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ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS XXI[*]. SOME π-PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF VARIOUS TRANSITION METALS

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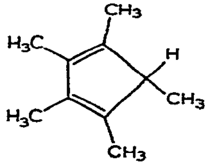
INTRODUCTION

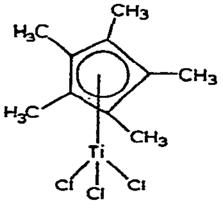
Hundreds of π-cyclopentadienyl derivatives are now known, including derivatives of all of the transition metals (for reviews on the chemistry of π-cyclopentadienylmetal compounds see refs. 2–5). However, with the exception of substitution products of ferrocene[6–9] and cymantrene[***]. metal π-complexes with substituted π-cyclopentadienyl groups have received much less attention. A few π-methylcyclopentadienyl complexes have been prepared and compared with the corresponding unsubstituted π-cyclopentadienyl derivatives[11].

Of particular interest are metal complexes with completely substituted π-cyclopentadienyl groups, since these are the cases where the substituents should have the maximum effect on chemical and physical properties. Some π-pentaphenylcyclopentadienyl complexes of iron have been reported[12]. By exhaustive substitution of ferrocene and cymantrene in several steps, the π-pentaethylcyclopentadienyl derivatives $[(C_2H_5)_5C_5]_2Fe$[13] and $(C_2H_5)_5C_5Mn(CO)_3$[14] have been prepared. Otherwise pentasubstituted π-cyclopentadienyl derivatives appear to be unknown[†].

In 1960 deVries[16] reported the preparation of pentamethylcyclopentadiene (I) from commercially available organic intermediates by means of a five-step synthesis. The following two considerations prompted the study of the syntheses of π-pentamethylcyclopentadienyl derivatives from pentamethylcyclopentadiene:



(I)



(II)

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[*] For Part XX of this series see ref. 1.

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[***] No comprehensive review on cymantrene, $C_5H_5Mn(CO)_3$, is yet available. Recent results (leading to earlier references if desired) may be found in ref. 10.

[†] Completely substituted π-cyclopentadienyl derivatives with *electronegative* substituents such as fluorine and methoxycarbonyl do not appear to be stable. As an indication of this, hexafluorocyclopentadiene has been found to react with various metal carbonyls[15] to give hexafluorocyclopentadiene olefin complexes rather than π-pentafluorocyclopentadienyl complexes.

(1) In 1961 Röhl, Lange, Gössl, and Roth[17] reported the preparation of the titanium compound $C_{10}H_{15}TiCl_3$ by heating titanium tetrachloride with various butenes at 300°. The single sharp proton NMR resonance of this compound indicated it to be π-pentamethylcyclopentadienyltrichlorotitanium (II). Apparently the pentamethylcyclopentadienyl moiety is formed by an unusual condensation reaction of the butene molecules under the very vigorous reaction conditions*. It appeared desirable to check this possibility by a synthesis of π-(pentamethylcyclopentadienyl)-trichlorotitanium (II) from pentamethylcyclopentadiene.

(2) Fischer and co-workers have found that hexamethylbenzene forms much more stable π-complexes with various metals than unsubstituted benzene. Thus $(CH_3)_6C_6Cr(CO)_3$ was found to be the most stable of the arenechromium tricarbonyls[18]. Subsequently Fischer and co-workers utilized the great relative stability of π-hexamethylbenzene complexes to synthesize π-arene complexes of types not formed by unsubstituted benzene. The first example of this was the synthesis of the zerovalent iron complex[19] $[(CH_3)_6C_6]_2Fe$. Later studies dealt with similar complexes of cobalt[20] and rhodium[21]. Extrapolation of these observations suggests that π-pentamethylcyclopentadienyl derivatives of transition metals could be prepared of types different from known unsubstituted π-cyclopentadienyl derivatives.

A further consideration in the selection of π-pentamethylcyclopentadienyl as the type of completely substituted π-cyclopentadienyl derivative for study was the low molecular weight of the methyl substituents which sometimes makes the complexes sufficiently volatile for purification by sublimation.

A previous paper[22] from this Laboratory on olefin complexes of tungsten carbonyl described the reaction between $(CH_3CN)_3W(CO)_3$ and pentamethylcyclopentadiene to give the π-pentamethylcyclopentadienyl derivative $(CH_3)_5C_5$-$W(CO)_3H$. This paper describes some research initiated in 1962 on the preparation and properties of several π-pentamethylcyclopentadienyl compounds of representative types. Limitations in the availability of large quantities of pentamethylcyclopentadiene have prevented us from exploring as wide a variety of its reactions with metal derivatives as would be of interest. However, even this rather limited study has resulted in the discovery of the novel compound $[C_5(CH_3)_5Mo(CO)_2]_2$ of a type unknown in unsubstituted π-cyclopentadienyl chemistry. This molybdenum compound appears to contain an unusual type of molybdenum–molybdenum triple bond.

EXPERIMENTAL

General

Microanalyses (Table 1) were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra (Table 2) were generally taken in potassium bromide pellets and recorded on a Perkin–Elmer Model 21 spectrometer. In addition the metal carbonyl stretching frequencies (Table 2) were investigated in greater detail in cyclohexane solutions and recorded on a Beckman IR-9 spectrometer with grating optics and a scale expanded by a factor of 4. Proton NMR spectra (Table 1) were taken in carbon disulfide or chloroform solutions with hexamethyldi-

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* The potentially highly corrosive nature of titanium tetrachloride on metal autoclaves at the necessary temperature of 300° has discouraged attempts to repeat this reaction.

TABLE 1

SOME π-PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES

Compound	*Color*	*M.p.*	*Analyses (%)*					*Proton NMR*[a] *(τ)*	
				C	*H*	*O*	*Metal*	*π-$(CH_3)_5C_5$*[b]	*π-C_5H_5 analogue*
$(CH_3)_5C_5TiCl_3$[c]	red	225–227°	Calcd.:	41.5	5.2		16.5	7.66	3.29[f]
			Found:	41.6	4.9		16.6	(CS_2)	($CHCl_3$)
$[(CH_3)_5C_5]_2Fe$	yellow	291–295°	Calcd.:	73.6	9.2		17.2	8.38	6.00
			Found:	74.0	9.1		17.0	(CS_2)	(CS_2)
$[(CH_3)_5C_5Fe(CO)_2]_2$	red-violet	dec. ~280°	Calcd.:	58.3	6.1	13.0	22.6	8.38	5.27
			Found:	57.8	5.8	13.5	22.8	(CS_2)	($CHCl_3$)
$(CH_3)_5C_5Co(CO)_2$	red	56–58°	Calcd.:	57.6	6.0	12.8	23.6	8.11	5.00
			Found:	58.0	5.8	13.1	23.3	(CS_2)	(CS_2)
$(CH_3)_5C_5Re(CO)_3$	white	151–153°	Calcd.:	38.5	3.7	11.8	45.9	7.85	4.63
			Found:	38.8	3.6	12.2	44.6	(CS_2)	(CS_2)
$(CH_3)_5C_5Mo(CO)_3CH_3$	orange	141–145° (dec.)	Calcd.:	50.9	5.4	14.6	29.1	8.13[e]	4.75
			Found:	50.2	5.2	15.2	29.2	(CS_2)	(CS_2)
$[(CH_3)_5C_5Mo(CO)_2]_2$[d]	red	dec. ~273°	Calcd.:	50.2	5.2	11.2	33.4	8.11	Unknown
			Found:	50.0	5.5	11.8	32.8	($CHCl_3$)	

[a] Solvent given in parenthesis. [b] Proton NMR spectrum of free pentamethylcyclopentadiene: resonances at τ 7.63 (quartet, J 8 cps with further fine structure), τ 8.25–8.30 (complex: two discernible peaks), and τ 9.06 (doublet, J 8 cps) in CS_2 solution of relative intensities 1:12:3 due to the single allylic proton, the four vinylic methyl groups, and the one allylic methyl group, respectively. [c] Cl calcd. 36.8; found 37.2%. [d] Mol.wt. calcd. 574; found 514 (Mechrolab vapor pressure osmometer in chloroform solution). [e] A singlet was also observed at τ 10.03 due to the protons of the methyl groups bonded directly to the molybdenum atom. [f] Value for the closely related $C_5H_5TiCl_2OCH(CH_3)_2$.

siloxane (τ 9.95) as an internal standard and recorded on a Varian A-60 spectrometer. Ultraviolet spectra were taken in cyclohexane or dichloromethane solutions in 0.1 to 10 mm cells and recorded on a Cary Model 14 spectrometer. Mass spectra were taken at 70 e.v. electron energies on an Associated Electrical Industries MS-9 mass spectrometer. Melting points were obtained in capillaries and are uncorrected.

A nitrogen atmosphere was routinely provided for the following operations: (*a*) carrying out reactions, (*b*) handling filtered solutions of organometallic compounds, and (*c*) admitting to evacuated vessels.

Reagents. Pentamethylcyclopentadiene was prepared from 2-bromo-2-butene (Columbia Organic Chemicals, Co., Columbia, S. Carolina), tiglaldehyde (Fisher Scientific Company), lithium metal, methyl iodide, active manganese dioxide[23], and various common acids, solvents, and inorganic chemicals using the procedure of deVries[16] which contains the following five steps: (*a*) Reaction of the tiglaldehyde with 2-butenyllithium (from 2-bromo-2-butene and lithium) in diethyl ether followed by hydrolysis to give di-2-buten-2-ylcarbinol, $[CH_3CH{=}C(CH_3)]_2CHOH$ (47% yield). (*b*) Oxidation of the di-2-buten-2-ylcarbinol with active manganese dioxide in pentane to give di-2-buten-2-yl ketone, $[CH_3CH{=}C(CH_3)]_2C{=}O$, (51% yield). This step was the bottleneck in the synthesis of pentamethylcyclopentadiene since very large quantities of active manganese dioxide were required. (*c*) Ring closure of the

TABLE 2

INFRARED SPECTRA OF π-PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES (cm^{-1})

Compound	*$\nu(CO)^{a,b}$*	*$\nu(CH)^{c}$*	*Other^{c}*
$(CH_3)_5C_5TiCl_3$		2915 (vvw) 2865 (vvw)	1477 (vw), 1421 (vw), 1374 (w), 1015 (vw), 1005 (vw), 755 (m)
$[(CH_3)_5C_5]_2Fe$		2910 (m) 2900 (m) 2850 (s)	1467 (m), 1444 (m), 1420 (m), 1371 (s), 1350 (vw), 1065 (w), 1026 (s)
$[(CH_3)_5C_5Fe(CO)_2]_2$	1932 (s) [2007 (m), 1962 (s)] 1764 (s)^{d} [1796 (s)]^{d}	2925 (sh) 2850 (vw)	1468 (m), 1440 (m), 1420 (m), 1380 (s), 1368 (s), 1150 (vw), 1070 (m), 1025 (s), 949 (vw), 797 (vw)
$(CH_3)_5C_5Co(CO)_2$	2011 (s), 1949 (s) [2033 (s), 1972 (s)]	2925 (vw) 2865 (vw)	1450 (vw), 1375 (w), 1022 (vw)
$(CH_3)_5C_5Re(CO)_3$	2017 (s), 1925 (vs) [2034 (s), 1941 (vs)]	2930 (w) 2880 (m)	1480 (m), 1449 (m), 1420 (vw), 1397 (vw), 1380 (s), 1150 (vw), 1120 (vw), 1100 (vw), 1066 (w), 1031 (s), 947 (vw)
$(CH_3)_5C_5Mo(CO)_3CH_3$	2014 (s), 1929 (vs) [2028 (s), 1944 (vs)]	2915 (w) 2860 (w)	1471 (m), 1442 (w), 1418 (vw), 1374 (s), 1150 (w), 1066 (w), 1028 (m), 903 (w), 874 (w), 792 (vw), 761 (m)
$[(CH_3)_5C_5Mo(CO)_2]_2$	1940 (s), 1907 (m), 1874 (m), 1846 (m)	2930 (w) 2870 (w)	1471 (m), 1445 (w), 1419 (w), 1376 (s), 1115 (w), 1022 (m), 906 (m), 878 (m), 766 (m)

[a] Cyclohexane solutions on a Beckman IR-9 spectrometer with grating optics. [b] The ν(CO) frequencies of the corresponding unsubstituted π-C_5H_5 derivative taken under identical conditions are given in square brackets [ ]. [c] Potassium bromide pellets on a Perkin–Elmer Model 21 spectrometer. [d] Bridging carbonyl stretching frequency.

di-2-buten-2-yl ketone with a mixture of formic acid and phosphoric acid to give tetramethylcyclopentenone (62% yield). (*d*) Reaction of the tetramethylcyclopentenone with methyllithium in diethyl ether to give pentamethylcyclopentenol. (*e*) Dehydration of the pentamethylcyclopentenol with iodine to give pentamethylcyclopentadiene [56% overall yield for steps (*d*) and (*e*)]. Thus from 210 g of tiglaldehyde (the limiting component), we obtained 27.5 g of pentamethylcyclopentadiene for a 8.3% overall yield for the five steps. Pentamethylcyclopentadiene, unlike cyclopentadiene itself, is stable to dimerization and could be stored at −10° for four years without significant change.

The metal carbonyls $Fe(CO)_5$, $Mo(CO)_6$, and $Co_2(CO)_8$ were commercial samples. The rhenium compound $Re(CO)_5Cl$ was prepared from K_2ReCl_6, copper powder, and carbon monoxide at high pressures and temperatures using the published procedure[24].

Butyllithium was purchased from Alfa Inorganics, Beverly, Massachusetts, and used within one month of purchase. Tetrahydrofuran was redistilled over lithium aluminum hydride immediately before use.

Preparation of π-$(CH_3)_5C_5TiCl_3$

A mixture of 0.83 ml (0.68 g, 5 mmoles) of pentamethylcyclopentadiene and 25 ml of dry benzene was treated with 4.0 ml (9.3 mmoles) of ~22% butyllithium in hexane. After stirring for a few minutes, the resulting suspension of ~5 mmoles of lithium pentamethylcyclopentadienide was treated with 0.7 ml (1.21 g, 6.4 mmoles) of titanium tetrachloride. After stirring for two days at room temperature, the reaction mixture was filtered by gravity washing the brown residue with two 15 ml portions of benzene. Solvent was removed from the red filtrate at ~25°/25 mm. The resulting red crystals were washed with two 20 ml portions of pentane precooled in a −78° bath and then sublimed at 100°/0.1 mm to give 0.22 g (15% yield) of red crystalline $(CH_3)_5C_5TiCl_3$, m.p. 225–227°.

Preparation of $[\pi\text{-}(CH_3)_5C_5]_2Fe$

A solution of ferrous chloride was obtained by boiling 5 h under reflux a mixture of 0.54 g (3.3 mmoles) of anhydrous ferric chloride, 0.10 g (1.8 mmoles) of iron powder, and 25 ml of tetrahydrofuran. This solution was treated with a solution of ~5 mmoles of lithium pentamethylcyclopentadienide obtained by adding 4 ml (9.3 mmoles) of ~22% butyllithium in hexane to a mixture of 0.83 ml (0.68 g, 5 mmoles) of pentamethylcyclopentadiene and 25 ml of tetrahydrofuran at −78° and allowing to warm to room temperature. The resulting reaction mixture was boiled under reflux for ~24 h to insure complete reaction. After cooling to room temperature, solvent was removed at ~25°/25 mm. Direct sublimation of the brown solid residue at 100–120°/0.1 mm for several hours gave up to 0.46 g (57% yield based on pentamethylcyclopentadiene) of a yellow crystalline sublimate of $[(CH_3)_5C_5]_2Fe$, m.p. 291–295°.

Preparation of $[\pi\text{-}(CH_3)_5C_5Fe(CO)_2]_2$

A mixture of 0.83 ml (0.68 g, 5 mmoles) of pentamethylcyclopentadiene, 2.0 ml (2.92 g, 15 mmoles) of pentacarbonyliron, and 40 ml of 2,2,5-trimethylhexane was boiled 48 h under reflux with magnetic stirring. After cooling to room temperature the reaction mixture was filtered by gravity and the black residue washed with 50 ml of toluene. Solvent was removed from the red-violet combined 2,2,5-trimethylhexane/toluene solutions at 25°/0.1 mm. The crystalline residue was recrystallized twice from mixtures of dichloromethane and hexane to give 0.59 g (48% yield) of red-violet crystalline $[(CH_3)_5C_5Fe(CO)_2]_2$.

Preparation of $\pi\text{-}(CH_3)_5C_5Co(CO)_2$

A mixture of 2.0 g (5.8 mmoles) of $Co_2(CO)_8$, ~12 ml of toluene, 0.83 ml (0.68 g, 5 mmoles) of pentamethylcyclopentadiene, and 50 ml of hexane was exposed for ~18 h in a quartz tube to the radiation from a 450 watt mercury ultraviolet lamp. Solvent was then removed from the reaction mixture at ~25°/25 mm. The residue was extracted with ~50 ml of pentane and the filtered pentane extracts cooled overnight in a −78° bath. A small amount (~0.009 g) of black crystals (apparently $Co_4(CO)_{12}$) were obtained. These were removed by filtration. The air-sensitive dark red-brown filtrate was evaporated to dryness at ~20°/25 mm leaving dark red-brown crystals. These were transferred into a sublimer with the aid of 6 ml of pentane in three portions. After removing this pentane at ~25°/25 mm, the residue was sublimed at 30–50°/0.1 mm for about 3 h to give 0.17 g (13.6% yield) of a red acicular sublimate of $(CH_3)_5C_5Co(CO)_2$, m.p. 56–58°. This compound gradually turned blue upon exposure to air and oxidized still more rapidly in solution.

Preparation of π-$(CH_3)_5C_5Re(CO)_3$

A solution of ~5 mmoles of lithium pentamethylcyclopentadienide was prepared by treating a mixture of 0.83 ml (0.68 g, 5 mmoles) of pentamethylcyclopentadiene and 25 ml of tetrahydrofuran with 4.0 ml (9.3 mmoles) of 22% butyllithium at −78° and allowing the mixture to warm to room temperature. This solution of lithium pentamethylcyclopentadienide was treated with 1.9 g (5 mmoles) of $Re(CO)_5Cl$. After refluxing for 24 h at the boiling point, solvent was removed at ~25°/25 mm. The residue was extracted with three 50 ml portions of dichloromethane and solvent removed from the filtered extracts at ~25°/25 mm. The residue was extracted with 50 ml of boiling hexane in three portions. The extracts were filtered and the filtrate cooled overnight in a −78° bath. The resulting white crystals were filtered, dried, and then purified by sublimation at 80–120°/0.1 mm to give 0.087 g (4.3% yield) of a white sublimate of $(CH_3)_5C_5Re(CO)_3$, m.p. 151–153°.

Preparation of π-$(CH_3)_5C_5Mo(CO)_3CH_3$

A solution of 5 mmoles of lithium pentamethylcyclopentadienide in ~50 ml of tetrahydrofuran prepared as described above for the preparation of $(CH_3)_5C_5Re(CO)_3$ was refluxed ~36 h at the boiling point with 1.32 g (5 mmoles) of hexacarbonylmolybdenum. The resulting yellow-brown solution of $Li[Mo(CO)_3C_5(CH_3)_5]$ was stirred at room temperature for 5 h with excess (1 ml, 2.28 g, 16.1 mmoles) of methyl iodide*. Solvent was then removed at ~25°/25 mm. The residue was extracted with three 50 ml portions of dichloromethane. Solvent was removed from the filtered extracts at ~25°/25 mm. The resulting yellow-brown residue was extracted with ~50 ml of boiling hexane. The filtered extracts were cooled overnight in a −78° bath. The yellow crystals which separated were filtered and dried. The product was sublimed once at 100°/0.1 mm for 4 h and then a second time at 70°/0.1 mm for ~18 h to give finally 0.54 g (33% yield) of orange crystalline π-$(CH_3)_5C_5Mo(CO)_3CH_3$, m.p. 141–145° (dec.).

Preparation of [π-$(CH_3)_5C_5Mo(CO)_2]_2$

A mixture of 1.32 g (5 mmoles) of hexacarbonylmolybdenum, 0.83 ml (0.68 g, 5 mmoles) of pentamethylcyclopentadiene, and 40 ml of 2,2,5-trimethylhexane was refluxed ~20 h at the boiling point with magnetic stirring. After cooling to room temperature, the red crystals were filtered and sucked dry. These red crystals were heated overnight at 50–60°/0.1 mm in a sublimer to assure removal of any unreacted $Mo(CO)_6$. Generally none was found to be present. The red residue was then extracted with 50 ml of boiling hexane in three portions. The filtered extracts were cooled overnight in a −78° bath to precipitate red crystals of the product. These were filtered, dried, and recrystallized again from hot hexane by a similar procedure to give 0.57 g (40% yield) of red crystalline $[(CH_3)_5C_5Mo(CO)_2]_2$. Upon heating, this material blackened at about 273° without melting. The color of this compound was considerably lighter than that of $[C_5H_5Mo(CO)_3]_2$.

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* Treatment of this crude $Li[Mo(CO)_3C_5(CH_3)_5]$ with glacial acetic acid instead of methyl iodide gave white crystalline air-sensitive $(CH_3)_5C_5Mo(CO)_3H$ analogous to the previously[22] reported $(CH_3)_5C_5W(CO)_3H$.

*Ultraviolet and visible spectra**

A. $(CH_3)_5C_5TiCl_3$: Maxima at 246 mμ (33,000) and 459 mμ (2200) in dichloromethane solution (yellow-orange).

B. $[(CH_3)_5C_5]_2Fe$: Maxima at 222 mμ (35,000) and 420 mμ (120) in cyclohexane solution (yellow).

C. $[(CH_3)_5C_5Fe(CO)_2]_2$: Maxima at 363 mμ (11,000) and 534 mμ (1300) in dichloromethane solution (red).

D. $(CH_3)_5C_5Re(CO)_3$: Maximum at 263 mμ (3100) in cyclohexane solution (colorless).

E. $CH_3Mo(CO)_3C_5(CH_3)_5$: Maximum at 323 mμ (2300) in cyclohexane solution (very pale yellow).

F. $[(CH_3)_5C_5Mo(CO)_2]_2$: Maxima at 231 mμ (18,500) and 283 mμ (11,000) in cyclohexane solution (yellow).

*Mass spectra***

A. $[(CH_3)_5C_5]_2Fe$: The following major ions with $m/e > 160$ were observed: $C_{20}H_{30}Fe^+$ (m/e 326, rel. int. 280), $C_{19}H_{27}Fe^+$ (m/e 311, rel. int. 15), $C_{18}H_{24}Fe^+$ (m/e 296, rel. int. 3), and $C_{20}H_{30}Fe^{++}$ (m/e 163, rel. int. 39).

B. $[(CH_3)_5C_5Mo(CO)_2]_2$: The following major ions with $m/e > 230$ were observed: $(C_{10}H_{15})_2Mo_2(CO)_4^+$ (m/e 574, rel. int. 30), $(C_{10}H_{15})_2Mo_2(CO)_3^+$ (m/e 546, rel. int. 4), $(C_{10}H_{15})_2Mo_2(CO)_2^+$ (m/e 518, rel. int. 41), $(C_{10}H_{15})_2Mo_2CO^+$ (m/e 490, rel. int. 2), $(C_{10}H_{15})_2Mo_2^+$ (m/e 462, rel. int. 124) and $(C_{10}H_{15})_2Mo_2^{++}$ (m/e 231, rel. int. 55).

DISCUSSION

The use of lithium pentamethylcyclopentadienide as a reagent for the preparation of the π-pentamethylcyclopentadienyl compounds $[(CH_3)_5C_5]_2Fe$, $(CH_3)_5C_5Re(CO)_3$, and $(CH_3)_5C_5Mo(CO)_3CH_3$ exactly parallels the use of sodium cyclopentadienide for the preparation of the analogous unsubstituted π-cyclopentadienyl derivatives $(C_5H_5)_2Fe$[25], $C_5H_5Re(CO)_3$[26], and $CH_3Mo(CO)_3C_5H_5$[27]. Several failures in the early stages of this work suggest that close attention to detail is necessary to obtain $[(CH_3)_5C_5]_2Fe$ from $LiC_5(CH_3)_5$ and ferrous chloride. Possibly steric interaction between the two π-pentamethylcyclopentadienyl rings hinders the preparation of bis-π-pentamethylcyclopentadienyl derivatives with two rings bonded to the same metal atom.

The reaction between lithium pentamethylcyclopentadienide and excess titanium tetrachloride gives the mono-π-pentamethylcyclopentadienyl derivative $(CH_3)_5C_5TiCl_3$. This reaction superficially appears anomalous since sodium cyclopentadienide and titanium tetrachloride give[28] the di-π-cyclopentadienyl derivative $(C_5H_5)_2TiCl_2$. However, this difference may arise from the 1:2 mole ratio of titanium tetrachloride to sodium cyclopentadienide used for the preparation of $(C_5H_5)_2TiCl_2$ as contrasted with the excess of titanium tetrachloride relative to the lithium penta-

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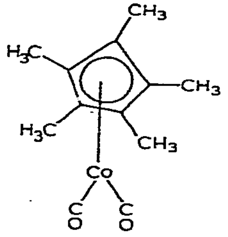
* Extinction coefficients are given in parentheses.

** The masses of the ions containing ^{56}Fe and ^{96}Mo are reported here. However, ions containing the other isotopes were observed with approximately the expected relative intensities.

methylcyclopentadienide used for the preparation of $(CH_3)_5C_5TiCl_3$. Furthermore, cyclopentadienylation of titanium tetrachloride with milder reagents such as magnesium cyclopentadienide gives[29] the mono-π-cyclopentadienyl derivative $C_5H_5TiCl_3$.

The melting point (225°) of our $(CH_3)_5C_5TiCl_3$ obtained from titanium tetrachloride and lithium pentamethylcyclopentadienide is somewhat higher than that (~200°) reported by Röhl *et al.*[17] for their $(CH_3)_5C_5TiCl_3$, obtained from various butenes and titanium tetrachloride*. However, comparison of the other properties indicate the two compounds to be identical. Our $(CH_3)_5C_5TiCl_3$ like that of Röhl *et al.*[17] exhibited a single proton resonance confirming the formulation as a π-pentamethylcyclopentadienyl derivative.

Interesting π-cyclopentadienylmetal carbonyls are often obtained by heating various metal carbonyls with cyclopentadiene**. The reactions between certain metal carbonyls and pentamethylcyclopentadiene were explored in an attempt to prepare similar π-pentamethylcyclopentadienylmetal carbonyls***. This led to the discovery of dark red very volatile air-sensitive crystalline $(CH_3)_5C_5Co(CO)_2$ (III) which appears to be completely analogous to $C_5H_5Co(CO)_2$[32,33].



(III)

The compound $[(CH_3)_5C_5Fe(CO)_2]_2$ superficially appears to be likewise analogous to the well-known[33,34] $[C_5H_5Fe(CO)_2]_2$. However, the metal carbonyl stretching frequencies of the infrared spectra of the two compounds in cyclohexane solution are distinctly different. [for a discussion of the infrared spectrum of $[C_5H_5Fe(CO)_2]_2$ see ref. 35]. The spectrum of the pentamethylcyclopentadienyl derivative $[(CH_3)_5C_5Fe(CO)_2]_2$ exhibits only one band [1932 (s) cm^{-1}] in the terminal metal carbonyl stretching region and only one band [1764 (s) cm^{-1}] in the bridging metal carbonyl stretching region. This is consistent with the structure (IV) with the π-pentamethylcyclopentadienyl rings in *trans* positions. By contrast, the π-cyclopentadienyl analogue $[C_5H_5Fe(CO)_2]_2$ exhibits two ν(CO) frequencies [2007 (m) and 1962 (s) cm^{-1}]. This additional ν(CO) frequency suggests either a less symmetrical structure or an equilibrium mixture of isomers for $[C_5H_5Fe(CO)_2]_2$ in solution [for a brief comparison of the structures of $[C_5H_5M(CO)_2]_2$ (M = Fe, Ru, and Os) compounds based on infrared spectroscopy see ref. 36].

Cyclopentadiene (produced spontaneously in the dedimerization of dicyclo-

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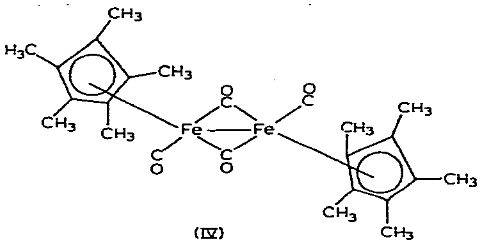
* It likewise appears difficult to obtain exact values for the melting point of the unsubstituted π-cyclopentadienyl analogue $C_5H_5TiCl_3$[29,30].

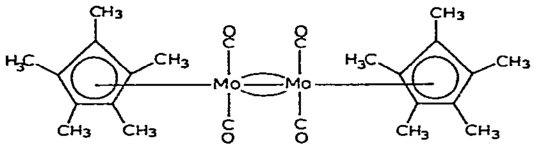
** For examples of the preparation of $[C_5H_5Mo(CO)_3]_2$, $[C_5H_5Fe(CO)_2]_2$, and $C_5H_5Co(CO)_2$ from the appropriate metal carbonyl and cyclopentadiene or dicyclopentadiene see ref. 31.

*** The previously reported[22] preparation of $(CH_3)_5C_5W(CO)_3H$ from $(CH_3CN)_3W(CO)_3$ and pentamethylcyclopentadiene is closely related to these reactions between metal carbonyls and pentamethylcyclopentadiene.

pentadiene) reacts with hexacarbonylmolybdenum to give the red-violet compound $[C_5H_5Mo(CO)_3]_2$ with three carbonyl groups for each molybdenum atom[37,38]. In contrast to this behavior pentamethylcyclopentadiene was found to react with hexacarbonylmolybdenum to give red $[(CH_3)_5C_5Mo(CO)_2]_2$ with only two carbonyl groups for each molybdenum atom. Apparently the greater steric requirements of the π-pentamethylcyclopentadienyl group more severely limits the number of carbonyl groups that can be attached to the metal atom.

The metal carbonyl region of the infrared spectrum of $[(CH_3)_5C_5Mo(CO)_2]_2$ exhibits four carbonyl stretching frequencies. Assuming the two $(CH_3)_5C_5Mo(CO)_2$ residues to be equivalent*, the infrared spectrum in this region resembles that found for $C_5H_5Mo(CO)_2T$ compounds where T is a bidentate or tridentate ligand rather than a unidentate ligand[39]. This supports the postulation of structure (V) with a molybdenum–molybdenum triple bond for $[(CH_3)_5C_5Mo(CO)_2]_2$. Assuming that the π-pentamethylcyclopentadienyl ligand like the π-cyclopentadienyl ligand occupies three coordination positions, the molybdenum atoms in $[(CH_3)_5C_5Mo(CO)_2]_2$ are formally octacoordinate molybdenum (IV) as in the $[Mo(CN)_8]^{4-}$ anion and possess the favored rare gas configuration. The alternative structure (VI) for $[(CH_3)_5C_5Mo(CO)_2]_2$ with a molybdenum–molybdenum single bond, formally hexacoordinate molybdenum (II), and each molybdenum atom possessing two electrons less than the favored rare gas configuration would represent a $C_5R_5Mo(CO)_2T$ derivative with a monodentate T ligand and thus would only be expected to exhibit two metal carbonyl stretching frequencies[38] rather than the observed four.


(IV)


(V)

The π-pentamethylcyclopentadienyl derivatives were found to possess appreciably higher melting points than the corresponding π-cyclopentadienyl derivatives. This effect was most dramatically demonstrated by $(CH_3)_5C_5Co(CO)_2$ which was a crystalline solid at room temperature (m.p. 56°) in contrast to the liquid $C_5H_5Co(CO)_2$ (m.p. −22°).

The metal carbonyl stretching frequencies of the π-(pentamethylcyclopentadienyl)metal carbonyls were 14 to 17 cm^{-1} less than those of the corresponding π-cyclopentadienylmetal carbonyls in cases where a direct comparison could be made $[C_5H_5Re(CO)_3$ and $C_5R_5Mo(CO)_3CH_3]$. This corresponds to about a 3 cm^{-1} reduction for each substitution of a hydrogen atom with a methyl group. This compares with the reduction for each methyl group of about 4 cm^{-1} in the metal carbonyl stretching frequencies of the methylated arenetungsten tricarbonyl complexes $(CH_3)_nC_6H_{6-n}W(CO)_3$ ($n = 0$ to 3 inclusive)[22] and is consistent with other[40]

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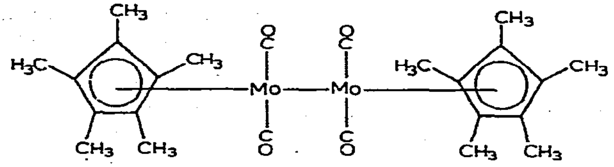
* The assumption of the equivalence of the two $(CH_3)_5C_5Mo(CO)_2$ residues is supported by the single methyl resonance in the proton NMR spectrum of $[(CH_3)_5C_5Mo(CO)_2]_2$.



(VI)

ν(CO) data on the arenemetal carbonyls. Increasing the number of electron-repelling methyl groups increases the electron density on the metal atom. This increases the π-bonding of the metal atom with the carbon monoxide ligands which in turn lowers the carbon–oxygen bond order and hence the ν(CO) frequency.

The most conspicuous feature of the infrared spectra of the π-pentamethylcyclopentadienyl compounds arising from the π-pentamethylcyclopentadienyl ligands is a band in the range 1370–1380 cm^{-1}. Weaker and more variable bands around 1440 cm^{-1} and around 1020 cm^{-1} also appeared characteristic of this ligand.

As expected, the π-pentamethylcyclopentadienyl derivatives all exhibit a sharp singlet proton NMR resonance in the range τ 7.6 to 8.4 (Table 1) due to the fifteen equivalent methyl protons. This contrasts with the clear distinction between the four vinylic methyl groups and the one allylic methyl group apparent in the NMR spectrum of free pentamethylcyclopentadiene (Table 1, footnote *b*). The correlation coefficient *r* between the positions of the methyl resonances in the π-pentamethylcyclopentadienyl compounds and of the singlet π-cyclopentadienyl resonances in analogous unsubstituted π-cyclopentadienyl compounds was +0.925 for the six cases where valid comparisons could be made. This indicates a strong degree of positive correlation. However, the appreciable deviation of this figure from 1.0 indicates that the factors influencing the chemical shifts of the NMR resonances of π-C_5H_5 and π-$(CH_3)_5C_5$ groups in analogous compounds are not identical.

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SUMMARY

Titanium tetrachloride reacts with lithium pentamethylcyclopentadienide in benzene solution to give red $(CH_3)_5C_5TiCl_3$ identical to the product previously obtained[17] from titanium tetrachloride and butenes at elevated temperatures. Ferrous chloride reacts with lithium pentamethylcyclopentadienide in boiling tetrahydrofuran to give yellow $[(CH_3)_5C_5]_2Fe$ (decamethylferrocene). Pentamethylcyclopentadiene reacts with pentacarbonyliron in boiling 2,2,5-trimethylhexane to give red-violet $[(CH_3)_5C_5Fe(CO)_2]_2$. Ultraviolet irradiation of pentamethylcyclopentadiene with $Co_2(CO)_8$ in hexane solution gives deep red crystalline $(CH_3)_5C_5Co(CO)_2$. Lithium pentamethylcyclopentadienide reacts with $Re(CO)_5Cl$ to give white $(CH_3)_5$-

$C_5Re(CO)_3$. Lithium pentamethylcyclopentadienide reacts with hexacarbonylmolybdenum in boiling tetrahydrofuran to give the $[C_5(CH_3)_5Mo(CO)_3]^-$ anion identified by conversion to the orange methyl derivative $CH_3Mo(CO)_3C_5(CH_3)_5$ with methyl iodide. However, pentamethylcyclopentadiene itself reacts with hexacarbonylmolybdenum to give red crystalline $[(CH_3)_5C_5Mo(CO)_2]_2$. This latter complex is postulated to contain a novel type of molybdenum–molybdenum triple bond.

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