Journal of Organometallic Chemistry, 60 (1973) 125–137

PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF TRANSITION METALS

IV. SOME NEW (PENTAMETHYLCYCLOPENTADIENYL)METAL CARBONYL DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN: REACTIVITY OF BIMETALLIC COMPOUNDS WITH METAL–METAL TRIPLE BONDS[*]

R. B. KING, A. EFRATY[**] and W. M. DOUGLAS[***]
Department of Chemistry, University of Georgia, Athens, Georgia, 30602, (U.S.A.)
(Received February 12th, 1973)

SUMMARY

Some reactions of $[(CH_3)_5C_5M(CO)_2]_2$ (M = Cr and Mo) and $(CH_3)_5C_5M(CO)_3CH_3$ (M = Mo and W) are described. Reactions of the bimetallic derivatives $[(CH_3)_5C_5M(CO)_2]_2$ (M = Cr and Mo) generally result in complete cleavage of the metal–metal triple bond often with carbonyl transfer to give monometallic $(CH_3)_5C_5M(CO)_3X$ derivatives. Thus treatment of $[(CH_3)_5C_5M(CO)_2]_2$ (M = Cr and Mo) with sodium amalgam in tetrahydrofuran at room temperature gives the anions $[(CH_3)_5C_5M(CO)_3]^-$ identified by reactions with $(C_6H_5)_3SnCl$, $HgCl_2$ and $Hg(CN)_2$ to give the corresponding yellow $(CH_3)_5C_5M(CO)_3R$ derivatives [R = $(C_6H_5)_3Sn$, ClHg, and 1/2 Hg]. Reactions of $[(CH_3)_5C_5M(CO)_2]_2$ (M = Cr and Mo) with iodine at room temperature give the corresponding violet to red tricarbonyl iodides $(CH_3)_5C_5M(CO)_3I$ (M = Cr and Mo). Reactions of $[(CH_3)_5C_5M(CO)_2]_2$ (M = Cr and Mo) with nitric oxide at room temperature give the corresponding orange nitrosyls $(CH_3)_5C_5M(CO)_2NO$ (M = Cr and Mo). The methyl derivatives $(CH_3)_5C_5M(CO)_3CH_3$ (M = Mo and W) react with iodine to give the iodides $(CH_3)_5C_5M(CO)_3I$ (M = Mo and W) and $(CH_3)_5C_5W(CO)_2I_3$ and with sulfur dioxide to give the yellow *S*-sulfinates $(CH_3)_5C_5M(CO)_3SO_2CH_3$ (M = Mo and W). The reaction of acetylpentamethylcyclopentadiene with $(CH_3CN)_3W(CO)_3$ in boiling methylcyclohexane gives the yellow σ-acetyl derivative $(CH_3)_5C_5W(CO)_3(COCH_3)$ in low yield in addition to the previously reported σ-methyl derivative $(CH_3)_5C_5W(CO)_3CH_3$.

INTRODUCTION

Reactions of acetylpentamethylcyclopentadiene[2,3] or pentamethylcyclo-

---

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

[**] Post-doctoral research associate 1968–1971. Present address: School of Chemistry, Rutgers University, New Brunswick, New Jersey, 08903, U.S.A.

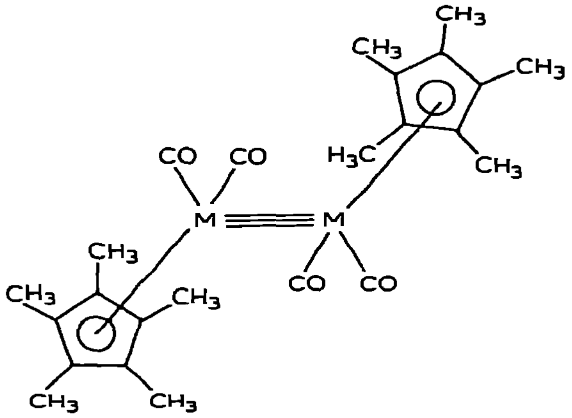
[***] Post-doctoral research associate 1971–1973.

TABLE 1

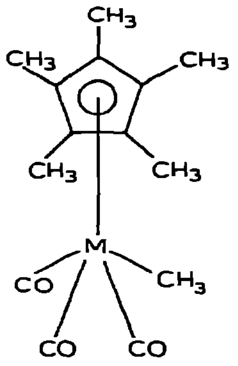
SOME NEW PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN PREPARED IN THIS WORK

Compound	*Color*	*M.p.* (°C)	*Analyses found (calcd.) (%)*					*Mol. wt. found (calcd.)*
			C	*H*	*O*	*Metal*	*Other*	
(A). Chromium compounds								
$Me_5C_5Cr(CO)_3SnPh_3$	Yellow	162–164	59.8 (59.9)	4.8 (4.6)	7.8 (7.7)	Cr, 8.3 (8.4)	Sn, 19.0 (19.2)	
$[Me_5C_5Cr(CO)_3]_2Hg$	Yellow	Dec. > 255	41.8 (42.1)	4.1 (4.0)				
$Me_5C_5Cr(CO)_3HgCl$	Yellow	Dec. > 90	30.8 (30.7)	3.0 (3.0)		Cr, 10.4 (10.2)	Hg, 40.0 (39.5)	501 (506) (Me_2CO)
$Me_5C_5Cr(CO)_3I$	Violet	Dec. > 110	37.4 (39.2)	4.1 (3.8)	11.7 (12.1)	Cr, 12.0 (13.0)		
$Me_5C_5Cr(CO)_2NO$	Orange	84	53.0 (52.8)	5.6 (5.5)	17.7 (17.7)	Cr, 19.0 (19.1)	N, 5.1 (5.1)	266 (273) (CH_2Cl_2)
(B) Molybdenum compounds								
$Me_5C_5Mo(CO)_3SnPh_3$	Yellow	154–156	57.0 (55.9)	4.7 (4.5)			Sn 17.8 (17.9)	
$[Me_5C_5Mo(CO)_3]_2Hg$	Yellow		37.7 (37.6)	3.6 (3.6)	11.6 (11.5)	Mo, 23.1 (23.2)	Hg, 24.1 (24.1)	
$Me_5C_5Mo(CO)_3I$	Red	208–210 (dec.)	35.3 (35.3)	3.1 (3.4)	10.9 (10.8)	Mo, 21.6 (21.7)	I, 28.6 (28.7)	
$Me_5C_5Mo(CO)_2NO$	Orange	87– 88	45.1 (45.4)	4.7 (4.7)		Mo, 30.2 (30.3)	N, 4.4 (4.4)	
$Me_5C_5Mo(CO)_3SO_2Me$	Yellow	125–127	43.2 (42.7)	4.4 (4.6)	20.2 (20.3)		S, 8.0 (8.1)	
(C). Tungsten compounds								
$Me_5C_5W(CO)_3COMe$	Yellow	108	40.6 (40.4)	4.0 (4.3)	14.4 (14.3)	W, 41.3 (41.2)		434 (446) ($CHCl_3$)
$Me_5C_5W(CO)_3I$	Deep red	Dec. > 125	30.1 (29.4)	2.9 (2.8)	9.1 (9.1)	W, 34.5 (34.8)	I, 23.4 (23.9)	
$Me_5C_5W(CO)_2I_3$	Brown	223–226	19.3 (19.0)	2.2 (2.0)	5.1 (4.2)	W, 22.2 (24.3)	I, 51.1 (50.4)	
$[Me_5C_5W(CO)_3]_2Hg$	Yellow	170–172	32.0 (31.2)	2.4 (3.0)	7.8 (9.6)	W, 36.2 (36.4)	Hg, 19.7 (20.0)	
$Me_5C_5W(CO)_3SO_2Me$	Yellow	129–131 (dec.)	34.9 (34.9)	3.9 (3.7)		W, 38.0 (38.2)	S, 6.8 (6.6)	482 (482) ($CHCl_3$)

pentadiene[4] with the hexacarbonyls of chromium and molybdenum give derivatives of the stoichiometry $[R_5C_5M(CO)_2]_2$ (R = CH_3, M = Cr and Mo). This stoichiometry is unusual since the corresponding unsubstituted cyclopentadienylmetal carbonyl derivatives of these metals have the stoichiometry $[R_5C_5M(CO)_3]_2$ (R = H, M = Cr[5], Mo[6] and W[6]). The presence of a metal–metal triple bond in the pentamethylcyclopentadienyl derivatives $[R_5C_5M(CO)_2]_2$ (R = CH_3; M = Cr and Mo) was originally[2,3,4] postulated in order to give the chromium or molybdenum atoms the favored 18-electron[7] rare gas configuration. A recent X-ray crystallography study on the chromium derivative[8] $[(CH_3)_5C_5Cr(CO)_2]_2$ indicated structure (I) (M = Cr). Features of particular significance in this structure were the very short chromium–chromium distance (2.276 Å) indicative of chromium–chromium triple bonding and four terminal carbonyl groups (Cr–C = 1.79 ± 0.01 Å) relatively close (Cr–C = 2.45 Å in some cases) to the chromium atom to which they are not bonded.



(I)



(II)

The unusual structural features of the compounds $[(CH_3)_5C_5M(CO)_2]_2$ [(I): M = Cr and Mo] make their chemical reactivity of interest particularly with regard to the following questions: (1) Will a metal-metal triple bond in structure (I) undergo addition reactions with appropriate reagents similar to the carbon–carbon triple bond in alkynes? (2) Does the close proximity of the carbonyl groups in structure (I) to the metal atom to which they are not bonded lead to unusual intramolecular carbonyl transfer reactions? This paper describes some reactions of the compounds $[(CH_3)_5C_5M(CO)_2]_2$ [(I) M = Cr and Mo] directed towards the clarification of these questions. Some simple reactions are also described of the σ-methyl derivatives $(CH_3)_5C_5M(CO)_3CH_3$ [(II): M = Mo and W], which are products of the reactions of acetylpentamethylcyclopentadiene with $Mo(CO)_6$ and $(CH_3CN)_3W(CO)_3$[2,3].

EXPERIMENTAL

Microanalyses (Table 1) were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, Germany; Meade Microanalytical Laboratory, Amherst, Massachusetts; and Mr. W. Swanson and co-workers of the microanalytical laboratory at

TABLE 2

SPECTROSCOPIC PROPERTIES OF SOME PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

Compound	*Infrared spectrum* (cm^{-1})		*Proton NMR spectrum*(τ)		
	Solvent	*ν(CO) and ν(NO)*	*Solvent*	Me_5C_5	*Other*
$Me_5C_5Cr(CO)_3SnPh_3$	c-C_6H_{12}	1972 s, 1911 s, 1893 s	$CDCl_3$	8.23	C_6H_6: ≈2.7(m), 2.98 (t)
$Me_5C_5Mo(CO)_3SnPh_3$	CH_2Cl_2	1988 s, 1915 s, 1891 s	$CDCl_3$	8.14	C_6H_5: 2.6 (br), 2.85 (br)
$[Me_5C_5Cr(CO)_3]_2Hg$	CH_2Cl_2	1966 m, 1940 s, 1870 s(br)	$CDCl_3$	8.15	
$[Me_5C_5Mo(CO)_3]_2Hg$	CH_2Cl_2	1979 m, 1950 s, 1875 s(br)	$CDCl_3$	8.02	
$[Me_5C_5W(CO)_3]_2Hg$	CH_2Cl_2	1994 s, 1903 s(br)	$CDCl_3$	7.85	
$Me_5C_5Cr(CO)_3HgCl$	CH_2Cl_2	1985 s, 1910 s(br)	$CDCl_3$	8.08	
$Me_5C_5W(CO)_3(COMe)$	c-C_6H_{12}	2005 , 1912 s, 1639 m	$CDCl_3$	7.96	CH_3CO: 7.47 s
$Me_5C_5Cr(CO)_3I$	Pentane	2022 s, 1965 s, 1932 s	$CDCl_3$	8.09	
$Me_5C_5Mo(CO)_3I$	c-C_6H_{12}	2036 s, 1960 s, 1939 s	$CDCl_3$	7.95	
$Me_5C_5W(CO)_3I$	CH_2Cl_2	2030 s, 1936 s(br)	$CDCl_3$	7.87	
$Me_5C_5W(CO)_2I_3$	CH_2Cl_2	2056 s, 2004 s	$CDCl_3$	7.84	
$Me_5C_5Mo(CO)_3SO_2Me$	CH_2Cl_2	2041 s, 1959 s(br)	$CDCl_3$	7.93	CH_3SO_2: 7.07 s
$Me_5C_5W(CO)_3SO_2Me$	CH_2Cl_2	2039 s, 1947 s(br)			
$Me_5C_5Cr(CO)_2NO$	CS_2	2010 s, 1932 s, 1680 s[a]	$CDCl_3$	8.21	
$Me_5C_5Mo(CO)_2NO$	Pentane	2015 s, 1935 s, 1665 s[a]	$CDCl_3$	8.04	

[a] ν(NO) frequency.

the University of Georgia. Molecular weight determinations (Table 1) were determined by the commercial laboratories listed above using vapor pressure osmometry in the indicated solvents. Infrared spectra in the 2200–1500 cm.$^{-1}$ ν(CO) and ν(NO) region (Table 2) were taken in the indicated solvents and recorded on a Perkin–Elmer Model 621 spectrophotometer with grating optics. The NMR spectra (Table 2) were taken in chloroform-*d* solution and recorded at 60 MHz. on a Perkin–Elmer–Hitachi R-20 spectrometer. Melting points were taken on samples 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*) filling evacuated vessels containing organometallic compounds.

The pentamethylcyclopentadienylmetal carbonyls $[(CH_3)_5C_5M(CO)_2]_2[(I)$: M=Cr and Mo] and $(CH_3)_5C_5Mo(CO)_3CH_3[(II)$: M=Mo] were prepared from acetylpentamethylcyclopentadiene and the corresponding metal hexacarbonyl[2,3]. The raw materials needed for these syntheses and other reagents used in this work were purchased from the usual commercial sources indicated in previous papers.

Reactions of $(CH_3CN)_3W(CO)_3$ *with acetylpentamethylcyclopentadiene*

This reaction was previously[2,3] reported to give the σ-methyl derivative $(CH_3)_5C_5W(CO)_3CH_3[(II)$: M=W]. A more careful investigation of this reaction as shown below indicates that it gives not only the σ-methyl derivative $(CH_3)_5C_5W(CO)_3CH_3$ but also the σ-acetyl derivative $(CH_3)_5C_5W(CO)_3(COCH_3)$.

A mixture of 4.0 g (10.21 mmoles) of freshly prepared $(CH_3CN)_3W(CO)_3$, 1.76 g (10 mmoles) of acetylpentamethylcyclopentadiene, and 150 ml of methylcyclohexane was boiled under reflux for 48 h. Solvent was then removed from the reaction mixture at 40°/35 mmHg. The residue was extracted with three 50 ml portions of boiling hexane. The filtered hexane extracts were chromatographed on a 2 × 60 cm Florisil column. Elution of the first yellow band with hexane followed by evaporation of the eluate gave 1.5 g (36% yield) of yellow $(CH_3)_5C_5W(CO)_3CH_3$. After removal of the $(CH_3)_5C_5W(CO)_3CH_3$, the second yellow band was eluted with a 1/1 mixture of dichloromethane and hexane and the eluate evaporated to dryness at 25°/35 mmHg. A hexane solution of the residue was chromatographed on a 2 × 60 cm Florisil column. After development of this second chromatogram with 500 ml of hexane, the yellow band was eluted with a 1/3 mixture of dichloromethane and hexane. Evaporation of this eluate followed by sublimation at 70°/0.1 mmHg gave 0.1 g (2.3% yield) of yellow $(CH_3)_5C_5W(CO)(COCH_3)$.

Preparation of $Na[(CH_3)_5C_5Cr(CO)_3]$ from $[(CH_3)_5C_5Cr(CO)_2]_2$

A solution of 0.6 g (1.23 mmoles) of $[(CH_3)_5C_5Cr(CO)_2]_2$ in 100 to 200 ml of redistilled tetrahydrofuran was stirred vigorously with excess (≈10 ml) of dilute (0.7 to 1%) sodium amalgam. The original green color of the $[(CH_3)_5C_5Cr(CO)_2]_2$ soon became violet and more gradually yellow-brown. After stirring for 1 to 3 h the excess amalgam was removed and the resulting yellow-brown solution of $Na[(CH_3)_5C_5Cr(CO)_3]$ used for experiments such as those described below.

Reaction of $Na[(CH_3)_5C_5Cr(CO)_3]$ with $(C_6H_5)_3SnCl$

A solution of $Na[(CH_3)_5C_5Cr(CO)_3]$ prepared from 0.65 g (1.34 mmoles) of $[(CH_3)_5C_5Cr(CO)_2]_2$ as described above was treated dropwise with a solution of 1.03 g (2.68 mmoles) of triphenyltin chloride in 30 ml of redistilled tetrahydrofuran. After stirring for 4½ h, solvent was removed from the reaction mixture at 25°/35 mmHg. The residue was extracted with two 100 ml portions of hot hexane. The solution was chromatographed on a 2 × 60 cm Florisil column. The yellow band was eluted with 1/9 to 1/3 mixtures of dichloromethane and hexane. These eluates were evaporated and the product recrystallized several times from mixtures of dichloromethane and hexane to give 0.32 g (19% yield) of yellow $(CH_3)_5C_5Cr(CO)_3Sn(C_6H_5)_3$.

Repetition of this reaction in an atmosphere of carbon monoxide rather than nitrogen resulted in a 27% yield of $(CH_3)_5C_5Cr(CO)_3Sn(C_6H_5)_3$.

Reaction of $Na[(CH_3)_5C_5Cr(CO)_3]$ with $Hg(CN)_2$

A solution of $Na[(CH_3)_5C_5Cr(CO)_3]$ prepared from 0.6 g (1.23 mmoles) of $[(CH_3)_5C_5Cr(CO)_2]_2$ as described above was treated with a solution of 0.35 g (1.38 mmoles) of mercury(II) cyanide in 50 ml of redistilled tetrahydrofuran. After stirring for 45 min chromatography followed by crystallization similar to the isolation of $(CH_3)_5C_5Cr(CO)_3Sn(C_6H_5)_3$ described above gave a 10% yield of yellow $[(CH_3)_5C_5Cr(CO)_3]_2Hg$.

Reaction of $Na[(CH_3)_5C_5Cr(CO)_3]$ with $HgCl_2$

A solution of $Na[(CH_3)_5C_5Cr(CO)_3]$ prepared from 0.6 g (1.23 mmoles) of $[(CH_3)_5C_5Cr(CO)_2]_2$ as described above was treated dropwise with a solution of

0.3 g (1.10 mmoles) of mercury(II) chloride in 50 ml of tetrahydrofuran. After stirring for 2 h chromatography (second yellow band) followed by crystallization similar to the isolation of $(CH_3)_5C_5Cr(CO)_3Sn(C_6H_5)_3$ described above gave an 8% yield of yellow $(CH_3)_5C_5Cr(CO)_3HgCl$.

Reaction of $[(CH_3)_5C_5Cr(CO)_2]_2$ *with iodine*

A solution of 1.0 g (2.06 mmoles) of $[(CH_3)_5C_5Cr(CO)_2]_2$ in 50 ml of dichloromethane was treated dropwise with a solution of 0.50 g (1.95 mmoles as I_2) of iodine in 100 ml of dichloromethane over 60 min. After stirring for an additional 30 min, solvent was removed from the reaction mixture at 25°/35 mmHg. A solution of the residue in a 1/4 mixture of dichloromethane and hexane was chromatographed on a 2 × 60 cm Florisil column. A green band first appeared on the column, but this decomposed upon development of the chromatogram. The major red-violet band which followed was eluted with a 1/3 mixture of dichloromethane and hexane. Concentration of the filtered red-violet eluate at ≈25°/40 mmHg followed by cooling to −78° gave 0.065 g (8% yield) of violet crystalline $(CH_3)_5C_5Cr(CO)_3I$. Attempts to recrystallize this compound led to significant decomposition.

Reaction of $[(CH_3)_5C_5Cr(CO)_2]_2$ *with nitric oxide*

Nitric oxide was passed for 15 min through a solution of 0.75 g (1.57 mmoles) of $[(CH_3)_5C_5Cr(CO)_2]_2$ in 125 ml of carbon disulfide. Solvent was removed from the reaction mixture at ≈25°/35 mmHg. A pentane solution of the residue was chromatographed on a 2 × 50 cm Florisil column. The orange band which first appeared was eluted with pentane. Evaporation of this eluate at ≈25°/35 mmHg followed by sublimation at 25°/0.01 mmHg gave 0.104 g (12% yield) of orange crystalline $(CH_3)_5C_5Cr(CO)_2NO$.

After removal of the orange band of $(CH_3)_5C_5Cr(CO)_2NO$, the chromatogram was eluted with 1/5 to 1/3 mixtures of diethyl ether and pentane. Evaporation of the eluates followed by sublimation at 70°/0.01 mmHg gave 0.084 g of a rather unstable deep red-brown solid. The infrared spectrum of this red-brown solid exhibited strong $\nu(NO)$ frequencies at 1784 and 1681 cm^{-1} indicating this second product to be a $(CH_3)_5C_5Cr(NO)_2X$ derivative.

A sample of this red-brown $(CH_3)_5C_5Cr(NO)_2X$ derivative (≈0.1 g) was treated at −78° with the pentafluorophenyllithium solution obtained by stirring 1.4 ml (2.2 mmoles) of commercial 15% n-butyllithium in hexane with 0.5 g (3.0 mmoles) of pentafluorobenzene in ≈50 ml of diethyl ether. After stirring for 1 h at −78°, solvent was removed from the reaction mixture at 25°/35 mmHg. The residue was chromatographed on a 2 × 50 cm Florisil column in 30–60° petroleum ether. Elution of the first yellow band with a 1/4 mixture of chloroform and petroleum ether followed by a low temperature crystallization from a minimum of petroleum ether gave a trace (≈0.002 g) of a green solid, m.p. 127–130°.

An analytically pure sample of this green solid could not be obtained. However, the mass spectrum of this solid (Perkin–Elmer–Hitachi RMU-6: chamber temperature 210°, sample temperature 125°) indicated it to be the expected pentafluorophenyl derivative $(CH_3)_5C_5Cr(NO)_2C_6F_5$. Major ions observed include $C_{10}H_{15}Cr(NO)_2C_6F_5^+$ (*m/e* 414, relative intensity 8), $C_{10}H_{15}CrNOC_6F_5^+$ (*m/e* 384, relative intensity 30), $C_{10}H_{15}CrC_6F_5^+$ (*m/e* 354, relative intensity 18), $C_{10}H_{15}CrF^+$ (*m/e* 206, relative intensity 87), and $C_6F_5H^+$ (*m/e* 168, relative intensity 168).

Reduction of $[(CH_3)_5C_5Mo(CO)_2]_2$ *with sodium amalgam followed by reaction with triphenyltin chloride*

A solution of 0.4 g (0.7 mmoles) of $[(CH_3)_5C_5Mo(CO)_2]_2$ in 200 ml of redistilled tetrahydrofuran was stirred with excess sodium amalgam for 2 h. Excess amalgam was then removed. The resulting solution was treated dropwise with a solution of 0.27 g (0.7 mmoles) of triphenyltin chloride in 50 ml of redistilled tetrahydrofuran. After stirring for an additional 1 h, solvent was removed from the reaction mixture at ≈25°/35 mmHg. A filtered solution of the residue in a minimum of a 1/3 mixture of dichloromethane and hexane was chromatographed on a 2 × 60 cm Florisil column. Trace amounts of a pale band of $[(CH_3)_5C_5Mo(CO)_2]_2$ were first eluted from the chromatogram with a 1/3 mixture of dichloromethane and hexane. The more major yellow band of the product was eluted with dichloromethane. After evaporation of the eluate at ≈25°/35 mmHg the product was crystallized from ≈20 ml of boiling hexane to give 0.047 g (5% yield) of yellow $(CH_3)_5C_5Mo(CO)_3Sn(C_6H_5)_3$, which was dried at 100°/0.1 mmHg.

Reaction of $[(CH_3)_5C_5Mo(CO)_2]_2$ *with iodine*

A solution of 0.40 g (0.7 mmoles) of $[(CH_3)_5C_5Mo(CO)_2]_2$ in ≈20 ml of dichloromethane was treated dropwise at room temperature with a solution of 0.165 g (0.65 mmoles as I_2) of iodine in 100 ml of dichloromethane over a period of 30 min. After stirring for an additional 30 min, solvent was removed at ≈25°/35 mmHg. An extract of the residue in hot hexane was chromatographed on a 2 × 60 cm Florisil column. The red band was eluted with a 1/3 mixture of dichloromethane and hexane. Slow evaporation of the red-orange eluate at ≈25°/35 mmHg gave 0.15 g (26% yield) of red crystalline $(CH_3)_5C_5Mo(CO)_3I$.

Reaction of $[(CH_3)_5C_5Mo(CO)_2]_2$ *with nitric oxide*

Nitric oxide was passed through a solution of 0.40 g (0.7 mmoles) of $[(CH_3)_5C_5Mo(CO)_2]_2$ in 100 ml of cyclohexane for 7 min. Solvent was then removed at 25°/35 mmHg. A pentane extract of the residue was chromatographed on a 2 × 60 cm Florisil column. Elution of the orange band with cyclohexane followed by evaporation of the eluate at 25°/35 mmHg and sublimation of the residue at 40°/0.05 mmHg gave 0.16 g (37% yield) of orange crystalline $(CH_3)_5C_5Mo(CO)_2NO$, m.p. 87–88°.

Ultraviolet irradiation of $(CH_3)_5C_5Mo(CO)_3CH_3$

A solution of 0.4 g (1.21 mmoles) of $(CH_3)_5C_5Mo(CO)_3CH_3$ in 75 ml of redistilled tetrahydrofuran in a Pyrex flask was exposed to the irradiation from an ultraviolet lamp for $6\frac{1}{2}$ h in air rather than under nitrogen as usual. Solvent was then removed from the reaction mixture at 25°/35 mmHg. A solution of the residue in a ≈1/4 mixture of dichloromethane and hexane was chromatographed on a 2 × 60 cm Florisil column. The initial red band was eluted with the same solvent mixture. Evaporation of this eluate followed by removal of any $(CH_3)_5C_5Mo(CO)_3CH_3$ by sublimation at 70°/0.1 mmHg gave 0.07 g (20% yield) of red $[(CH_3)_5C_5Mo(CO)_2]_2$, m.p. 271° (lit.[4] dec. 273°).

A similar ultraviolet irradiation of a solution of 0.5 g (1.51 mmoles) of $(CH_3)_5C_5Mo(CO)_3CH_3$ in a mixture of 30 ml of 1,5-cyclooctadiene and 75 ml of cyclohexane gave 0.05 g (11.5% yield) of red $[(CH_3)_5C_5Mo(CO)_2]_2$ rather than a cyclooctadiene-molybdenum complex.

Reactions of the methyl derivatives $(CH_3)_5C_5M(CO)_3CH_3$ ($M = Mo$ and W) with sulfur dioxide

The methyl derivative $(CH_3)_5C_5Mo(CO)_3CH_3$ (1.2 g, 3.97 mmoles) was stirred with 75 to 100 ml of liquid sulfur dioxide at −40° to −50° for 5 h. The reaction mixture was then warmed to room temperature to allow the sulfur dioxide to evaporate. A solution of the residue in a 1/3 mixture of dichloromethane and hexane was chromatographed on a 1.5 × 50 cm Florisil column. Minor side products were removed from the chromatogram with diethyl ether. The major yellow band remaining was then eluted with acetone. Evaporation of the eluate at 25°/35 mmHg followed by recrystallization from a mixture of dichloromethane and hexane gave 0.84 g (58% yield) of golden yellow $(CH_3)_5C_5Mo(CO)_3SO_2CH_3$.

A similar reaction of 0.5 g (0.96 mmoles) of $(CH_3)_5C_5W(CO)_3CH_3$ with excess sulfur dioxide gave 0.021 g (4.5 % yield) of yellow $(CH_3)_5C_5W(CO)_3SO_2CH_3$.

Reaction of $(CH_3)_5C_5Mo(CO)_3CH_3$ with iodine

A solution of 7.25 g (22 mmoles) of $(CH_3)_5C_5Mo(CO)_3CH_3$ in 50 ml of dichloromethane was treated dropwise with a solution of 5.5 g (21.7 mmoles as I_2) of iodine in 300 ml of dichloromethane over a period of 45 min. The reaction mixture was then boiled under reflux for 11 h. Solvent was removed from the reaction mixture at 25°/35 mmHg. The residue was taken up in a 1/1 mixture of dichloromethane and hexane and chromatographed on a 2.5 × 60 cm Florisil column. The orange band was eluted with the same solvent mixture. Evaporation of the eluate followed by recrystallization from a mixture of dichloromethane and hexane gave 4.0 g (44% yield) of dark red $(CH_3)_5C_5Mo(CO)_3I$.

Reaction of $(CH_3)_5C_5W(CO)_3CH_3$ with iodine

A solution of 0.85 g (1.92 mmoles) of $(CH_3)_5C_5W(CO)_3CH_3$ in 20 ml of dichloromethane was treated dropwise with a solution of 0.48 g (1.88 mmoles as I_2) of iodine in 100 ml of dichloromethane over a period of 30 min. After stirring for an additional 12 h at room temperature, the solution was concentrated to 60 ml at 25°/35 mmHg. Addition of 80 ml of hexane gave a brown precipitate. A solution of this precipitate in a 1/1 mixture of dichloromethane and hexane was chromatographed on a Florisil column. The dark brown band was eluted with a 1/1 to 2/1 mixture of dichloromethane and hexane. Slow evaporation of the eluate at 25°/35 mmHg gave 0.125 g (≈13% yield) of brown $(CH_3)_5C_5W(CO)_2I_3$.

The filtrate from the original separation of the $(CH_3)_5C_5W(CO)_2I_3$ was chromatographed on a 2 × 35 cm Florisil column. The orange band was eluted with a 1/1 mixture of dichloromethane and hexane. Evaporation of the eluate at 25°/35 mmHg gave 0.153 g (15% yield) of deep red $(CH_3)_5C_5W(CO)_3I$.

Preparation of $[(CH_3)_5C_5Mo(CO)_3]_2Hg$

A mixture of 0.55 g (1.24 mmoles) of $(CH_3)_5C_5Mo(CO)_3I$, 15 ml (204 g, 62 mmoles of sodium) of 0.7% sodium amalgam, and 100 ml of redistilled tetrahydrofuran was stirred vigorously for 1 h. Excess amalgam was removed and the reaction mixture treated dropwise at −30° with 0.55 g (1.24 mmoles) of $(CH_3)_5C_5Mo(CO)_3I$ dissolved in 20 ml of redistilled tetrahydrofuran. After stirring the reaction mixture for 30 min at −30° and at 25° for 1 h, the solvent was removed at 25°/35 mmHg. An extract of the residue in a 1/8 mixture of dichloromethane and hexane was chromatographed on a 2×60 cm alumina column. The yellow band was eluted with a 1/8 mixture of dichloromethane and hexane. Evaporation of the eluate gave 0.070 g (6.8% yield) of yellow $[(CH_3)_5C_5Mo(CO)_3]_2Hg$.

After removal of the $[(CH_3)_5C_5Mo(CO)_3]_2Hg$, an orange band remained on the chromatogram. Elution of this band with a 1/1 to 2/1 mixture of dichloromethane and hexane followed by evaporation of the eluate gave ≈0.15 g (13.7% recovery) of unreacted $(CH_3)_5C_5Mo(CO)_3I$.

Preparation of $[(CH_3)_5C_5W(CO)_3]_2Hg$

A mixture of 0.30 g (0.57 mmoles) of $(CH_3)_5C_5W(CO)_3I$, 15 ml (204 g, 62 mmoles of sodium) of 0.7% sodium amalgam, and 100 ml of redistilled tetrahydrofuran was stirred vigorously for 90 min. After removal of excess amalgam, a solution of 1.0 g (3.68 mmoles) of mercuric chloride in ≈40 ml of redistilled tetrahydrofuran was added dropwise at 25°. After stirring for an additional hour, the solvent was removed at ≈40°/35 mmHg. The residue was extracted with a 1/6 mixture of dichloromethane and hexane and the extracts chromatographed on a ≈2×60 cm Florisil column. The yellow band was eluted with the solvent mixture. Evaporation of the eluate gave ≈0.15 g (≈52% yield) of yellow crystalline $[(CH_3)_5C_5W(CO)_3]_2Hg$.

DISCUSSION

A. Reactions of the bimetallic derivatives $[(CH_3)_5C_5M(CO)_2]_2$ *[(I): M = Cr and Mo]*

All of the reactions of the bimetallic derivatives $[(CH_3)_5C_5M(CO)_2]_2$[(I): M = Cr and Mo] observed in this work involve cleavage of the metal–metal triple bond. In many cases, intramolecular carbonyl transfer to give a pentamethylcyclopentadienylmetal tricarbonyl derivative $(CH_3)_5C_5M(CO)_3X$ is observed. For example, reaction of $[(CH_3)_5C_5Cr(CO)_2]_2$ with sodium amalgam in tetrahydrofuran under nitrogen at room temperature causes the original green color to become yellow-brown through an intermediate violet stage. The presence of the tricarbonyl anion $[(CH_3)_5C_5Cr(CO)_3]^-$ in this yellow-brown solution is shown by its reactions with triphenyltin chloride to give yellow $(CH_3)_5C_5Cr(CO)_3Sn(C_6H_5)_3$, with mercuric chloride to give yellow $(CH_3)_5C_5Cr(CO)_3HgCl$, and with mercuric cyanide to give yellow $[(CH_3)_5C_5Cr(CO)_3]_2Hg$ in yields of 8 to 20%. The reaction of $[(CH_3)_5C_5Cr(CO)_2]_2$ with sodium amalgam in tetrahydrofuran under carbon monoxide rather than nitrogen proceeded similarly to give a yellow-brown solution which gave only a slightly higher yield of the triphenyltin derivative $(CH_3)_5C_5Cr(CO)_3Sn(C_6H_5)_3$ upon reaction with triphenyltin chloride. Reactions of the anion $[(CH_3)_5C_5Cr(CO)_3]^-$ with the halides $(C_6H_5)_2PCl$, $(CH_3)_3SiCl$, $(CH_3)_2SnCl_2$, $ClCH_2SCH_3$, AsF_3, acetyl chloride, and hexafluorobenzene failed to give new organochromium compounds in quantities sufficient for characterization. The molybdenum derivative $[(CH_3)_5C_5Mo(CO)_2]_2$ also reacts with sodium amalgam in tetrahydrofuran to give a solution containing the $[(CH_3)_5C_5Mo(CO)_3]^-$ anion as indicated by its reaction with triphenyltin chloride to give $(CH_3)_5C_5Mo(CO)_3Sn(C_6H_5)_3$. Similar chemistry is known[9,10] of the unsubstituted cyclopentadienylmetal tricarbonyl anions $[C_5H_5M(CO)_3]^-$ (M = Cr and Mo) prepared either by reaction of sodium cyclopentadienide with the metal hexacarbonyls or by sodium reduction of the cyclopentadienylmetal tricarbonyl dimers $[C_5H_5M(CO)_3]_2$.

Reactions of the bimetallic derivatives [$(CH_3)_5C_5M(CO)_2]_2$[(I): M = Cr and Mo] with halogens also result in cleavage of the metal–metal triple bond. The iodine cleavage of the bimetallic derivatives [$(CH_3)_5C_5M(CO)_2]_2$[(I): M = Cr and Mo] also involves intramolecular carbonyl transfer to give the pentamethylcyclopentadienylmetal tricarbonyl iodides $(CH_3)_5C_5M(CO)_3I$ (M = Cr and Mo). The purple chromium derivative $(CH_3)_5C_5Cr(CO)_3I$, like the unsubstituted cyclopentadienyl derivative[11] $C_5H_5Cr(CO)_3I$, was rather unstable in solution and thus was obtained only in rather low yield and could not be completely purified by recrystallization because of decomposition in solution. Titration of [$(CH_3)_5C_5Cr(CO)_2]_2$ with bromine in dichloromethane solution resulted in the gradual appearance of new infrared ν(CO) frequencies at 2033 s, 1971 s, and 1949 s cm^{-1} which may be assigned to the bromide $(CH_3)_5C_5Cr(CO)_3Br$ on the basis of comparison with the frequencies found for the iodide $(CH_3)_5C_5Cr(CO)_3I$ (Table 2). However, attempts to isolate a pure sample of $(CH_3)_5C_5Cr(CO)_3Br$ from this solution led instead to a blue carbonyl-free solid with analyses not corresponding to a simple empirical formula. This observation is consistent with the relative instability of $C_5H_5Cr(CO)_3X$ (X = halide) derivatives[11].

Another characteristic reaction of the bimetallic derivatives [$(CH_3)_5C_5M(CO)_2]_2$ [(I): M = Cr and Mo] is the cleavage of the metal–metal triple bond with nitric oxide to give the orange monometallic derivatives $(CH_3)_5C_5M(CO)_2NO$ (M = Cr and Mo). The reactivity of the chromium derivative [$(CH_3)_5C_5Cr(CO)_2]_2$ towards nitric oxide to give $(CH_3)_5C_5Cr(CO)_2NO$ resembles the reported[12] reactivity of the unsubstituted cyclopentadienylchromium derivative [$C_5H_5Cr(CO)_3]_2$ towards nitric oxide to give $C_5H_5Cr(CO)_2NO$. However, the reactivity of the molybdenum derivative [$(CH_3)_5C_5Mo(CO)_2]_2$ towards nitric oxide to give $(CH_3)_5C_5Mo(CO)_2NO$ contrasts with the reported[12] inertness of the unsubstituted cyclopentadienylmolybdenum derivative [$C_5H_5Mo(CO)_3]_2$ towards nitric oxide. This suggests that the molybdenum–molybdenum triple bond in [$(CH_3)_5C_5Mo(CO)_2]_2$[(I): M = Mo] is more susceptible to cleavage with chemical reagents (at least of certain types) than the molybdenum–molybdenum single bond in [$C_5H_5Mo(CO)_3]_2$.

The reaction between [$(CH_3)_5C_5Cr(CO)_2]_2$[(I) M = Cr] and nitric oxide in carbon disulfide solution besides giving orange $(CH_3)_5C_5Cr(CO)_2NO$ gave also an unstable brown less volatile but still sublimable solid. The instability of this second product prevented reliable and consistent elemental analyses from being obtained. The infrared spectrum of this brown solid exhibited two ν(NO) frequencies at 1784 and 1681 cm^{-1} consistent with its formulation as a $(CH_3)_5C_5Cr(NO)_2X$ derivative [*e.g.* reported[13] ν(NO) for $C_5H_5Cr(NO)_2Cl$ at 1823 and 1715 cm^{-1}]. Reaction of this brown solid with pentafluorophenyllithium gave a trace of a volatile green solid shown by its mass spectrum to be the pentafluorophenyl derivative $(CH_3)_5C_5Cr(NO)_2$-C_6F_5. The yield of this product was insufficient for complete characterization.

An extensive search was made for reactions of the bimetallic derivatives [$(CH_3)_5C_5M(CO)_2]_2$[(I): M = Cr and Mo] involving addition to the metal–metal triple bond without cleavage but no such reactions were found. The following reactions of [$(CH_3)_5C_5Cr(CO)_2]_2$ resulted in unchanged [$(CH_3)_5C_5Cr(CO)_2]_2$ as the only organometallic product in quantities sufficient for unambiguous identification:

(1). [$(CH_3)_5C_5Cr(CO)_2]_2$ and cyclooctatetraene or cycloheptatriene in boiling methylcyclohexane for 24 h.

(2). $[(CH_3)_5C_5Cr(CO)_2]_2$ and trimethyl phosphite in boiling methylcyclohexane for 48 h.
(3). $[(CH_3)_5C_5Cr(CO)_2]_2$ and triphenylphosphine in boiling octane for 30 h.
(4). $[(CH_3)_5C_5Cr(CO)_2]_2$ and tetraphenylbiphosphine in boiling hexane for 24 h.
(5). $[(CH_3)_5C_5Cr(CO)_2]_2$ and diphenylacetylene in boiling octane for 22 h.
(6). $[(CH_3)_5C_5Cr(CO)_2]_2$ and boiling carbon disulfide for 132 h.
(7). $[(CH_3)_5C_5Cr(CO)_2]_2$ and sulfur in boiling carbon disulfide for 50 h.
(8). Ultraviolet irradiation of $[(CH_3)_5C_5Cr(CO)_2]_2$ with diphenylsilane in tetrahydrofuran for 20 h.
(9). $[(CH_3)_5C_5Cr(CO)_2]_2$ and gaseous hydrogen chloride in cyclohexane at room temperature.

Reactions of $[(CH_3)_5C_5Cr(CO)_2]_2$ (0.4 to 0.5 g) with potential addends such as tetracyanoethylene, dimethyl acetylenedicarboxylate, dicobalt octacarbonyl, dimethyl disulfide and tetraphenylbiphosphine in boiling methylcyclohexane for $\approx$20 h gave only traces ($\approx$0.01 g) of new products which could not be identified because of the extremely limited quantities available. Similar addition reactions of the molybdenum derivative $[(CH_3)_5C_5Mo(CO)_2]_2$ [(I): M = Mo] under similar conditions to potential addends such as diphenylacetylene, 1,7-cyclododecadiyne, and trimethyl phosphite gave no products in quantities sufficient for characterization. These extensive observations indicate that the metal–metal triple bonds in the $[(CH_3)_5C_5M(CO)_2]_2$ [(I): M = Cr and Mo] derivatives do not normally undergo addition reactions without concurrent and complete cleavage of the metal–metal triple bond. There is therefore no analogy between the chemistry of the metal–metal triple bond in the $[(CH_3)_5C_5M(CO)_2]_2$ [(I): M = Cr and Mo] derivatives and the chemistry of the carbon–carbon triple bond in alkynes.

B. Reactions of the σ-methyl derivatives $(CH_3)_5C_5M(CO)_3CH_3$ (M = Mo and W)

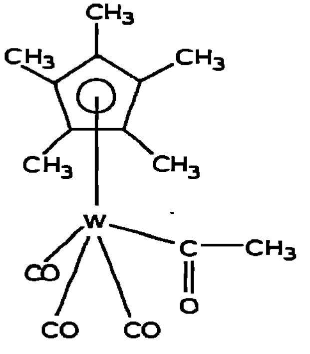
A byproduct from the preparation of $[(CH_3)_5C_5Mo(CO)_2]_2$[(I): M = Mo] by the reaction between acetylpentamethylcyclopentadiene and $Mo(CO)_6$ is the methyl derivative $(CH_3)_5C_5Mo(CO)_3CH_3$. Similarly, the reaction of acetylpentamethylcyclopentadiene with $(CH_3CN)_3W(CO)_3$ is reported[2,3] to give the analogous σ-methyl derivative $(CH_3)_5C_5W(CO)_3CH_3$ [(II): M = W]. Several reactions of these methyl derivatives have been investigated. The reactions of $(CH_3)_5C_5M(CO)_3CH_3$ [(II): M = Mo and W] with liquid sulfur dioxide to give the sulfinates $(CH_3)_5C_5M(CO)_3SO_2CH_3$ are further examples of a well-established[14] type of insertion reaction of transition metal alkyls. The much lower yield of $(CH_3)_5C_5W(CO)_3SO_2CH_3$ from the reaction of the tungsten compound $(CH_3)_5C_5W(CO)_3CH_3$ [(II): M = W] with liquid sulfur dioxide relative to the yield of $(CH_3)_5C_5Mo(CO)_3SO_2CH_3$ from the analogous reaction of the analogous molybdenum compound $(CH_3)_5C_5Mo(CO)_3CH_3$[(II): M = Mo] may relate to the greater strength of tungsten–carbon bonds relative to molybdenum–carbon bonds[15].

The methyl derivatives $(CH_3)_5C_5M(CO)_3CH_3$[(II): M = Mo and W] also react with iodine in dichloromethane at room temperature with simple cleavage of the methyl–metal bond to give the tricarbonyl iodides $(CH_3)_5C_5M(CO)_3I$. The molybdenum compound $(CH_3)_5C_5Mo(CO)_3I$ is identical to the product obtained from $[(CH_3)_5C_5Mo(CO)_2]_2$ and iodine as discussed above. The reaction of the tungsten compound $(CH_3)_5C_5W(CO)_3CH_3$ [(II): M = W] with iodine also gave small quantities of the dicarbonyl triiodide $(CH_3)_5C_5W(CO)_2I_3$ analogous to a series of known[10] dicarbonyl trihalides of the type $C_5H_5M(CO)_2X_3$ (M = Mo and W; X = Cl, Br, and I) containing unsubstituted cyclopentadienyl rings. The infrared ν(CO) frequencies (2056 and 2004 cm^{-1}) of $(CH_3)_5C_5W(CO)_2I_3$ resemble closely those found for $C_5H_5W(CO)_2I_3$ (2068 and 2027 cm^{-1}) with the small downward shift expected for complete methyl substitution for hydrogen on the cyclopentadienyl ring[4].

The halides $(CH_3)_5C_5M(CO)_3I$ (M = Mo and W) are useful intermediates for the preparation of the mercury derivatives $[(CH_3)_5C_5M(CO)_3]_2Hg$ (M = Mo and W) by procedures involving sodium amalgam reduction as described in the Experimental Section. The complete series of three mercury derivatives $[(CH_3)_5C_5M(CO)_3]_2Hg$ (M = Cr, Mo, and W) is thus available. The patterns of the infrared ν(CO) frequencies in the three mercury derivatives $[(CH_3)_5C_5M(CO)_3]_2Hg$ (M = Cr, Mo, and W) change noticeably upon descending the column of the periodic table probably because of different coupling between the stretches of the carbonyl groups bonded to different metal atoms.

Ultraviolet irradiation of the methylmolybdenum derivative $(CH_3)_5C_5Mo(CO)_3CH_3$ was investigated as a possible low temperature synthetic approach to the unknown tricarbonyl dimer $[(CH_3)_5C_5Mo(CO)_3]_2$ analogous to the well-known[6] $[C_5H_5Mo(CO)_3]_2$. However, only the dicarbonyl dimer $[(CH_3)_5C_5Mo(CO)_2]_2$ [(I): M = Mo] was obtained. Another possible low-temperature synthetic approach to the unknown tricarbonyl dimer $[(CH_3)_5C_5Mo(CO)_3]_2$ is the reduction of $(CH_3)_5C_5Mo(CO)_3I$ with sodium amalgam followed by reaction of the presumably generated $[(CH_3)_5C_5Mo(CO)_3]^-$ with more $(CH_3)_5C_5Mo(CO)_3I$. However, this approach gave instead the mercury derivative $[(CH_3)_5C_5Mo(CO)_3]_2Hg$ as discussed above. From these somewhat limited observations we suspect that the unknown (pentamethylcyclopentadienyl)molybdenum tricarbonyl dimer $[(CH_3)_5C_5Mo(CO)_3]_2$ is unstable even at room temperature with respect to decarbonylation giving $[(CH_3)_5C_5Mo(CO)_2]_2$ [(I): M = Mo] in contrast to the unsubstituted cyclopentadienylmolybdenum tricarbonyl dimer $[C_5H_5Mo(CO)_3]_2$[6].

The $(CH_3)_5C_5W(CO)_3CH_3$ [(II): M = W] used for this work was isolated from the first yellow band from chromatography of the mixture obtained by heating acetylpentamethylcyclopentadiene with $(CH_3CN)_3W(CO)_3$ in boiling methylcyclohexane. A second weaker and more strongly adsorbed yellow band was also observed



(III)

in this chromatogram. This was identified as the σ-acetyl derivative $(CH_3)_5C_5W(CO)_3(COCH_3)$ (III) by elemental analyses and the presence of an acyl $\nu(CO)$ frequency at 1639 cm^{-1} in addition to the usual terminal $\nu(CO)$ frequencies for a $(CH_3)_5C_5W(CO)_3$ group. The mass spectrum of $(CH_3)_5C_5W(CO)_3(COCH_3)$ was essentially identical to the mass spectrum reported[3] for the σ-methyl derivative $(CH_3)_5C_5W(CO)_3CH_3$ [(II): M=W] indicating decarbonylation within the mass spectrometer. The isolation of the σ-acetyl tungsten derivative $(CH_3)_5C_5W(CO)_3(COCH_3)$ (III) from the reaction of acetylpentamethylcyclopentadiene with $(CH_3CN)_3W(CO)_3$ resembles the previously observed[2,3] isolation of the σ-acetyliron derivative $(CH_3)_5C_5Fe(CO)_2(COCH_3)$ from the reaction of acetylpentamethylcyclopentadiene with $Fe_2(CO)_9$ and is consistent with the previously discussed[2,3] general scheme for the reactions of acetylpentamethylcyclopentadiene with metal carbonyls.

ACKNOWLEDGEMENT

We are indebted to the National Science Foundation for partial support of this work under Grant GP-31347X.

REFERENCES

1 R. B. King, A. Efraty, and W. M. Douglas, *J. Organometal. Chem.*, 56 (1973) 345.
2 R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 93 (1971) 4950.
3 R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 94 (1972) 3773.
4 R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 8 (1967) 287.
5 E. O. Fischer and W. Hafner, *Z. Naturforsch. B*, 10 (1955) 140.
6 F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 27 (1957) 809.
7 R. B. King, *Advan. Chem. Ser.*, 62 (1967) 203.
8 J. Potenza, P. Giordano, D. Mastropaolo, A. Efraty, and R. B. King, *J. Chem. Soc., Chem. Commun.*, (1972) 1333.
9 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
10 R. B. King, *Accounts Chem. Res.*, 3 (1970) 417.
11 A. R. Manning and D. J. Thornhill, *J. Chem. Soc. A*, (1971) 637.
12 E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch. B*, 10 (1955) 598.
13 R. B. King, *Organometal. Syn.*, 1 (1965) 161.
14 A. Wojcicki, *Accounts. Chem. Res.*, 4 (1971) 344.
15 R. B. King, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 905.
16 R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, (1966) 1606; M. L. H. Green and W. E. Lindsell, *J. Chem. Soc. A*, (1967) 686.