by acid-catalyzed ring contraction were intermediates in this reaction. This suggested that other 5-

(5) L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

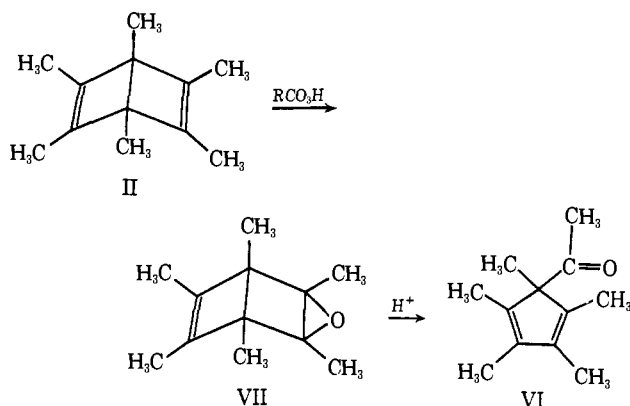
(6) For a summary of much of the known cyclopentadienylmetal carbonyl chemistry, see R. B. King, "Transition Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

(7) J. W. Kang and P. M. Maitlis, *J. Amer. Chem. Soc.*, **90**, 3259 (1968).

(8) J. W. Kang, K. Moseley, and P. M. Maitlis, *ibid.*, **91**, 5970 (1969).

substituted pentamethylcyclopentadienes of the type V might react with transition metal derivatives to form pentamethylcyclopentadienyl derivatives with removal of the substituent in the 5 position and that a promising source of such 5-substituted pentamethylcyclopentadienes of type V might be ring contraction reactions of the commercially available hexamethylbicyclo[2.2.0]hexadiene (II).

One such 5-substituted pentamethylcyclopentadiene of type V is 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene (VI) which can be prepared from the commercially available hexamethylbicyclo[2.2.0]hexadiene (II) by conversion to the monoepoxide VII followed by acid-catalyzed rearrangement according to the following sequence.^{9,10}



This conversion of hexamethylbicyclo[2.2.0]hexadiene (II) to acetylpentamethylcyclopentadiene (VI) can be performed in about 40% yield in a single laboratory operation by reaction of II with a peroxycarboxylic acid, preferably the commercially available and relatively stable *m*-chloroperoxybenzoic acid, since an acidic peroxy compound can serve the dual purpose of providing the oxygen for the epoxidation and the necessary acid to catalyze the rearrangement.

We have prepared a supply of acetylpentamethylcyclopentadiene (VI) and studied its reactions with the more readily available metal carbonyls in hydrocarbon solvents at elevated temperatures. As already indicated in our preliminary communication,² this reaction provides a convenient source of many pentamethylcyclopentadienyl metal carbonyls. Using this new synthetic method we have now been able to expand the scope of known pentamethylcyclopentadienyl metal carbonyls so that derivatives of chromium,² molybdenum,^{1,2} tungsten,² manganese,² rhenium,¹ iron,^{1,2} cobalt,¹¹ and iridium⁸ are now known. This paper describes the details of our study of the reactions between acetylpentamethylcyclopentadiene and various metal carbonyls. Later papers in this series will discuss the chemistry of the pentamethylcyclopentadienyl metal carbonyls made readily available for the first time by this new synthetic method.

Experimental Section

Microanalyses were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Meade Microanalytical Lab-

(9) H. N. Junker, W. Schäfer, and H. Nidenbrück, *Chem. Ber.*, **100**, 2508 (1967).

(10) L. A. Paquette and G. R. Krow, *Tetrahedron Lett.*, 2139 (1968).

(11) J. W. Kang and P. M. Maitlis, *J. Organometal. Chem.*, **26**, 393 (1971).

Table I. Infrared Spectra of New Pentamethylcyclopentadienyl Metal Carbonyl Derivatives Prepared in This Work

Compound	Infrared spectrum, cm^{-1}		
	$\nu(\text{CO})^a$	$\nu(\text{CH})^b$	Other ^b
$[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$	1876 (s), 1857 (s)	2986 (vw), 2960 (vw), 2918 (w)	1482 (w), 1448 (vw, sh), 1436 (w, sh), 1423 (w), 1401 (w), 1386 (m), 1379 (m), 1260 (w), 1118 (vw, sh), 1098 (vw), 1070 (w), 1027 (m), 798 (vw), 749 (vw)
$\text{CH}_3\text{W}(\text{CO})_5\text{C}_5(\text{CH}_3)_5$	2013 (s), 1920 (vs)	2981 (vw, sh), 2967 (vw), 2924 (vw), 2897 (vw)	1491 (w), 1474 (w), 1454 (vw), 1418 (vw), 1404 (vw, sh), 1398 (vw, sh), 1388 (m), 1381 (m), 1180 (vw), 1073 (vw), 1036 (w), 944 (vw), 905 (vw), 801 (vw)
$(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_5$	2017 (s), 1928 (vs)	2987 (w), 2966 (vw), 2927 (w)	1489 (w), 1475 (vw), 1453 (w), 1431 (w), 1386 (m), 1076 (w), 1035 (m)
$[(\text{CH}_3)_5\text{C}_5\text{COCH}_3\text{Fe}(\text{CO})_5]$	2041 (s), 1975 (s), 1966 (s), 1703 (m) ^c	2972 (w), 2920 (w), 2861 (vw)	1467 (vw), 1450 (w), 1382 (m), 1352 (m), 1288 (vw), 1255 (vw), 1190 (w), 1105 (vw), 1088 (vw), 1068 (w), 1027 (w), 961 (w), 798 (vw)
$\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$	2009 (s), 1945 (s), 1636 (m) ^d	2985 (vw), 2963 (vw), 2918 (vw, br)	1490 (vw), 1455 (vw, br), 1401 (vw, br), 1384 (m), 1365 (vw), 1326 (m), 1061 (m), 1033 (w), 1028 (w), 971 (vw), 910 (m)

^a These $\nu(\text{CO})$ frequencies were measured in pentane or hexane solutions. ^b These frequencies ($3500\text{--}700\text{ cm}^{-1}$) were measured in KBr pellets. ^c Acetyl (ketonic) carbonyl group. ^d Metal acyl carbonyl group (measured in a KBr pellet).

oratory, Amherst, Mass. Infrared spectra (Table I) were taken in potassium bromide pellets and in saturated hydrocarbon solvents (pentane or hexane) and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Proton nmr spectra were taken in CDCl_3 or C_6D_6 solutions and recorded at 100 Mc on a Varian HA-100 spectrometer. Melting points were obtained in capillaries and are uncorrected.

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with metal carbonyl derivatives; (b) handling filtered solutions of organometallic compounds; (c) admitting to evacuated vessels containing organometallic compounds.

Hexamethylbicyclo[2.2.0]hexadiene was purchased from Columbia Organic Chemicals, Columbia, S. C., and from Henley and Co., New York, N. Y. *m*-Chloroperoxybenzoic acid was purchased from Columbia Organic Chemicals, Columbia, S. C. The following metal carbonyls were purchased from the indicated commercial sources: $\text{Fe}(\text{CO})_5$ (GAF Corp., New York, N. Y.), $\text{Co}_2(\text{CO})_8$ (Strem Chemical Co., Danvers, Mass.), $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ (Pressure Chemical Co., Pittsburgh, Pa.). The $\text{Mn}_2(\text{CO})_{10}$ was prepared from commercial $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ (Ethyl Corp., New York, N. Y.) by the published procedure.¹² The metal carbonyls $\text{Fe}_2(\text{CO})_9$ ¹³ and $(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$)¹⁴ were prepared by the cited published procedures.

Preparation of 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene (VI). The procedure given below appears to be more reliable and convenient than the reported⁹ procedure for the conversion of hexamethylbicyclo[2.2.0]hexadiene (II) to acetylpentamethylcyclopentadiene (VI).

A solution of 219 g (1.08 mol) of commercial 85% *m*-chloroperoxybenzoic acid in 2 l. of chloroform was added dropwise to a solution of 174 g (1.07 mol) of hexamethylbicyclo[2.2.0]hexadiene in 250 ml of toluene at 0° over a 3–4-hr period. The reaction mixture was kept at 0° for an additional 3–4 hr and finally was stirred at ambient temperature ($\sim 25^\circ$) for at least an additional 24 hr. The resulting white precipitate (mainly *m*-chlorobenzoic acid) was then removed by filtration. The chloroform was removed from the filtrate at 40° (35 mm). The residual toluene solution was treated with 500 ml of pentane. The filtered toluene–pentane solution was washed with four 250-ml portions of 10% aqueous sodium hydroxide followed by two 250-ml portions of water. Solvents were removed from the dried (anhydrous MgSO_4) organic layer at 50° (35 mm). The remaining liquid was distilled at 4 mm. The fraction boiling at $75\text{--}95^\circ$ (4 mm) consisted of 80 g of crude acetylpentamethylcyclopentadiene. This product was dissolved in 50 ml of pentane and the pentane solution cooled for several hours in a -78° bath. The resulting white crystals were removed by filtration and dried to give 70 g (37% yield) of pure acetylpentamethylcyclopentadiene (VI), mp $53\text{--}54^\circ$ (lit.⁹ mp $50\text{--}52^\circ$). Evaporation of the filtrate from this crystallization gave 10 g of impure acetylpentamethylcyclopentadiene

(VI) as a viscous yellow oil; this impure material could also be used for the preparation of pentamethylcyclopentadienyl metal carbonyls. Very pure acetylpentamethylcyclopentadiene could be obtained by sublimation of the recrystallized material at $30\text{--}40^\circ$ (0.01 mm).

The proton nmr spectrum of acetylpentamethylcyclopentadiene (VI) in CDCl_3 solution exhibited resonances at τ 8.18, 8.33, 8.46, and 8.92 of relative intensities 2:2:1:1 corresponding to the two pairs of nonequivalent olefinic methyl groups, the singlet acetyl methyl group, and the single methyl group attached to an sp^3 carbon atom, respectively.

Reaction of $\text{Cr}(\text{CO})_6$ with Acetylpentamethylcyclopentadiene (VI). A mixture of 9.0 g (41.0 mmol) of hexacarbonylchromium, 6.0 g (33.7 mmol) of acetylpentamethylcyclopentadiene (VI), and 150 ml of 2,2,5-trimethylhexane was boiled under reflux for 55 hr. Solvent was removed at 50° (35 mm). The resulting green residue was extracted with three 150-ml portions of boiling hexane. The volume of the filtered hexane extracts was reduced to 50 ml. The concentrated extracts were cooled in a -78° bath for about 1 hr. The resulting precipitate was removed by filtration and dried at 25° (0.01 mm) to give 5.5 g (67% yield based on VI) of green crystalline $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$, dec pt $>200^\circ$, proton nmr τ (CH_3) 8.37 (CHCl_3).

Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{Cr}_2\text{O}_4$: C, 59.3; H, 6.2; Cr, 21.4; O, 13.2. Found: C, 59.4; H, 6.4; Cr, 21.2; O, 13.0.

Reactions of $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ with Acetylpentamethylcyclopentadiene (VI). A solution of 5.0 g (21.8 mmol) of $\text{Cr}(\text{CO})_6$ in 100 ml of acetonitrile was boiled under reflux for 18 hr. The acetonitrile was then removed at 50° (35 mm). The resulting $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ ¹⁴ was boiled under reflux for 24 hr with a solution of 4.0 g (22.5 mmol) of acetylpentamethylcyclopentadiene (VI) in 125 ml of methylcyclohexane. From the resulting reaction mixture 1.2 g (22.5% yield) of green crystalline $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$, identified by its infrared spectrum, was isolated by a procedure essentially identical with that described above for the reaction between $\text{Cr}(\text{CO})_6$ and VI.

Reaction of $\text{Mo}(\text{CO})_6$ with Acetylpentamethylcyclopentadiene (VI). A mixture of 9.0 g (34.0 mmol) of $\text{Mo}(\text{CO})_6$, 5.0 g (28.3 mmol) of acetylpentamethylcyclopentadiene (VI), and 175 ml of 2,2,5-trimethylhexane was boiled under reflux for 36 hr. Solvent was removed from the resulting reaction mixture at 50° (35 mm). The residue was extracted with four 100-ml portions of boiling hexane. Solvent was removed from the filtered hexane solution at $\sim 35^\circ$ (35 mm). The residue was sublimed at 70° (0.01 mm) with periodic removal of the yellow sublimate of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$. This sublimation was continued until no further sublimation occurred (about 2–3 days). The combined sublimes were recrystallized from hexane to give 3.9 g (42% yield) of yellow $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$, mp 140° dec (lit.¹ mp $141\text{--}145^\circ$ dec). The $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ was identified further by comparison of its infrared and proton nmr spectra with the reported¹ spectra.

The residue from the sublimation of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ consisted of $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$. This was purified by crystallization from a mixture of dichloromethane and hexane to give 1.6 g (19% yield) of red crystalline $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$, identified by comparison of its infrared and proton nmr spectra with those reported in the literature.¹

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(13) E. H. Bray and W. Hübel, *Inorg. Syn.*, **8**, 178 (1966).

(14) (a) D. P. Tate, J. M. Augl, and W. R. Knipple, *Inorg. Chem.*, **1**, 433 (1962); (b) R. B. King, *J. Organometal. Chem.*, **8**, 139 (1967).

Reaction of $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$ with Acetylpentamethylcyclopentadiene (VI). The $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$ prepared¹⁴ from 4.2 g (16 mmol) of $\text{Mo}(\text{CO})_6$ and 120 ml of acetonitrile was boiled under reflux for 24 hr with a solution of 2.75 g (15.5 mmol) of acetylpentamethylcyclopentadiene in 100 ml of methylcyclohexane. Solvent was removed from the reaction mixture at 50° (35 mm). The residue was extracted with two 100-ml portions of pentane. The pentane extracts were concentrated to ~75 ml and then chromatographed on a 2 × 60-cm Florisil column. The yellow band was eluted with pentane. Evaporation of the pentane eluate gave 1.9 g (37% yield) of $\text{CH}_3\text{Mo}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$, identified by its infrared spectrum. The infrared spectrum of the reaction mixture prior to chromatography indicated the absence of $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$.

Reaction of $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$ with Acetylpentamethylcyclopentadiene (VI). A mixture of 5.0 g (12.8 mmol) of freshly prepared $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$, 2.2 g (12.4 mmol) of acetylpentamethylcyclopentadiene (VI), and 125 ml of methylcyclohexane was boiled under reflux for 48 hr. Solvent was then removed from the reaction mixture at 50° (35 mm). A pentane solution of the residue was chromatographed on a 2 × 60-cm Florisil column. The pale yellow band was eluted slowly with pentane. Solvent was removed from the eluate at 25° (35 mm) and the residue sublimed at 45° (0.01 mm) to give 2.1 g (41% yield) of yellow $\text{CH}_3\text{W}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$, mp 170–171°.

Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{W}$: C, 40.2; H, 4.3; O, 11.5; W, 44.0. Found: C, 40.4; H, 4.4; O, 11.4; W, 43.9.

The proton nmr spectrum of $\text{CH}_3\text{W}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ in C_6D_6 solution exhibited resonances at τ 8.42 and 9.74 of relative intensities 5:1 corresponding to the five equivalent methyl groups of the pentamethylcyclopentadienyl ring and to the single methyl group bonded to the tungsten, respectively.

No other tungsten carbonyl products were detected in the above reaction mixture. If the reaction between $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$ and acetylpentamethylcyclopentadiene (VI) was carried out in boiling 2,2,5-trimethylhexane (124°) rather than boiling methylcyclohexane (100°), the product $\text{CH}_3\text{W}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ was also obtained, but in only 3.3% yield. Hexacarbonyltungsten failed to react with acetylpentamethylcyclopentadiene (VI) upon prolonged boiling in 2,2,5-trimethylhexane or cyclooctane.

Reaction of $\text{Mn}_2(\text{CO})_{10}$ with Acetylpentamethylcyclopentadiene (VI). A mixture of 1.60 g (4.1 mmol) of $\text{Mn}_2(\text{CO})_{10}$, 0.77 g (4.6 mmol) of acetylpentamethylcyclopentadiene (VI), and 50 ml of 2,2,5-trimethylhexane was boiled under reflux for 48 hr. During the course of this reaction the original yellow color gradually became deep orange. Solvent was removed from the reaction mixture at 50° (35 mm). A pentane solution of the residue was chromatographed on a 2 × 30-cm Florisil column. The first yellow band was eluted from the column with hexane. Evaporation of the eluate gave unreacted $\text{Mn}_2(\text{CO})_{10}$. A second yellow band was eluted from the chromatography column with diethyl ether. Evaporation of the eluate followed by low-temperature crystallization from pentane and sublimation at 30° (0.01 mm) gave 0.15 g (12% yield based on VI) of pale yellow crystalline $(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$, mp 77.5°, proton nmr τ (CH_3) 8.14 (CDCl_3). If the reaction was scaled up, the yield of $(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$ appeared to fall.

Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{MnO}_3$: C, 57.0; H, 5.5; Mn, 20.1; O, 17.6. Found: C, 57.2; H, 5.6; Mn, 18.7; O, 17.4.

Reaction of $\text{Fe}(\text{CO})_5$ with Acetylpentamethylcyclopentadiene (VI). A mixture of 25 ml (36.5 g, 186 mmol) of $\text{Fe}(\text{CO})_5$, 7.5 g (42 mmol) of acetylpentamethylcyclopentadiene (VI), and 200 ml of 2,2,5-trimethylhexane was boiled under reflux for 24 hr. Solvent was removed from the reaction mixture at 50° (35 mm). The dry residue was extracted with a mixture of 200 ml of dichloromethane and 200 ml of hexane. Evaporation of the filtered extract at 25° (35 mm) followed by drying at 60° (0.01 mm) gave 7.3 g (71% yield based on VI) of red-violet $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]_2$, identified on comparison of its infrared and nmr spectra with the reported¹ spectra. The $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]_2$ could be purified further by crystallization from a mixture of dichloromethane and hexane.

Reaction of $\text{Fe}_2(\text{CO})_9$ with Acetylpentamethylcyclopentadiene (VI). A mixture of 4.3 g (11.8 mmol) of $\text{Fe}_2(\text{CO})_9$, 2.0 g (11.2 mmol) of acetylpentamethylcyclopentadiene (VI), and 100 ml of pentane was stirred at room temperature (~25°) for ~14 hr. Solvent was removed from the filtered reaction mixture at 25° (35 mm). A solution of the oily residue in a minimum volume of pentane was chromatographed on a 2 × 60-cm Florisil column. The chromatogram was developed with pentane or hexane. Elution of the first yellow band with hexane containing 10–20% dichloromethane followed by evaporation of the eluate at 25° (35 mm) gave 0.93 g (25% yield based on VI) of the liquid diene complex

$[(\text{CH}_3)_5\text{C}_5\text{COCH}_3\text{Fe}(\text{CO})_3]$. The analytical sample, a yellow waxy solid, was purified further by additional chromatography followed by evaporative distillation at 75–80° (0.01 mm) and crystallization from pentane.

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{FeO}_4$: C, 56.6; H, 5.7; Fe, 17.6; O, 20.1. Found: C, 56.3; H, 5.6; Fe, 17.6; O, 20.7.

The proton nmr spectrum of $[(\text{CH}_3)_5\text{C}_5\text{COCH}_3\text{Fe}(\text{CO})_3]$ in C_6D_6 solution exhibited resonances at τ 8.07, 8.19, 8.63, and 9.41 of relative intensities 1:2:2:1 corresponding to the acetyl methyl group, the two pairs of nonequivalent complexed olefinic methyl groups, and the single methyl group attached to an sp^3 carbon atom, respectively.

After removal of the $[(\text{CH}_3)_5\text{C}_5\text{COCH}_3\text{Fe}(\text{CO})_3]$ from the chromatography column, the second yellow band was eluted with diethyl ether. Evaporation of the eluate at 25° (35 mm) followed by low-temperature crystallization from pentane gave 0.29 g (8.5% yield based on VI) of pale yellow crystalline $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$, mp 72–73°.

Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{FeO}_3$: C, 57.8; H, 6.2; Fe, 19.3; O, 16.5. Found: C, 57.8; H, 6.2; Fe, 19.2; O, 16.7.

The proton nmr spectrum of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ in C_6D_6 solution exhibited resonances at τ 7.54 and 8.54 of relative intensities 1:5 corresponding to the single acetyl methyl group and the five equivalent methyl groups of the pentamethylcyclopentadienyl ring.

The reaction between $\text{Fe}_2(\text{CO})_9$ and acetylpentamethylcyclopentadiene (VI) was repeated in different saturated hydrocarbon solvents at different temperatures. In boiling hexane (68°, reaction time 24 hr) a 15% yield of $[(\text{CH}_3)_5\text{C}_5\text{COCH}_3\text{Fe}(\text{CO})_3]$ and a 5% yield of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ was obtained. In boiling heptane (98°, reaction time 30 hr) a 13% yield of $[(\text{CH}_3)_5\text{C}_5\text{COCH}_3\text{Fe}(\text{CO})_3]$, a 1.7% yield of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$, and a 2.3% yield of $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]_2$ were obtained. In boiling 2,2,5-trimethylhexane (124°, reaction time 32 hr) no $[(\text{CH}_3)_5\text{C}_5\text{COCH}_3\text{Fe}(\text{CO})_3]$, a 1% yield of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$, and a 34% yield of $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]_2$ were obtained.

Reaction of $\text{Co}_2(\text{CO})_8$ with Acetylpentamethylcyclopentadiene (VI). A mixture of 12.9 g (37.7 mmol) of $\text{Co}_2(\text{CO})_8$, 5.2 g (29.3 mmol) of acetylpentamethylcyclopentadiene (VI), and 150 ml of cyclohexane was boiled under reflux for 22–87 hr. Solvent was then removed from the reaction mixture at 40° (35 mm). The residue was extracted with three 50-ml portions of pentane. The concentrated pentane solution was chromatographed on a 2 × 60-cm alumina column. The orange band was eluted with pentane. The red pentane eluate was concentrated to 40 ml and then cooled in a –78° bath for several hours. The resulting crystals were then removed by filtration and dried to give 4.3 g (59% yield based on VI) of red crystalline $(\text{CH}_3)_5\text{C}_5\text{Co}(\text{CO})_3$, mp 55–56° (lit.¹ mp 56–58°).

Attempted Reactions of Nickel Carbonyls with Acetylpentamethylcyclopentadiene (VI). Excess $\text{Ni}(\text{CO})_4$ (5 ml) failed to react with acetylpentamethylcyclopentadiene (VI) (0.85 g) upon prolonged stirring in 2,2,5-trimethylhexane (75 ml) at room temperature (~25°). Upon gradual heating of this mixture to the boiling point only complete decomposition to give a black precipitate of metallic nickel was observed. An analogous attempt to react $[\text{C}_5\text{H}_7\text{NiCO}]_2$ with acetylpentamethylcyclopentadiene (VI) gave similar negative results.

Mass Spectra. The mass spectra listed below were taken at 70 eV on a Perkin-Elmer Hitachi RMU-6 mass spectrometer with a chamber temperature of 220°. Relative intensities and sample temperatures are given in parentheses.

A. $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$ (~200°): $[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2(\text{CO})_3]^+$ (35), $[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2(\text{CO})_2]^+$ (0.8), $[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2\text{CO}]^+$ (10), $[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2]^+$ (100), $[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}^+]$ (88), $(\text{CH}_3)_5\text{C}_5\text{CrC}_5(\text{CH}_3)_4^+$ (4), $(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_5^+$ (17), $(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2^+$ (24), $(\text{CH}_3)_5\text{C}_5\text{CrCO}^+$ (33), $(\text{CH}_3)_5\text{C}_5\text{Cr}^+$ (77), $\text{C}_{10}\text{H}_{13}\text{Cr}^+$ (76), $\text{C}_9\text{H}_{12}\text{Cr}^+$ (17), $\text{C}_9\text{H}_{11}\text{Cr}^+$ (18), $\text{C}_8\text{H}_{11}\text{Cr}^+$ (8), $\text{C}_8\text{H}_9\text{Cr}^+$ (5), $\text{C}_{10}\text{H}_{16}^+$ (11), $\text{C}_{10}\text{H}_{15}^+$ (18), $\text{C}_9\text{H}_{14}^+$ (32), $\text{C}_{10}\text{H}_{13}^+$ (48), $\text{C}_9\text{H}_{13}^+$ (18), $\text{C}_9\text{H}_{11}^+$ (73), C_8H_9^+ (23), $\text{C}_{10}\text{H}_{10}\text{Cr}^{2+}$ (12), C_7H_9^+ (11), C_7H_7^+ (29), C_6H_7^+ (10), C_6H_5^+ (11) and Cr^+ (~100). Meta-stable ions at m/e 353 w $\{[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2(\text{CO})_3]^+ \rightarrow [(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2\text{CO}]^+ + \text{CO}\}$, 348 s $\{[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2\text{CO}]^+ \rightarrow [(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2^+ + \text{CO}]\}$, 277 vw $\{[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}_2]^+ \rightarrow [(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}^+ + \text{Cr}]\}$, and 292 vw $\{[(\text{CH}_3)_5\text{C}_5\text{C}_2\text{Cr}^+ \rightarrow (\text{CH}_3)_5\text{C}_5\text{CrC}_5(\text{CH}_3)_4^+ + \text{CH}_3]\}$.

B. $\text{CH}_3\text{W}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ (~100°): $\text{CH}_3\text{W}(\text{CO})_2\text{C}_5(\text{CH}_3)_5^+$ (21), $(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_3^+$ (5), $\text{CH}_3\text{W}(\text{CO})_2\text{C}_5(\text{CH}_3)_5^+$ (31), $\text{C}_{10}\text{H}_{14}\text{W}(\text{CO})_2^+$ (~14), $\text{C}_{10}\text{H}_{13}\text{W}(\text{CO})_2^+$ (~21), $\text{C}_{10}\text{H}_{12}\text{W}^+$ (? (37), $\text{C}_{10}\text{H}_{14}\text{WCO}^+$ (50), $\text{C}_{11}\text{H}_{16}\text{W}^+$ (100), $\text{C}_{10}\text{H}_{14}\text{W}^+$ (72), $\text{C}_{10}\text{H}_{13}\text{W}^+$ (~35), $\text{C}_{10}\text{H}_8\text{W}^+$ (~20), $\text{C}_9\text{H}_7\text{W}^+$ (~4), $\text{C}_9\text{H}_6\text{W}^+$ (~4), $\text{C}_9\text{H}_5\text{W}^+$ (~4), $\text{C}_8\text{H}_5\text{W}^+$ (~10), $\text{C}_8\text{H}_3\text{W}^+$ (~11), $\text{C}_7\text{H}_5\text{W}^+$ (~5), $\text{C}_7\text{H}_3\text{W}^+$ (~4), $\text{C}_6\text{H}_3\text{W}^+$ (~10), $\text{C}_6\text{H}_2\text{W}^+$ (~6), $\text{C}_5\text{H}_2\text{W}^+$ (~4), $\text{C}_5\text{H}_3\text{W}^+$ (~6), $\text{C}_5\text{H}_2\text{W}^+$ (~4), $\text{C}_3\text{H}_2\text{W}^+$ (5), $\text{C}_2\text{H}_2\text{W}^+$ (1.6), $\text{C}_{10}\text{H}_{14}\text{W}(\text{CO})_2^{2+}$ (5), $\text{C}_{10}\text{H}_{14}\text{WCO}^{2+}$

(~8), $C_{10}H_nW^+$ ($n = 10, 9, 8$; not clearly separated; approximate relative intensity 10), $C_9H_8W^{2+}$ (10), $C_8H_6W^{2+}$ (14), $C_{10}H_{14}^+$ (47), $C_9H_{13}^+$ (24), $C_9H_{11}^+$ (100), $C_8H_9^+$ (19), $C_8H_7^+$ (7), $C_7H_9^+$ (9), $C_7H_7^+$ (27), $C_6H_7^+$ (11), and $C_6H_5^+$ (17).

C. $(CH_3)_5C_5Mn(CO)_3$ (80°): $(CH_3)_5C_5Mn(CO)_3^+$ (27), $(CH_3)_5C_5Mn(CO)_2^+$ (11), $(CH_3)_5C_5Mn(CO)_2^+$ (2.1), $(CH_3)_5C_5Mn(CO)_3^+$ (1.9), $(CH_3)_4C_5Mn(CO)_2^+$ (1.1), $(CH_3)_5C_5Mn(CO)_3^+$ (1.4), $(CH_3)_5C_5MnCO^+$ (20), $(CH_3)_4C_5MnCO^+$ (11), $(CH_3)_5C_5Mn(CO)_2^+$ (2.5), $(CH_3)_5C_5Mn^+$ (100), $(CH_3)_4C_5Mn^+$ (42), $C_{10}H_{15}^+$ (93), $C_9H_{13}^+$ (42), $C_9H_{11}^+$ (15), $C_8H_{11}^+$ (6.3), $C_8H_9^+$ (18), $C_7H_9^+$ (6.3), $C_7H_7^+$ (16), $C_6H_7^+$ (8.4), $C_6H_5^+$ (9.1), MnH^+ (8.4), and Mn^+ (32). Metastable ions at m/e 221 s [$(CH_3)_5C_5Mn(CO)_3^+ \rightarrow (CH_3)_5C_5Mn(CO)_2^+ + CO$], 206 w [$(CH_3)_5C_5Mn(CO)_3^+ \rightarrow (CH_3)_5C_5Mn(CO)_2^+ + CO$], 193 m [$(CH_3)_5C_5Mn(CO)_2^+ \rightarrow (CH_3)_5C_5MnCO^+ + CO$], 165.5 w [$(CH_3)_5C_5MnCO^+ \rightarrow (CH_3)_5C_5Mn^+ + CO$], 151 w [$(CH_3)_4C_5MnCO^+ \rightarrow (CH_3)_4C_5Mn^+ + CO$], 96 vs [$(CH_3)_5C_5Mn^+ \rightarrow (CH_3)_5C_5^+ + Mn$], 84.8 m [$C_{10}H_{15}^+ \rightarrow C_8H_{11}^+ + C_2H_4$], 71.8 w [$C_9H_{13}^+ \rightarrow C_7H_9^+ + C_2H_4$], and 58.3 w [$C_8H_{11}^+ \rightarrow C_6H_7^+ + C_2H_4$].

D. $CH_3COFe(CO)_2C_5(CH_3)_5$ (80°): $[(CH_3)_5C_5]Fe^+$ (21), $CH_3COFe(CO)_2C_5(CH_3)_5^+$ (0.3), $(CH_3)_5C_5Fe(CO)_3^+$ (0.5), $CH_3Fe(CO)_2C_5(CH_3)_5^+$ (21), $(CH_3)_5C_5Fe(CO)_2^+$ (3.7), $CH_3COFeCO_2C_5(CH_3)_5^+$ (21), $(CH_3)_5C_5FeCO^+$ (12), $CH_3FeC_5(CH_3)_5^+$ (16), $(CH_3)_5C_5Fe^+$ (100), $C_9H_{10}Fe^+$ (18), $C_{11}H_{18}^+$ (100), $C_{10}H_{15}^+$ (160), $C_9H_{13}^+$ (35), $C_9H_{11}^+$ (110), $C_8H_{11}^+$ (25), $C_8H_9^+$ (43), $C_7H_9^+$ (23), $C_7H_7^+$ (40), $C_6H_7^+$ (13), $C_6H_5^+$ (23), $C_6H_3^+$ (12), and Fe^+ (11). Metastable ions at m/e 209.3 w [$CH_3Fe(CO)_2C_5(CH_3)_5^+ \rightarrow CH_3FeCO_2C_5(CH_3)_5^+ + CO$], 159 m [$(CH_3)_5C_5Fe^+ \rightarrow C_9H_{10}Fe^+ + H_2 + CH_3$], and 85.0 ($C_{10}H_{15}^+ \rightarrow C_8H_{11}^+ + C_2H_4$).

Discussion

The data presented in this paper indicate that the reactions of acetylpentamethylcyclopentadiene with metal carbonyls proceed according to the general scheme outlined in Scheme I which consists of the following four-step sequence: (A) coordination of the 1,3-diene system of the acetylpentamethylcyclopentadiene to give the diene complex A; (B) migration of the acetyl group from a ring carbon atom to the transition metal atom with concurrent displacement of one carbonyl group to give the monohapto¹⁵ acetyl derivative B; (C) decarbonylation of the monohapto acetyl derivative B to give the monohapto methyl derivative C (this decarbonylation step presumably occurs by the established¹⁶ methyl migration mechanism where the acetyl methyl group migrates from the acyl carbonyl group to the metal atom with concurrent displacement of one of the terminal carbonyl groups); (D) rupture of the transition metal–methyl σ bond to form a pentamethylcyclopentadienyl metal carbonyl fragment D with loss of the methyl group that was bonded to the transition metal in intermediate C [the resulting pentamethylcyclopentadienyl metal carbonyl fragment D may undergo dimerization (e.g., formation of $[(CH_3)_5C_5Fe(CO)_2]_2$) or dimerization and decarbonylation (e.g., formation of $[(CH_3)_5C_5Cr(CO)_2]_2$) in order for the central metal atom to attain a favored electronic configuration (generally the 18-electron rare gas configuration¹⁷). The principal evidence for this sequence for the reactions of acetylpentamethylcyclopentadiene (VI) with various metal carbonyls is based on the isolation and characterization of the three types of intermediates A, B, C when the reactions between certain metal carbonyls and acetylpentamethylcyclopentadiene are done under conditions too mild for the entire reaction sequence of Scheme I. The relative rates of the reaction steps A–D

(15) For a description of this nomenclature, see F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968).

(16) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

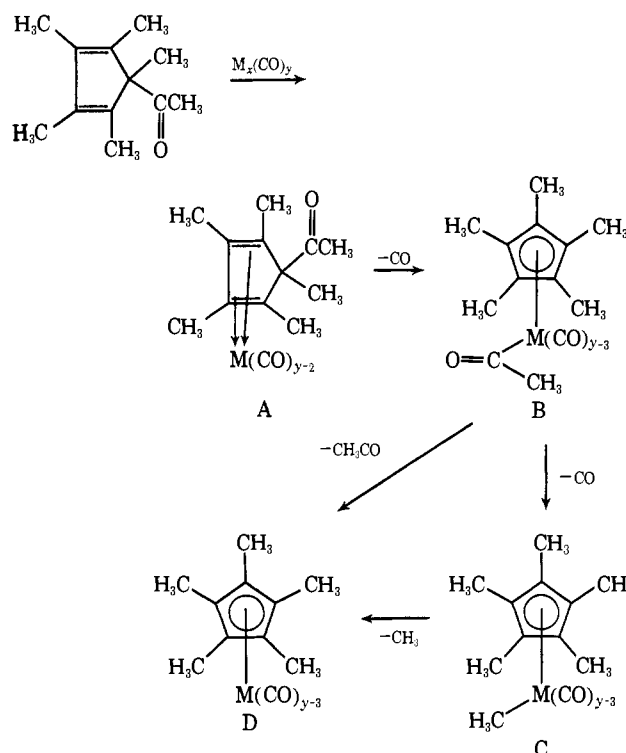
(17) R. B. King, *Advan. Chem. Ser.*, No. 62, 203 (1967).

above will determine whether any of the intermediate compounds can be isolated from a given system.

The one example of an intermediate diene complex of acetylpentamethylcyclopentadiene (VI) of type A (Scheme I) is the yellow waxy $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ (VIII) which is obtained in about 25% yield by reaction of $Fe_2(CO)_9$ with acetylpentamethylcyclopentadiene (VI) in pentane at room temperature. The proton nmr spectrum of $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ shows the four methyl resonances expected for structure VIII rather than the simpler nmr spectrum observed in all of the derivatives with a pentahapto pentamethylcyclopentadienyl ring. The infrared spectrum of $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ (Table I) exhibits the $\nu(CO)$ pattern in the metal carbonyl region expected for a diene iron tricarbonyl derivative.¹⁸ In addition, a $\nu(CO)$ frequency at 1703 cm^{-1} is observed arising from the acetyl group in the coordinated acetylpentamethylcyclopentadiene. An attempt to obtain the mass spectrum of $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ using a chamber temperature of 220° as in the case of the other mass spectra studied in this work resulted instead in decomposition giving free acetylpentamethylcyclopentadiene.

The one example of an intermediate monohapto acetyl derivative of type B (Scheme I) is the pale yellow

Scheme I. Generalized Scheme for the Reactions of 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene with Metal Carbonyls

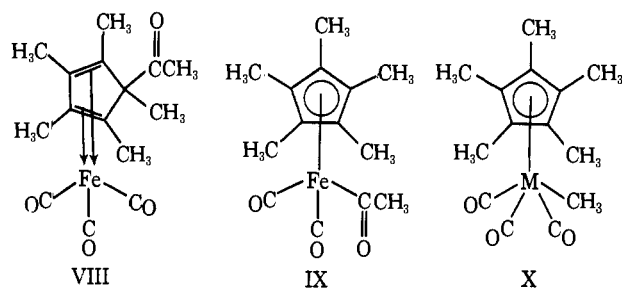


crystalline $CH_3COFe(CO)_2C_5(CH_3)_5$ (IX), a minor product (up to 9% yield) from the reaction of $Fe_2(CO)_9$ with acetylpentamethylcyclopentadiene (VI). The proton nmr spectrum of $CH_3COFe(CO)_2C_5(CH_3)_5$ (IX) exhibited a resonance at τ 7.54 which can be assigned to the methyl protons of the monohapto acetyl group. The acyl carbonyl of the acetyl group exhibited a $\nu(CO)$

(18) See, for example, J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 3955 (1963).

infrared frequency at 1636 cm^{-1} , a characteristic region for acyl groups directly bonded to transition metals.¹⁹ In addition, the two terminal metal carbonyl $\nu(\text{CO})$ frequencies expected for a $\text{YFe}(\text{CO})_2\text{C}_5\text{R}_5$ derivative were observed.²⁰

Examples of intermediate monohapto methyl derivatives of type C (Scheme I) are the yellow crystalline compounds $\text{CH}_3\text{M}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ (X; M = Mo and



W) obtained from reactions of $\text{Mo}(\text{CO})_6$ or $(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3$ (M = Mo and W) with acetylpentamethylcyclopentadiene (VI). The molybdenum compound $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ (X; M = Mo) had properties identical with authentic material¹ prepared by reaction of $\text{Mo}(\text{CO})_6$ with lithium pentamethylcyclopentadiene followed by addition of excess methyl iodide.

Further evidence for the general scheme outlined in Scheme I for the reactions of acetylpentamethylcyclopentadiene (VI) with metal carbonyls is provided by a study of the reactions of $\text{Fe}_2(\text{CO})_9$ with acetylpentamethylcyclopentadiene (VI) in inert saturated hydrocarbon solvents at four different temperatures within the range 25° (room temperature) to 124° (boiling 2,2,5-trimethylhexane). As the temperature was increased successively from 25 through 68° and 98 to 124° , the yield of the diene complex $[(\text{CH}_3)_5\text{C}_5\text{COCH}_3]\text{Fe}(\text{CO})_3$ (VII) of type A (Scheme I) decreased from 25 through 15% and 13% to zero. Similarly the yield of the monohapto acetyl derivative $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ (IX) of type B (Scheme I) during this successive temperature increase decreased from 8.5 through 5% and 1.7% to 1% . However, the yield of the final pentamethylcyclopentadienyliron carbonyl $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]$ during this successive temperature increase increased from zero through 2.3% (at 98°) to 34% (at 124°). No evidence for any methyl derivative $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ of type C (Scheme I) was observed in any of these experiments suggesting that this stage was essentially bypassed in the reactions of iron carbonyls with acetylpentamethylcyclopentadiene. The yields of $[(\text{CH}_3)_5\text{COCH}_3]\text{Fe}(\text{CO})_3$ (VII), $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ (IX), and $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]$ from the reaction between $\text{Fe}_2(\text{CO})_9$ and acetylpentamethylcyclopentadiene (VI) as a function of reaction temperatures suggest that VII and VIII are formed in the early stages of the reaction and are converted to $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]$ in the later stages of the reaction in accord with the scheme outlined in Scheme I and discussed above.

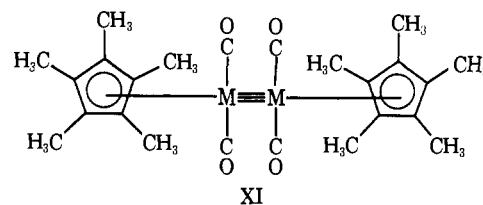
The reactions between acetylpentamethylcyclopentadiene (VI) and various metal carbonyls provide more convenient synthetic routes to the previously reported¹ pentamethylcyclopentadienylmetal carbonyls $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]$, $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]$, and $(\text{CH}_3)_5\text{C}_5\text{Co}(\text{CO})_2$.

(19) R. B. King, *J. Amer. Chem. Soc.*, **85**, 1918 (1963).

(20) R. B. King, *Inorg. Chim. Acta*, **2**, 454 (1968).

In addition, the new pentamethylcyclopentadienylmetal carbonyls $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]$ and $(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$ were also prepared. However, attempts to prepare a pentamethylcyclopentadienylnickel carbonyl by reaction of either $\text{Ni}(\text{CO})_4$ or $[\text{C}_5\text{H}_5\text{Ni}(\text{CO})_2]$ with acetylpentamethylcyclopentadiene were unsuccessful.

The new pentamethylcyclopentadienylchromium carbonyl $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]$ is an air-stable green solid which is readily soluble in saturated hydrocarbons such as pentane in contrast to the sparingly soluble cyclopentadienylchromium carbonyl $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]$.²¹ The stoichiometry of $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]$ parallels that of $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]$ but is different from that of the unsubstituted derivative $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]$. The proton nmr spectrum of $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]$ exhibits a single sharp methyl resonance at τ 8.37 indicating diamagnetism and a symmetrical pentamethylcyclopentadienyl ring (at least on an nmr time scale). The infrared spectrum of $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]$ exhibits two strong terminal $\nu(\text{CO})$ frequencies but no bridging $\nu(\text{CO})$ frequencies and resembles that of the purest samples of $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]$.²² The mass spectrum of $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]$ did not exhibit a molecular ion. Instead the highest m/e ion was $[(\text{CH}_3)_5\text{C}_5\text{Cr}_2(\text{CO})_3]^+$ formed by loss of one CO group from the molecular ion. Metastable ions support the fragmentation of $[(\text{CH}_3)_5\text{C}_5\text{Cr}_2(\text{CO})_3]^+$ by the following four-step sequence: (1) loss of two carbonyl groups to give $[(\text{CH}_3)_5\text{C}_5\text{Cr}_2\text{CO}]^+$; (2) loss of the final carbonyl group to give $[(\text{CH}_3)_5\text{C}_5\text{Cr}_2]^+$; (3) loss of a chromium atom to give $[(\text{CH}_3)_5\text{C}_5\text{Cr}]^+$; (4) loss of a methyl group to give $(\text{CH}_3)_5\text{C}_5\text{CrC}_5(\text{CH}_3)_4^+$. The monometallic ions $(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_n^+$ ($n = 3, 2, 1$, and 0) were also observed suggesting facile cleavage of the chromium–chromium bond. However, the observation of significant abundances of the bimetallic ions $[(\text{CH}_3)_5\text{C}_5\text{Cr}_2(\text{CO})_n]^+$ ($n = 3, 1$, and 0) in the mass spectrum of $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]$ contrasts with the failure²³ to observe any bimetallic ions in the mass spectrum of $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]$. This suggests that the chromium–chromium bond is stronger in $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]$ than in $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]$ in accord with the structure XI (M = Cr) with a chromium–



chromium triple bond analogous to the structure XI (M = Mo) proposed^{1,24} for the molybdenum analog $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]$. We hope to clarify the nature of these compounds by an X-ray crystal structure determination.

The mass spectra of the other new pentamethylcyclopentadienylmetal carbonyl derivatives $\text{CH}_3\text{W}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$, $(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$, and $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5(\text{CH}_3)_5$ were also obtained. These mass spectra were similar

(21) E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allg. Chem.*, **282**, 47 (1955).

(22) Recent studies suggest that the reported (ref 1) bands of $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]$ at 1940 and 1907 cm^{-1} arise from decomposition leaving the bands at 1874 and 1846 cm^{-1} to correspond to the $\nu(\text{CO})$ frequencies of the pure compound.

(23) R. B. King, *J. Amer. Chem. Soc.*, **88**, 2075 (1966).

(24) R. B. King, *Chem. Commun.*, 986 (1967).

to those of similar unsubstituted cyclopentadienylmetal carbonyl derivatives²⁵ with the added possibility (particularly noticeable in $(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$) of competitive successive losses of methyl groups from the pentamethylcyclopentadienyl ring. The decamethylferrocene ion $[(\text{CH}_3)_5\text{C}_5\text{H}_5]_2\text{Fe}^+$ was observed as a pyrolysis product in the mass spectrum of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5^-$

(25) R. B. King, *J. Amer. Chem. Soc.*, **90**, 1417 (1968).

$(\text{CH}_3)_5$ similar to the observation of the ferrocene ion $(\text{C}_5\text{H}_5)_2\text{Fe}^+$ as a pyrolysis product in the mass spectra of numerous cyclopentadienyliron carbonyl derivatives.²⁵

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Crystal Structure of $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$. A Comparison of Rhodium–Ethylene and Rhodium–Tetrafluoroethylene Bonding

Lloyd J. Guggenberger* and Richard Cramer

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Abstract: The molecular and crystal structures of π -cyclopentadienylethylenetetrafluoroethylenorhodium, $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$, have been determined from room-temperature X-ray diffractometer data. The molecule has idealized $C_s(m)$ symmetry with the rhodium atom coordinated to a cyclopentadienyl ring, an ethylene ligand, and a tetrafluoroethylene ligand. The rhodium to C_5H_5 ring plane distance is 1.899 Å. The ethylene ligand distances are 2.167 (2) Å for Rh–C and 1.358 (9) Å for C–C; the tetrafluoroethylene distances are 2.024 (2) Å for Rh–C and 1.405 (7) Å for C–C. The dihedral angle between the fluorine atom substituents is 74.3° , greater than for any observed metal–olefin substituent angles and close to the positions expected for “tetrahedral” geometry. The ethylene hydrogen atoms were located and refined, establishing the nonplanar geometry of the coordinated ethylene. The carbon atom geometry found for the ethylene ligand is nearly identical with that in ethylene oxide, $\text{C}_2\text{H}_4\text{O}$. The stereochemical implications with respect to bonding are examined; the large differences in rhodium–olefin distances are discussed in terms of increased π bonding to the tetrafluoroethylene ligand which exerts a significant trans influence (0.07 Å) on the cyclopentadienyl ring. Crystals of $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$ are monoclinic, space group $P2_1/c$, with four molecules per cell of dimensions $a = 7.262$ (4), $b = 9.101$ (4), $c = 16.879$ (9) Å, and $\beta = 118.49$ (9)°. The structure was solved by Patterson and Fourier techniques and refined by least squares to a conventional R of 0.031.

In recent years a great many metal–olefin complexes have been prepared and much has been inferred about the metal–olefin geometry from spectral evidence,¹ but there have been few systematic studies of the influence of olefin substitution on the metal–olefin stereochemistry. We report here the molecular and crystal structures of π -cyclopentadienylethylenetetrafluoroethylenorhodium, $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$, which is ideal for assessing the effects of fluoro substitution on rhodium–olefin geometry, since it contains both the substituted and unsubstituted olefins. The very electronegative fluorine substituents provide a valuable comparison with the available metal–olefin structural data on cyano-substituted olefins. Differences might be anticipated in view of the nature of the inductive and π -acceptor characteristics of the substituents. Of particular interest is the comparison of the geometries of the olefin carbon atoms and its relation to the σ - π vs. “metallocyclopropane” metal–olefin bonding models.

The preparation and interpretation of the nmr spectrum of $(\text{C}_2\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$ were reported earlier.² The nmr spectrum in particular suggested a sig-

nificant difference in metal–olefin bonding between the unsubstituted and tetrafluoro-substituted olefins. The coupling constants of the ethylene protons change little on coordination to rhodium, but the fluorine–fluorine couplings of tetrafluoroethylene change significantly following coordination to rhodium.

The structure of $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$ is compared with the available data from the recent structure determination of acetylacetonatoethylenetetrafluoroethylenorhodium, $(\text{C}_5\text{H}_7\text{O}_2)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$.³

Crystal Data and Structure Determination

Crystals of π -cyclopentadienylethylenetetrafluoroethylenorhodium, $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{F}_4)(\text{C}_2\text{H}_4)$, are monoclinic, space group $P2_1/c$, with cell dimensions of $a = 7.262$ (4), $b = 9.101$ (4), $c = 16.879$ (9) Å, and $\beta = 118.49$ (9)°. These parameters resulted from the least-squares refinement of 11 carefully measured reflections on the diffractometer. The observed and calculated densities for four molecules per cell are 1.94 and 2.01 g/cm³, respectively. There is no space group imposed molecular symmetry. All atoms were placed in the general positions $\pm(x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z)$.⁴

(1) F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969), and references therein for work on platinum and palladium complexes.

(2) R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 2519 (1969).

(3) J. A. Evans and D. R. Russell, *Chem. Commun.*, 197 (1971).

(4) “International Tables for X-ray Crystallography,” Vol. I, Kynoch Press, Birmingham, England, 1965, p 99.