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REACTIONS OF ALKALI-METAL DERIVATIVES OF METAL CARBONYLS VII*. REACTIONS OF THE SODIUM CYCLOPENTADIENYLTRICARBONYLMETALLATES OF MOLYBDENUM AND TUNGSTEN WITH CERTAIN ORGANIC POLYHALIDES**

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In 1963 the reactions between various α,ω-dibromoalkanes and the sodium salts $NaFe(CO)_2C_5H_5$ and $NaMn(CO)_5$ were reported[2,3]. Both of these sodium salts replaced both halogen atoms of the α,ω-dibromoalkanes in tetrahydrofuran solution at room temperature. In the case of the iron derivative compounds of the type $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ ($n = 3$, 4, 5, or 6) were obtained[2]. In all of these iron compounds all of the methylene groups, regardless of their distance from the iron atom, exhibited a single sharp proton NMR resonance. The reaction between $NaMn(CO)_5$ and 1,3-dibromopropane, also carried out in tetrahydrofuran solution, gave a golden yellow crystalline material of analogous stoichiometry, $(CH_2)_3[Mn(CO)_5]_2$. However, the three methylene groups in this manganese complex exhibited three proton NMR resonances of relative intensities 1 : 1 : 1[3]. On the basis of this anomalous NMR spectrum, the unusual structure (I) was proposed for $(CH_2)_3[Mn(CO)_5]_2$.

TABLE 1

SOME $Br(CH_2)_nM(CO)_3C_5H_5$ COMPOUNDS

Compound[a]	*M.p.*	*Yield (%)*	*Analyses (%)*				
				C	*H*	*O*	*Br*
$Br(CH_2)_3Mo(CO)_3C_5H_5$	85–87°	33	Calcd.	36.0	3.0	13.1	21.8
			Found	36.5	2.8	14.0	20.0
$Br(CH_2)_4Mo(CO)_3C_5H_5$	48–50°	17	Calcd.[b]	37.8	3.4	12.6	21.0
			Found	38.0	3.1	12.8	21.1
$Br(CH_2)_3W(CO)_3C_5H_5$	109–112°	23	Calcd.	29.0	2.4	10.5	17.6
			Found	29.4	2.6	11.3	16.4
$Br(CH_2)_4W(CO)_3C_5H_5$	66–68°	13	Calcd.[c]	30.7	2.8	10.2	17.0
			Found	30.0	2.7	10.5	15.9

[a] These compounds were obtained from $Br(CH_2)_nBr$ and $NaM(CO)_3C_5H_5$ in tetrahydrofuran solution at room temperature. [b] Molybdenum: calcd. 25.2; found 25.4%. [c] Molecular weight: calcd. 469; found 506 (Mechrolab vapor pressure osmometer in benzene solution).

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* For Part VI see ref. 1.

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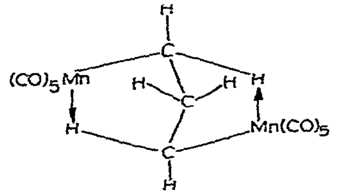
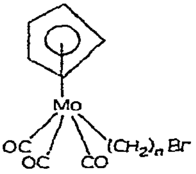
Hoping to clarify some of the above observations, the reactions of 1,3-dibromopropane and 1,4-dibromobutane with the metal carbonyl anions $NaM(CO)_3C_5H_5$ (M=Mo or W) were investigated in tetrahydrofuran solution at room temperature (Table 1). In all cases only one bromine atom was replaced by the transition metal atom resulting in compounds of the type $Br(CH_2)_nM(CO)_3C_5H_5$ (II: $n=3$ or 4; M=Mo or W). In these experiments no evidence for compounds of the type $(CH_2)_n[M(CO)_3C_5H_5]_2$ ($n=3$ or 4; M=Mo or W) was obtained.

These new compounds have physical properties corresponding to other $RM(CO)_3C_5H_5$ compounds[4]. Thus they are light yellow crystalline solids readily soluble in organic solvents. They are volatile in high vacuum at ~80°/0.1 mm; however, sublimation is not recommended for purification of the molybdenum compounds since decomposition to give $[C_5H_5Mo(CO)_3]_2$ or $C_5H_5Mo(CO)_3Br$ also occurs at 80°/0.1 mm. The infrared spectra of the $Br(CH_2)_nM(CO)_3C_5H_5$ compounds in cyclohexane solution like other $RM(CO)_3C_5H_5$ compounds exhibit two strong metal–carbonyl stretching frequencies (Table 2). However, the infrared spectra of the molybdenum compounds in cyclohexane solution in this region exhibit other weaker metal–carbonyl stretching frequencies indicative of decomposition. As is the case with other $RM(CO)_3C_5H_5$ compounds including the hydrides $HM(CO)_3C_5H_5$, the tungsten compounds are considerably more stable than their molybdenum analogues decomposing neither on sublimation at ~80°/0.1 mm nor in cyclohexane solution.



(I)



(II)

The proton NMR spectra (Table 3) of the $Br(CH_2)_nM(CO)_3C_5H_5$ compounds exhibit the expected methylene and π-C_5H_5 resonances of relative intensities consistent with their formulas. The triplet resonance arising from the two protons of one methylene group appears at appreciably lower fields (τ 6.6 to τ 6.9) than the protons of the remaining methylene groups (τ 8.0 to τ 8.5). Comparison with the published* spectra of alkyl halides suggests that this methylene group with lower field proton resonances is that adjacent to the bromine atom.

The replacement of only one bromine atom in 1,3-dibromopropane or 1,4-dibromobutane with $-M(CO)_3C_5H_5$ groups by reaction with $NaM(CO)_3C_5H_5$ (M = Mo or W) is hardly surprising. Chemical observations** and kinetic measurements[7] have both already indicated the sodium salts $NaM(CO)_3C_5H_5$ (M = Mo or W) to be less reactive than the sodium salts $NaMn(CO)_5$ and especially $NaFe(CO)_2C_5H_5$. The reactions of these sodium salts with 1,3-dibromopropane illustrate their different reactivities more clearly than past chemical observations.

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* Representative proton NMR spectra of organic halides may be found in ref. 5.

** For discussions of the chemistry of metal carbonyl anions see ref. 6.

TABLE 2

INFRARED SPECTRA OF NEW COMPOUNDS DESCRIBED IN THIS PAPER IN CM^{-1}

Compound	ν(CO)[a]	ν(CH)[b]	*Other bands*[b]
A. $Br(CH_2)_nM(CO)_3C_5H_5$ compounds			
$Br(CH_2)_3Mo(CO)_3C_5H_5$	2026(s) 1945(vs)[c]	3070(vvw) 2920(vw)	1423(w), 1415(w), 1295(w), 1205(w), 1115(vw), 1014(w), 1001(vw), 845(vw), 835(w), 820(m)
$Br(CH_2)_4Mo(CO)_3C_5H_5$	2025(s) 1947(vs)[c]	3060(vw) 2910(w) 2815(vw)	1430(sh), 1418(m), 1280(m), 1115(w), 1010(w), 1003(w), 830(w), 816(s)
$Br(CH_2)_3W(CO)_3C_5H_5$	2024(s) 1935(vs)	3060(vw) 2900(vw)	1420(m), 1300(m), 1207(m), 1140(sh), 1132(w), 1016(w, sh), 1010(m), 1001(vw), 944(vw), 850(w), 841(m), 834(m), 828(m), 756(vw)
$Br(CH_2)_4W(CO)_3C_5H_5$	2020(s) 1933(vs)	3050(vvw) 2890(w)	1422(sh), 1411(w), 1280(w), 1201(vw), 1122(w), 1009(w), 1000(vw), 827(m)
B. Other compounds			
$(CH_2)_3[Mn(CO)_4P(C_6H_5)_3]_2$	1987(m) 1956(s) 1940(sh) 1915(sh)[d]	3000(w)	1579(vw), 1562(vw), 1479(w), 1440(m), 1302(vw), 1180(vw), 1151(vw), 1085(m), 1069(vw), 1022(vw), 994(vw), 740(m), 721(vw), 692(m)
$\{C_3H_5[Fe(CO)_2C_5H_5]_2\}[PF_6]$	2044(s) 2019(s)[d]	3060(vw)	1495(m), 1426(w), 1410(w), 1387(m), 1350(vw), 1242(w), 1236(w), 1101(w), 1095(m), 1075(m), 1054(m), 1040(m), 1031(m), 1015(w), 933(w), 876(w), 856(m), 837(s)[e], 830(s)[e]

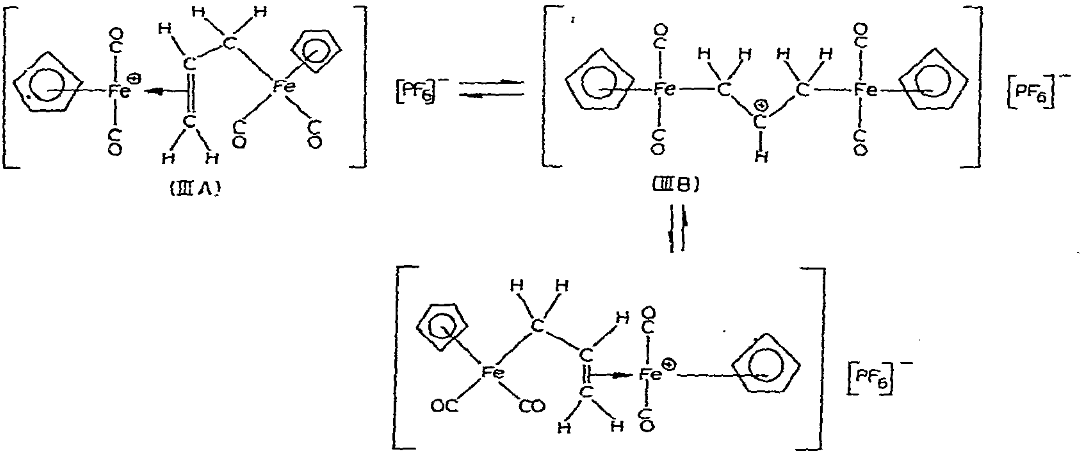
[a] Cyclohexane solution on a Beckman IR-9 spectrometer unless otherwise indicated. [b] KBr pellets on a Perkin–Elmer Model 21 spectrometer. [c] Weaker bands at ~1995 cm^{-1} due to decomposition products were also observed. [d] Halocarbon oil mulls on a Beckman IR-9 spectrometer. [e] ν(PF) of PF_6^- anion.

The availability of the compounds $Br(CH_2)_nM(CO)_3C_5H_5$ appeared to provide an opportunity to prepare novel compounds containing two different transition metal atoms by replacement of the residual bromine atom by treatment with a sodium salt of a more reactive metal carbonyl anion such as $NaMn(CO)_5$ or $NaFe(CO)_2C_5H_5$. However, treatment of $Br(CH_2)_3Mo(CO)_3C_5H_5$ with $NaMn(CO)_5$ in tetrahydrofuran at room temperature replaced both the bromine atom and the $-Mo(CO)_3C_5H_5$ group with $-Mn(CO)_5$ groups to give $(CH_2)_3[Mn(CO)_5]_2$ identical to an authentic sample[3] prepared from 1,3-dibromopropane and $NaMn(CO)_5$. Analogously, the compounds $Br(CH_2)_nMo(CO)_3C_5H_5$ ($n = 3$ or 4) reacted with $NaFe(CO)_2C_5H_5$ in tetrahydrofuran solution at room temperature to give the known[2] compounds $(CH_2)_n[Fe(CO)_2C_5H_5]_2$. These reactions, although synthetically valueless, are significant in representing a novel type of transmetallation reaction in transition metal organometallic chemistry. Alternatively they may be regarded as involving the transfer of an organic ligand σ-bonded to a transition metal in contrast to the cyclopentadienyl and tetraphenylcyclobutadiene transfer reactions reported by Maitlis, Efraty, and Games[8] which involve the transfer of an organic ligand π-bonded to a transition metal.

Green and Nagy[9] report the abstraction as hydride of a β-hydrogen atom in compounds of the types $RFe(CO)_2C_5H_5$ and $RMn(CO)_5$ with triphenylmethyl salts to give cations of the types $[C_5H_5Fe(CO)_2(\text{olefin})]^+$ and $[(CO)_5Mn(\text{olefin})]^+$. The iron compound $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ reacts with triphenylmethyl hexafluorophosphate, $[(C_6H_5)_3C][PF_6]$, in dichloromethane solution to give orange crystalline $[C_5H_5Fe(CO)_2CH_2CHCH_2Fe(CO)_2C_5H_5][PF_6]$.

The limited solubility of this new iron complex has prevented observation of the complete proton NMR spectrum. However, the resonance corresponding to the equivalent π-cyclopentadienyl protons can be observed in a saturated $(CD_3)_2CO$ solution at τ 4.58. These acetone solutions are unstable and develop additional resonances at τ 3.83 and eventually also τ 5.10 due to the decomposition products.

The equivalence of the two π-cyclopentadienyl groups in $[C_5H_5Fe(CO)_2 \cdot CH_2CHCH_2Fe(CO)_2C_5H_5][PF_6]$ indicates both iron atoms to be equivalent. This is consistent with structure (IIIB), a carbonium ion salt where the positive charge is localized on the central carbon atom of the three-carbon chain. However, in view of the stability of $[C_5H_5Fe(CO)_2(\text{olefin})]^+$ salts relative to carbonium ion salts, a more attractive representation of $[C_5H_5Fe(CO)_2CH_2CHCH_2Fe(CO)_2C_5H_5] \cdot [PF_6]$ involves a dynamic equilibrium between the carbonium salt (IIIB) and the two "mirror-image" $[C_5H_5Fe(CO)_2(\text{olefin})]^+$ salts (IIIA) and (IIIC). Attempts to split the π-C_5H_5 resonance in (III) by cooling were not successful: at −25° the π-C_5H_5 resonance remained a singlet and below −25° the solubility of (III) in acetone solution was insufficient for observation of an NMR spectrum.



(IIIA)

(IIIB)

(IIIC)

The manganese compound $(CH_2)_3[Mn(CO)_5]_2$ (I) did not deposit a precipitate upon reaction with triphenylmethyl hexafluorophosphate in dichloromethane solution at room temperature for several days. After several weeks a yellow solid had separated but an infrared spectrum showed the absence of metal carbonyl groups. This material thus cannot be $[(CO)_5MnCH_2CHCH_2Mn(CO)_5][PF_6]$ or other manganese carbonyl salt. The behavior of $(CH_2)_3[Mn(CO)_5]_2$ (I) and $(CH_2)_3$-

$[Fe(CO)_2C_5H_5]_2$ upon treatment with triphenylmethyl hexafluorophosphate are distinctly different in line with the different structures of the iron and manganese compounds.

The reaction between $(CH_2)_3[Mn(CO)_5]_2$ (I) and triphenylphosphine was investigated in order to see whether replacement of carbonyl groups in (I) with triphenylphosphine ligands would alter the unusual structure. Orange-yellow $(CH_2)_3[Mn(CO)_4P(C_6H_5)_3]_2$ was obtained from this reaction. Unfortunately, this material was too sparingly soluble in organic solvents for observation of the proton NMR resonances arising from the methylene protons. It is thus not clear whether structure (I) is preserved upon replacement of carbonyl groups with triphenylphosphine ligands.

A few exploratory reactions between $NaMo(CO)_3C_5H_5$ and other types of polyhalides were carried out. These studies showed that chlorocarbons with allylic chlorine atoms such as hexachlorocyclopentadiene and hexachloropropene act as chlorinating agents converting $NaMo(CO)_3C_5H_5$ into the known[4] $C_5H_5Mo(CO)_3Cl$. This new route to $C_5H_5Mo(CO)_3Cl$ does not appear to possess any obvious advantages over its known[4]* preparation from $C_5H_5Mo(CO)_3H$ and carbon tetrachloride.

EXPERIMENTAL

Microanalyses (Table 1) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. In general, infrared spectra (Table 2) were taken in potassium bromide pellets and recorded on a Perkin–Elmer Model 21 spectrometer with sodium chloride optics. In addition, the carbonyl stretching frequencies in the infrared spectra of selected compounds were investigated in greater detail in cyclohexane solutions or halocarbon oil mulls on a Beckman IR-9 spectrometer with grating optics. Ultraviolet spectra were taken in cyclohexane or dichloromethane

TABLE 3

PROTON N.M.R. SPECTRA (τ) OF $Br(CH_2)_nM(CO)_3C_5H_5$ COMPOUNDS (CS_2 solution)

Compound	*CH_2Br*[a]	*Other CH_2 groups*	*C_5H_5*[d]
$Br(CH_2)_3Mo(CO)_3C_5H_5$	6.83(7)[c,e]	~8.0[b,c], ~8.5[b,c]	4.87
$Br(CH_2)_4Mo(CO)_3C_5H_5$	6.61(6)[c,e]	8.11[c,f], 8.34[g,f]	4.68
$Br(CH_2)_3W(CO)_3C_5H_5$	6.75(7)[c,e]	~8.0[b,c], ~8.5[b,c]	4.63
$Br(CH_2)_4W(CO)_3C_5H_5$	6.65(6)[c,e]	8.16[c,f], 8.43[g,f]	4.65

[a] Coupling constants given in parentheses. [b] Complex asymmetric pattern of lines. [c] Relative intensity corresponding to one methylene group. [d] Sharp singlet. [e] Triplet. [f] Broad unresolved. [g] Relative intensity corresponding to two methylene groups.

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* We have developed an improved preparation of $C_5H_5Mo(CO)_3Cl$ based on this reaction between $C_5H_5Mo(CO)_3H$ and carbon tetrachloride which does not require isolation and purification of the rather unstable $C_5H_5Mo(CO)_3H$. Instead, the solution obtained by heating hexacarbonylmolybdenum with sodium cyclopentadienide in tetrahydrofuran is acidified with acetic acid and then reacted directly with carbon tetrachloride with ice cooling. Details of this improved procedure will be given in a future more appropriate publication.

solutions and recorded on a Cary Model 14 spectrometer. Proton NMR spectra (Table 3) were taken in carbon disulfide solution and recorded on a Varian A-60 spectrometer. Melting and decomposition points were taken 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; (*c*) admitting to evacuated vessels.

Reagents

Tetrahydrofuran and 1,2-dimethoxyethane such as used for the sodium salts of metal carbonyl anions were freshly redistilled over lithium aluminum hydride. 1,3-Dibromopropane, 1,4-dibromobutane, triphenylphosphine, hexachloropropene, and hexachlorocyclopentadiene were commercial samples. The reaction between triphenylcarbinol and hexafluorophosphoric acid in propionic anhydride solution[10] was used to prepare $[(C_6H_5)_3C][PF_6]$. The metal carbonyls $Fe(CO)_5$, $Mo(CO)_6$, and $W(CO)_6$ were purchased from Antara Division of General Aniline and Film (New York City), Climax Molybdenum Company (New York City), and Pressure Chemical Company (Pittsburgh, Pa.), respectively.

The sodium salts $NaM(CO)_3C_5H_5$ were obtained by the previously published procedure[4,11] of reacting the appropriate metal hexacarbonyl with sodium cyclopentadienide in boiling tetrahydrofuran (M = Mo) or 1,2-dimethoxyethane (M = W). Sodium amalgam (~1%) reductions of $[C_5H_5Fe(CO)_2]_2$ and $Mn_2(CO)_{10}$ in tetrahydrofuran solutions were used to prepare the sodium salts $NaFe(CO)_2C_5H_5$ and $NaMn(CO)_5$, respectively[4,11,12,13].

The iron compound $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ was prepared by the published procedure[2] from 1,3-dibromopropane and $NaFe(CO)_2C_5H_5$. The manganese compound $(CH_2)_3[Mn(CO)_5]_2$ was prepared by a modification of the published procedure[3] from 100 mmoles each of 1,3-dibromopropane and $NaMn(CO)_5$ and omitting the chromatography purification step previously used.

Preparation of the $Br(CH_2)_nM(CO)_3C_5H_5$ compounds ($n = 3$ or 4; M = Mo or W)

A tetrahydrofuran (M = Mo) or 1,2-dimethoxyethane (M = W) solution of the appropriate sodium salt $NaM(CO)_3C_5H_5$ (M = Mo: 100 mmoles; M = W: 20 mmoles) was stirred for about 16 h with an equimolar or up to 60% excess of 1,3-dibromopropane or 1,4-dibromobutane. Solvent was then removed at ~25°/30 mm. The residue was extracted with three 100 ml portions of dichloromethane. Solvent was removed from the filtered extracts at ~25°/30 mm.

In the cases of the $Br(CH_2)_3M(CO)_3C_5H_5$ compounds the crude product was extracted with 200 to 300 ml of boiling hexane in several portions. The filtered hexane extracts were cooled several hours in a −78° bath. The resulting crystals were filtered and recrystallized from hexane one or two additional times by the same procedure.

In the cases of the more soluble $Br(CH_2)_4M(CO)_3C_5H_5$ compounds the crude product was extracted with 70 (M = W) to 150 (M = Mo) ml of pentane at room temperature in several portions. The filtered extracts were cooled in a −78° bath for several hours. The crystals were filtered and crystallized an additional time by the same procedure.

In the two cases of the tungsten compounds, the product obtained after the first pentane or hexane crystallization was heated at ~70°/0.1 mm overnight to assure removal of $W(CO)_6$. Small amounts of $Br(CH_2)_nW(CO)_3C_5H_5$ sublimed during this operation.

Yields, analyses, and melting points of the $Br(CH_2)_nM(CO)_3C_5H_5$ compounds are given in Table 1.

Reactions between $Br(CH_2)_nMo(CO)_3C_5H_5$ *and* $NaFe(CO)_2C_5H_5$

A mixture of 10 mmoles of $NaFe(CO)_2C_5H_5$ and 5 mmoles of $Br(CH_2)_n$-$Mo(CO)_3C_5H_5$ ($n = 3$ or 4) in 100 ml of tetrahydrofuran was stirred overnight for 16 h. Solvent was then removed from the reaction mixture in a water-pump vacuum. The residue was extracted with three 50-ml portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts in a water-pump vacuum. A filtered solution of the residue in 75 to 100 ml of diethyl ether was chromatographed on a 2×50 cm alumina column. The chromatogram was developed with diethyl ether. A yellow band of the $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ appeared followed by a brown-violet band of $[C_5H_5Fe(CO)_2]_2$. The yellow band was eluted with diethyl ether. Solvent was removed from the filtered eluate at ~25°/30 mm.

The orange crystalline residue of crude $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ ($n = 3$ or 4) was extracted with 50 ml of boiling hexane in three portions. The filtered extracts were cooled at −15° to −78° for ~16 h. The resulting orange crystals were filtered and dried to give 0.46 g (23% yield) of $(CH_2)_3[Fe(CO)_2C_5H_5]_2$, m.p. 96–98° (lit.[2] m.p. 103–105°), or 0.58 g (28% yield) of $(CH_2)_4[Fe(CO)_2C_5H_5]_2$, m.p. 117–119° (lit.[2] m.p. 123–124°) depending on the $Br(CH_2)_nMo(CO)_3C_5H_5$ compound used as a starting material. The products were also identified by comparison of their infrared and proton NMR spectra with published[2] data.

Reaction between $Br(CH_2)_3Mo(CO)_3C_5H_5$ *and* $NaMn(CO)_5$

A mixture of 1.83 g (5 mmoles) of $Br(CH_2)_3Mo(CO)_3C_5H_5$ and 10 mmoles of $NaMn(CO)_5$ in 100 ml of tetrahydrofuran was stirred 24 h at room temperature. Solvent was then removed at ~25°/30 mm giving a greenish residue. This residue was extracted with three 75-ml portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts leaving a yellow solid.

This solid product was extracted with 50 ml of pentane in three portions. The filtered pentane extracts were cooled to −78°. The yellow crystals which separated were filtered and finally sublimed at 70–80°/0.2 mm to give 0.76 g (35% yield) of $(CH_2)_3[Mn(CO)_5]_2$, m.p. 61–63° (lit.[3] m.p. 64–65°) as a yellow crystalline sublimate.

Preparation of $(CH_2)_3[Mn(CO)_4P(C_6H_5)_3]_2$

A mixture of 1.0 g (2.32 mmoles) of $(CH_2)_3[Mn(CO)_5]_2$, 1.5 g (5.73 mmoles) of triphenylphosphine, and 50 ml of methylcyclohexane was boiled 16 h under reflux. After cooling to room temperature, the yellow precipitate was filtered, washed with several portions of pentane, and dried. The crude precipitate was extracted with ~100 ml of dichloromethane in three portions and the filtered dichloromethane extracts treated with ~25 ml of hexane. Solvent was removed at ~25°/30 mm. The resulting yellow-orange crystals were washed with three 15-ml portions of pentane and then crystallized again similarly from a mixture of dichloromethane and hexane to give finally 0.85 g (41% yield) of yellow-orange $(CH_2)_3[Mn(CO)_4P(C_6H_5)_3]_2$, m.p. 203–206°. The conductivity of an acetone solution of this complex was no higher than that of pure acetone. [Found: C, 62.2; H, 3.7; Mn, 12.3; P, 6.8; mol. wt., 905 (Mechrolab vapor pressure osmometer in benzene solution). $C_{47}H_{36}Mn_2O_8P_2$ calcd.: C, 62.7; H, 4.0; Mn, 12.2; P, 6.9%; mol. wt., 900.]

Reaction between $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ *and* $[(C_6H_5)_3C][PF_6]$

Gravity filtered solutions of 1.58 g (4 mmoles) of $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ in ~75 ml of dichloromethane and of 1.55 g (4 mmoles) of $[(C_6H_5)_3C][PF_6]$ in ~75 ml of dichloromethane were mixed and stored at room temperature. Orange crystals gradually precipitated. After 18 h these were filtered, washed with two 15 ml portions of dichloromethane and dried. After a recrystallization from acetone/benzene followed by further dichloromethane washing, 1.34 g (62% yield) of orange $[C_5H_5Fe(CO)_2CH_2CHCH_2Fe(CO)_2C_5H_5][PF_6]$ was obtained. Upon heating, this compound decomposed above ~180° without melting. (Found: C, 37.4; H, 2.8; F, 20.5; Fe, 21.1; P, 5.7. $C_{17}H_{15}F_6Fe_2O_4P$ calcd.: C, 37.8; H, 2.8; F, 21.1; Fe, 20.7; P, 5.7%.)

Conductivity. A molar conductance of 255±3 $ohm^{-1}cm^2$ was found from measurements on acetone solutions of three concentrations in the range 4×10^{-4} to 1.8×10^{-3} *M*.

Reaction between $NaMo(CO)_3C_5H_5$ *and Hexachloropropene*

A solution of 50 mmoles of $NaMo(CO)_3C_5H_5$ in ~200 ml of tetrahydrofuran was treated at −78° with 12.5 g (50 mmoles) of hexachloropropene. The reaction mixture was then allowed to warm up slowly to room temperature and stirred at room temperature for ~24 h. Solvent was then removed in a water-pump vacuum and the residue extracted with three 75-ml portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts giving an orange crystalline residue. This residue was washed with four 20 ml portions of pentane and dried. The crude product was extracted with ~250 ml of boiling diethyl ether in six portions. The filtered ether extracts were cooled ~16 h in a −78° bath. The resulting orange crystals were filtered and dried to give 4.84 g of $C_5H_5Mo(CO)_3Cl$, m.p. 137–140° (dec.) (lit.[4] dec. 145°). Evaporation of the filtrate gave an additional 0.64 g of $C_5H_5Mo(CO)_3Cl$ making the total yield 5.48 g (39%). Identification of the product was confirmed by elemental analysis. (Found: C, 34.6; H, 1.7; Cl, 13.0. $C_8H_5ClMoO_3$ calcd.: C, 34.2; H, 1.8; Cl, 12.7%.)

A similar reaction of 50 mmoles of $NaMo(CO)_3C_5H_5$ and 18.7 g (68.5 mmoles) of hexachlorocyclopentadiene gave 4.09 g (29% yield) of $C_5H_5Mo(CO)_3Cl$. Black tarry by-products made isolation of pure $C_5H_5Mo(CO)_3Cl$ more difficult from this reaction than from the cleaner reaction between $NaMo(CO)_3C_5H_5$ and hexachloropropene.

*Ultraviolet spectra**

$Br(CH_2)_3W(CO)_3C_5H_5$: maximum at 308 mμ (2400) in cyclohexane solution (pale yellow). $Br(CH_2)_4W(CO)_3C_5H_5$: maximum at 310 mμ (2400) in cyclohexane

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* Extinction coefficients are given in parentheses.

solution (pale yellow). $(CH_2)_3[Mn(CO)_5]_2$: maxima at 340 mμ (13,900) and 365 mμ (14,400) in dichloromethane solution (yellow). $(CH_2)_3[Mn(CO)_4P(C_6H_5)_3]_2$: maximum at 373 mμ (33,000) in dichloromethane solution (yellow).

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SUMMARY

The halides $Br(CH_2)_nBr$ ($n = 3$ or 4) react with the sodium salts $NaM(CO)_3$-C_5H_5 (M = Mo or W) to give the yellow derivatives $Br(CH_2)_nM(CO)_3C_5H_5$. The molybdenum compounds $Br(CH_2)_nMo(CO)_3C_5H_5$ react with the sodium salts $NaMn(CO)_5$ and $NaFe(CO)_2C_5H_5$ with nucleophilic displacement of both the bromine atom and the $-Mo(CO)_3C_5H_5$ group to give the known compounds $(CH_2)_3[Mn(CO)_5]_2$ and $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ ($n = 3$ or 4), respectively. Triphenylphosphine displaces two carbonyl groups from $(CH_2)_3[Mn(CO)_5]_2$ to give yellow-orange sparingly soluble $(CH_2)_3[Mn(CO)_4P(C_6H_5)_3]_2$. Triphenylmethyl hexafluorophosphate abstracts hydride from $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ to give the orange salt $[C_5H_5Fe(CO)_2CH_2CHCH_2Fe(CO)_2C_5H_5][PF_6]$.

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