the electrolysis and spectrophotometry in experiment I were performed at lower temperatures than in preceding experiments.

There are not such discrete criteria to establish the validity of the visible spectrum of the cation, since the only change on standing is an initial general increase in absorbance. We feel, however, that the spectrum showing the smaller absorbance, that from experiment D (Figure 4), is probably the more accurate of the two.

Spectra of CpVTr.—Preparation and manipulation of solutions of CpVTr were carried out with the utmost care to exclude atmospheric oxygen. Since such solutions neither discolored nor changed absorbance over many hours, it is likely that the largest experimental errors occurred in measuring the volumes of the solutions. These errors are almost certainly no larger than 2%. We believe, therefore, that the peak positions and molar absorptivities for CpVTr are accurate in both the ultraviolet and the visible regions.

Spectra of CpVTr and CpVTr$^+$.—The electronic spectra of relatively few sandwich complexes are available in the literature. Presumably this paucity arises from the air sensitivity of many of these compounds and the difficulty involved in obtaining spectra of solutions free of decomposition products. Unfortunately, no quantitative data for the related molecules CpCrTr and CpCrTr$^+$ are available for comparison with the present work. (CpCrTr$^+$ is isoelectronic with CpVTr.) King and Bisnette[3c] do describe solutions of CpCrTr as deep blue and those of the corresponding cation as yellow; solutions of CpVTr are pale purple, while those of the cation are bright orange.

King and Stone[2] proposed that contributing resonance structures for CpVTr involved considerable separation of charge between the two rings. Hence, it might be tempting to regard the intense absorption in the ultraviolet region as an intramolecular charge-transfer band. Such a transition, however, would result in rather different dipole moments for the ground and excited states and should, therefore, be sensitive to solvent polarity.[27] The observation that CpVTr shows so nearly the same spectrum in acetonitrile and in isooctane seems to preclude such an assignment.

Acknowledgment.—The authors gratefully acknowledge the gift of a sample of CpVTr from Professors F. G. A. Stone and R. B. King and financial support of this research from the U. S. Army Research Office (Durham) through Grant DA-ORD-31-124-61-G20 and the National Science Foundation through Grant GP-4906.

[27] See, for example, J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co., Ltd., London, 1963, p 272.

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin

Chemistry of the Cyclopentadienylmetal Carbonyls. VII.[1] Nucleophilic Substitution Reactions of Cyclopentadienyliron, -tungsten, and -molybdenum Carbonyl Cations

By P. M. TREICHEL and R. L. SHUBKIN

Received January 15, 1967

Reactions of pentafluorophenyllithium and phenyllithium with the cationic species $C_5H_5Fe(CO)_3{}^+$, $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+$, $C_5H_5Fe(CO)_2py^+$, $C_5H_5Fe(CO)_2(CH_3CN)^+$, $C_5H_5M(CO)_4{}^+$, and $C_5H_5M(CO)_3L^+$ (M = Mo, W; $L = (C_6H_5)_3P$, $(C_6H_5)_3As$) have been studied. Depending on the nature of the metal and the ligands substituted on the metal, the reaction that occurs is: (a) reaction at a carbonyl to give an acyl metal derivative, (b) displacement of a ligand to give an aryl metal compound, (c) reaction at the cyclopentadienyl ring to give a 1-arylcyclopentadiene complex, and/or (d) reduction to give the corresponding biaryl and a dimeric cyclopentadienylmetal carbonyl. The reaction of $NaBH_4$ and $C_5H_5M(CO)_4{}^+$ gives $C_5H_5M(CO)_3H$ (M = Mo, W), in a reaction analogous to (b) above. The reaction of $NaBH_4$ and $C_5H_5M(CO)_3[(C_6H_5)_3P]^+$ surprisingly gives $C_5H_5M(CO)_2[(C_6H_5)_3P]CH_3$ (M = Mo, W) in high yield. A possible mechanism for this reaction is suggested.

Introduction

Reactions of nucleophilic reagents such as alkyl- or aryllithium compounds, or sodium borohydride, with low-valency transition metal complexes bearing a positive charge have been reported. These reactions proceed in three general pathways determined by the nature of the metal–ligand complex. The types of reactions observed are listed below.

(1) Reactions which Proceed with Attack on a Ligand.—These reactions vary widely; one general subclassification includes reaction on a delocalized hydrocarbon bonded to the metal. This category includes $NaBH_4$ or RLi reactions with $(C_5H_5)_2M^+$ (M = Co,[2] Rh[3]), $C_6H_6M(CO)_3{}^+$ (M = Mn,[4] Re[5]), $C_7H_7Cr(CO)_3{}^+$,[6]

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and metal derivatives of more complex hydrocarbons. Related reactions of methoxide ion with $C_5H_5Mn(CO)_2NO^+$,[7] and $Mn(CO)_4[(C_6H_5)_3P]_2^+$,[8] leading to carbomethoxy–metal complexes are reported also.

(2) **Reactions which Proceed with Displacement of a Ligand.**—The reaction of sodium borohydride with $C_5H_5Fe(CO)_3^+$ gives $C_5H_5Fe(CO)_2H$,[9] with displacement of carbon monoxide. It is possible that initially a formyl derivative $C_5H_5Fe(CO)_2CHO$ is formed here and that this then decarbonylates rapidly. This possible distinction is not important to this categorization however.

(3) **Reaction Occurring with Reduction to a Dinuclear Species.**—Borohydride reactions with $Co(CO)_3[(C_6H_5)_3P]_2^+$,[10] $C_5H_5Mn(CO)_2NO^+$,[11] and the chloride salt of $C_5H_5Fe(CO)_2(C_2H_4)^+$ [12] give $Co_2(CO)_6[(C_6H_5)_3P]_2$, $[C_5H_5Mn(CO)(NO)]_2$, and $[C_5H_5Fe(CO)_2]_2$, respectively. There is no available evidence to suggest intermediate hydride formation though this possibility cannot be excluded either.

Little effort has been made to evaluate the influence of various ligands on the nature of such nucleophilic reactions with a related series of complexes, yet quite clearly this is an interesting aspect of the over-all problem. This can be seen by a comparison of the borohydride reductions of $C_5H_5Fe(CO)_3^+$ and $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+$ which lead to $C_5H_5Fe(CO)_2H$ and $C_5H_6Fe(CO)_2[(C_6H_5)_3P]$, respectively.[9] A similar discrimination was reported in preliminary form by us[13] concerning reactions of these cations with pentafluorophenyllithium. We have chosen, therefore, to begin a systematic investigation of such reactions and report here results of work on cyclopentadienyliron, -molybdenum, and -tungsten cationic systems.

Experimental Section

The preparations of cyclopentadienyliron,[14] -molybdenum, and -tungsten[15,16] carbonyl cations have been described. Phenyllithium in a hexane–ether solvent was a commercial sample; pentafluorophenyllithium was prepared from butyllithium and bromopentafluorobenzene by the published method.[17] Except where indicated, tetrahydrofuran, freshly distilled from $LiAlH_4$, was used as solvent.

Chromatographic separations were carried out on alumina (Merck, acid washed) without further treatment.

Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. Proton nmr were recorded on a Varian A-60 spectrometer with tetramethylsilane as internal standard. Resonance peaks are recorded in τ units (tetramethylsilane = τ 10). Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institüt für Kohlenforschung, Mulheim, Germany. Molecular weights were determined in benzene with a Mechrolab vapor pressure osmometer at concentrations between 0.01 and 0.05 *m*. Melting points were observed on a Kofler micro hot stage.

All of the reactions described were run in a nitrogen atmosphere and nitrogen was admitted to all evacuated flasks as a routine precautionary measure.

Reaction of $C_5H_5Fe(CO)_3^+PF_6^-$ and C_6F_5Li.—A slurry of $C_5H_5Fe(CO)_3^+PF_6^-$ (0.8 g, 2.28 mmoles) was added slowly to a solution of pentafluorophenyllithium (4.56 mmoles) at −78°. The solution was stirred at this temperature for 1 hr and then at 0° for an additional 2 hr. Following filtration, the solution was evaporated to dryness on a rotary evaporator, dissolved in benzene (50 ml), washed with several small portions of water, dried over Na_2SO_4, filtered, concentrated, and chromatographed on alumina using 10% benzene in hexane as eluent. Four yellow bands developed.

The first band gave only a trace of yellow oil upon removal of the solvent. Overnight, a few large crystals formed in the oil, and these were used for microanalysis. Because of the extremely small amount of material available, complete characterization was not possible. The analytical and spectral data (Table I) indicate that this product is *exo*-$(1\text{-}C_6F_5)C_5H_5Fe(CO)_3$. *Anal.* Calcd for $C_{14}H_5F_5O_3Fe$: C, 45.19; H, 1.35; F, 25.54. Found: C, 45.45; H, 1.41; F, 27.55.

The second band gave the known compound $C_5H_5Fe(CO)_2C_6F_5$[18,19] (0.1 g, 12.7% yield), mp 139–141° (lit. 144.5–145°). The infrared and proton nmr data are in satisfactory agreement with the literature values. *Anal.* Calcd for $C_{13}H_5F_5FeO_2$: C, 45.38; H, 1.47; F, 27.61; mol wt, 344. Found: C, 45.59; H, 1.38; F, 27.38; mol wt, 351.

The third band gave the yellow crystalline perfluorobenzoyl-derivate, $C_5H_5Fe(CO)_2COC_6F_5$ (0.15 g, yield 17.6%), identified by analyses and spectra, mp 86–87°. *Anal.* Calcd for $C_{14}H_5F_5FeO_3$: C, 45.19; H, 1.35; F, 25.54; mol wt, 372. Found: C, 46.01; H, 1.45; F, 25.37; mol wt, 374.

The fourth band on the chromatography column yielded only a trace of compound which was not identified.

Decarbonylation of $C_5H_5Fe(CO)_2COC_6F_5$ under similar conditions (tetrahydrofuran solution, 25°, 18 hr) was not observed to occur. Neither did the carbonylation reaction of $C_5H_5Fe(CO)_2C_6F_5$ occur (tetrahydrofuran solution, 25°, 2.5 hr at 1 atm of CO pressure). In both reactions starting material was recovered quantitatively. These observations suggest that both $C_5H_5Fe(CO)_2COC_6F_5$ and $C_5H_5Fe(CO)_2C_6F_5$ are direct reaction products of the pentafluorophenyllithium reaction.

Reaction of $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+I^-$ and C_6F_5Li.—A slurry of $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+I^-$ (1.25 g, 2.2 mmoles) in tetrahydrofuran was added slowly to a solution of pentafluorophenyllithium (4.05 mmoles) at −78°. The temperature was raised to 0°, and the mixture was stirred for 3 hr. After the reaction mixture was filtered and the solvent was removed from the filtrate on the rotary evaporator, the resulting residual oil was dissolved in hexane, filtered, and chromatographed on alumina with hexane as eluent. A single yellow band eluted which was concentrated and cooled in Dry Ice to give yellow crystals of *exo*-$(1\text{-}C_6F_5)C_5H_5Fe(CO)_2[(C_6H_5)_3P]$ (0.75 g, yield 56.4%, mp 132.5–134.0°. *Anal.* Calcd for $C_{31}H_{20}F_5FeO_2P$: C, 61.41; H, 3.33; F, 15.67; P, 5.11; mol wt, 606. Found: C, 61.64; H, 3.50; F, 15.42; P, 5.00; mol wt, 610.

Reaction of $C_5H_5Fe(CO)_2(py)^+PF_6^-$ and C_6F_5Li.—Solid $C_5H_5Fe(CO)_2(py)^+PF_6^-$ (0.75 g, 1.87 mmoles) was added directly to a solution of pentafluorophenyllithium in 50 ml of tetrahydrofuran at −78°. After the reaction mixture was stirred for 1 hr at this temperature, it was warmed to room temperature and stirred for an additional 1 hr. The solvent was removed, and the residue was dissolved in benzene, filtered, and chromatographed on

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TABLE I

INFRARED AND PROTON NMR DATA

Fe compounds	Proton nmr (τ)[a]	Carbonyl str freq,[c] cm^{-1}	Other infrared freq,[c] cm^{-1}
exo-(1-C_6F_5)$C_5H_5Fe(CO)_3$	5.08 (2) mult H_β[b] 6.25 (1) mult H_{endo} 7.22 (2) mult H_α	2030 s, 1970 vs[d]	1650 m, 1490 vs, 1405 m, 1390 m, 1320 m, 1300 m, 1200 m, 1135 w, 1107 s, 1075 m, 1052 m, 985 s, 950 m, 900 m, 845 m, 720 m, 778 m, 660 vs, 560 s, 510 m, 480 w, 440 w[d]
exo-(1-C_6F_5)$C_5H_5Fe(CO)_2$-[$(C_6H_5)_3P$]	5.03 (2) mult H_β 5.85 (1) mult H_{endo} 7.40 (2) mult H_α	1990 vs, 1925 vs[e]	3070 w, 2940 w, 1650 w, 1527 m, 1490 s, 1438 s, 1405 vw, 1390 vw, 1300 w, 1262 w, 1200 w, 1108 s, 1092 s, 1078 w, 1055 w, 990 s, 950 w, 895 w, 692 s, 595 s, 558 s, 525 s, 505 w[e]
exo-(1-C_6H_5)$C_5H_5Fe(CO)_2$-[$(C_6H_5)_3P$]	2.66 (15) mult $(C_6H_5)_3P$ 2.97 (6) mult C_6H_5 4.85 (2) mult H_β 6.15 (1) mult H_{endo} 7.38 (2) mult H_α	1980 vs, 1920 vs[e]	3060 m, 2920 m, 1480 m, 1435 m, 1090 m, 1070 w, 1030 w, 998 vw, 720 w, 693 s, 625 w, 600 s, 565 m, 523 m, 510 w, 498 w
Mo and W compounds			
$C_5H_5Mo(CO)_3COC_6F_5$	4.50 singlet C_5H_5	2030 s, 1960 vs, 1645 m, 1625 s[e]	3120 vw, 1492 s, 1425 vs, 1400 w, 1300 m, 1100 s, 980 s, 935 w, 695 m, 622 m, 580 m, 555 s, 475 m[e]
$C_5H_5W(CO)_3COC_6F_5$	4.36 singlet C_5H_5	2025s, 1940 vs, 1645 w, 1615 m[f]	3120 w, 1510 m, 1490 m, 1300 w, 1102 m, 980 m, 940 w, 700 m, 620 w, 555 m, 530 w, 475 w, 445 m[f]
$C_5H_5Mo(CO)_2[(C_6H_5)_3P]$-$COC_6F_5$		1953 s, 1890 s, 1865 s, 1600 m	1295 vs, 1090 m, 970 m, 835 vw, 810 w, 752 w, 745 w, 695 m, 620 vw, 587 w, 560 w, 515 m, 495 w
$C_5H_5W(CO)_2[(C_6H_5)_3P]$-$COC_6F_5$	2.60 (15) mult $(C_6H_5)_3P$ 4.87 (5) C_5H_5 doublet ($J_{P-H} = 4.5$ cps)	1955 s, 1870 vs, 1595 m[e]	1510 w, 1090 m, 970 m, 840 vw, 815 w, 775 w, 745 w, 720 w, 695 m, 620 w, 580 vw, 560 w, 520 m, 505 w, 495 w
$C_5H_5W(CO)_2[(C_6H_5)_3As]$-$COC_6F_5$	2.66 mult $(C_6H_5)_3As$ 4.80 singlet C_5H_5	1955 s, 1870 vs, 1595 m[e]	1510 w, 1480 m, 1290 vw, 1092 m, 1070 w, 970 m, 840 vw, 815 w, 775 w, 740 m, 690 m, 670 m, 580 m, 555 m, 465 m
$C_5H_5W(CO)_2[(C_6H_5)_3P]Br$		2055 s, 1970 vs	1180 w, 1085 m, 995 w, 835 w, 815 w, 740 m, 685 m, 555 m, 520 s, 500 m, 485 w

[a] Deuteriochloroform solution except where noted; relative intensities are given in parentheses. [b] Benzene solvent, to obtain the solubility necessary to see the H_α, H_β, and H_{endo} protons. [c] Nujol mull, KBr cells except when noted. [d] Liquid film (probably impure). [e] CCl_4 solution. [f] $CHCl_3$ solution.

alumina (40 × 2.5 cm column) using benzene as eluent. Six distinct bands developed with good separation between them: (1) bright yellow, (2) light brown, (3) purple-brown, (4) orange, (5) yellow, (6) green. The first band gave 20 mg of $C_5H_5Fe(CO)_2C_6F_5$ (3.1% yield) identified by its infrared spectrum. The second band gave less than 5 mg of a red oil which was not identified. The third band gave *ca.* 10 mg of the dimer $[C_5H_5Fe(CO)_2]_2$ (3% yield), identified by its infrared spectrum. The fourth and fifth bands contained quantities of material too small to be isolated. The sixth band did not elute from the column.

Reaction of $C_5H_5Fe(CO)_2(CH_3CN)^+PF_6^-$ and C_6F_5Li.—Solid $C_5H_5Fe(CO)_2(CH_3CN)^+PF_6^-$ (1.5 g, 4.13 mmoles) was added directly to a tetrahydrofuran solution of pentafluorophenyllithium (4.5 mmoles). The solution was stirred 1 hr at −78° and then warmed to room temperature over a period of 1 hr. The solvent was removed, and the dark residual oil was dissolved in benzene, filtered, and chromatographed on alumina (55 × 3 cm column). Three bands eluted with benzene. The first gave 0.13 g of $C_5H_5Fe(CO)_2C_6F_5$ (9.2% yield), identified by its infrared spectrum. The second band was orange in color and gave only a trace of oil which was not identified. The third band gave a trace of $[C_5H_5Fe(CO)_2]_2$, identified by its infrared spectrum.

Reaction of $C_5H_5Fe(CO)_3^+PF_6^-$ and C_6H_5Li.—Solid $C_5H_5Fe(CO)_3^+PF_6^-$ (2.0 g, 5.7 mmoles) was slurried in 50 ml of freshly distilled tetrahydrofuran and cooled to 0°. Phenyllithium (9.8 mmoles) was added and the mixture was stirred at 0° for 1 hr. The solvent was removed with a rotary evaporator, and the residue was dissolved in benzene and chromatographed on alumina with benzene as eluent. Two bands eluted. The first band, barely discernible on the column, gave 0.4 g of biphenyl (2.6 mmoles). The second band gave 0.6 g of $[C_5H_5Fe(CO)_2]_2$ (1.67 mmoles, 58.6% yield).

Reaction of $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+I^-$ and C_6H_5Li.—A slurry of $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+I^-$ (2 g, 3.5 mmoles) was prepared in 50 ml of tetrahydrofuran at 0°. Phenyllithium (7.0 mmoles) was added and the reaction mixture was stirred at 0° for 1 hr and then an additional 3 hr at room temperature. The solvent was removed, and the residue was dissolved in benzene, filtered, and chromatographed on alumina (53 × 3 cm column). Three bands eluted with benzene. The second (red) and third (green) bands gave traces of $[C_5H_5Fe(CO)_2]_2$ and $C_5H_5Fe(CO)[(C_6H_5)_3P]I$, respectively. The first band (yellow) gave yellow crystals of *exo*-$(C_6H_5)C_5H_5Fe(CO)_2[(C_6H_5)_3P]$ (0.15 g) when cooled in hexane at −10°. The filtrate from this crystallization was rechromatographed on alumina with hexane as eluent until two yellow bands separated. These were eluted with 20% benzene in hexane. The first band gave 0.1 g of solid material which proved to be a mixture of $C_5H_5Fe(CO)_2C_6H_5$ (*ca.* 0.03 g, 3.5%) and triphenylphosphine. The iron compound was purified by sublimation from the mixture to a probe at 0°.

The second band gave an additional 0.1 g of *exo*-(1-C_6H_5)-$C_5H_5Fe(CO)_2[(C_6H_5)_3P]$, mp 172° (total, 0.25 g, 14% yield). *Anal.* Calcd for $C_{31}H_{25}FeO_2P$: C, 72.11; H, 4.88; P, 6.00; mol wt, 516. Found: C, 72.53; H, 5.02; P, 5.83; mol wt, 489.

Reaction of $C_5H_5Mo(CO)_4{}^+PF_6{}^-$ and C_6F_5Li.—A solution of pentafluorophenyllithium (2.6 mmoles) was prepared in 50 ml of tetrahydrofuran as previously described. Then solid $C_5H_5Mo(CO)_4{}^+PF_6{}^-$ (1.0 g, 2.4 mmoles) was added directly to the reaction flask, and stirring was continued at −78° for 1 hr. The temperature was allowed to rise slowly to room temperature over a period of 1 hr. The solvent was removed with a rotary evaporator, and the residue was taken up in benzene (15 ml). Chromatography on alumina (40 × 2.5 cm column), using 1:1 benzene–hexane as eluent, gave a red band followed by a yellow band. The red band yielded a few milligrams of $[C_5H_5Mo(CO)_3]_2$, identified by its infrared spectrum. The yellow band gave the yellow crystalline perfluorobenzoyl derivative, $C_5H_5Mo(CO)_3COC_6F_5$ (0.17 g, 16% yield). The product was recrystallized from hexane at −10°, mp 77°. *Anal.* Calcd for $C_{15}H_5F_5MoO_4$: C, 40.93; H, 1.15; F, 21.58. Found: C, 41.12; H, 1.44; F, 21.66.

The yellow crystals turned green overnight unless stored with rigorous exclusion of air. Reliable molecular weight data could not be obtained because of the instability of the product in solution.

Reaction of $C_5H_5W(CO)_4{}^+PF_6{}^-$ and C_6F_5Li.—The reaction of $C_5H_5W(CO)_4{}^+PF_6{}^-$ (1 g, 1.97 mmoles) and pentafluorophenyllithium (2.43 mmoles) was carried out and worked up in a manner analogous to that with the corresponding molybdenum cation. Two bands eluted from the chromatography column with benzene. The first (red) gave a trace of $[C_5H_5W(CO)_3]_2$, identified by its infrared spectrum. The second band (yellow) was evaporated to an oil and pentane added, causing crystallization. Recrystallization from hexane at −10° gave yellow crystals of the perfluorobenzoyl derivative, $C_5H_5W(CO)_3COC_6F_5$ (0.5 g, 49%), mp 98°. *Anal.* Calcd for $C_{15}H_5F_5WO_4$: C, 34.77; H, 0.97; F, 18.34; mol wt, 518. Found: C, 35.05; H, 1.01; F, 18.53; mol wt, 538.

Reaction of $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ and C_6F_5Li.—Solid $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ (1.0 g, 1.53 mmoles) was added directly to a solution of pentafluorophenyllithium (2.2 mmoles) and treated in a manner similar to that described for the tetracarbonyl cation. Stirring was continued an additional 1 hr at room temperature. Chromatography on alumina (40 × 2.5 cm column) with benzene as eluent showed three bands. The first band (red) gave only a trace of oil which was not identified. The second band (yellow) gave 0.15 g (14.5% yield) of a yellow crystalline product which was identified as the perfluorobenzoyl derivative $C_5H_5Mo(CO)_2[(C_6H_5)_3P]COC_6F_5$, mp 115–120° dec. The product decomposed slowly in air and more quickly in solution, which accounts for the rather poor molecular weight data. *Anal.* Calcd for $C_{32}H_{20}F_5MoO_3P$: C, 56.99; H, 2.99; mol wt, 674. Found: C, 57.36; H, 3.41; mol wt, 738.

The third chromatography band (orange) gave 0.05 g of the known compound $C_5H_5Mo(CO)_2[(C_6H_5)_3P]Br$, mp 167° (lit.[15] 163°). This identification was confirmed by the infrared spectrum and by an independent microanalysis. *Anal.* Calcd for $C_{25}H_{20}BrMoO_2$: C, 53.69; H, 3.60; P, 5.54. Found: C, 53.89; H, 3.81; P, 5.59.

Reaction of $C_5H_5W(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ and C_6F_5Li.—A slurry of $C_5H_5W(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ (0.6 g, 0.81 mmole) and pentafluorophenyllithium (1.2 mmoles) was allowed to react and worked up in a fashion similar to the reaction of the analogous molybdenum compound. Chromatography (alumina, benzene) gave first a very light, barely visible yellow band that could not be isolated. The bright yellow second band gave 0.25 g (40.5% yield) of $C_5H_5W(CO)_2[(C_6H_5)_3P]COC_6F_5$, which was rechromatographed and crystallized slowly from benzene–hexane at −10°, mp 125°. *Anal.* Calcd for $C_{32}H_{20}F_5WO_3P$: C, 50.41; H, 2.64; mol wt, 762. Found: C, 50.50; H, 2.77; mol wt, 782.

The third chromatography band (orange) was concentrated to about 20 ml. Addition of hexane gave 0.1 g (19% yield) of the previously unreported $C_5H_5W(CO)_2[(C_6H_5)_3P]Br$, mp 185°. *Anal.* Calcd for $C_{25}H_{20}BrWO_2P$: C, 46.39; H, 3.12; Br, 12.35. Found: C, 47.70; H, 3.31; Br, 12.51.

Reaction of $C_5H_5W(CO)_3[(C_6H_5)_3As]^+PF_6{}^-$ and C_6F_5Li.—A slurry of $C_5H_5W(CO)_3[(C_6H_5)_3As]^+PF_6{}^-$ (1.7 g, 2.17 mmoles) and pentafluorophenyllithium (2.5 mmoles) were allowed to react in the usual fashion. Chromatography (alumina, benzene) gave first a trace of $[C_5H_5W(CO)_3]_2$ and then a single yellow band which was crystallized to give 0.65 g (37% yield) of $C_5H_5W(CO)_2[(C_6H_5)_3As]COC_6F_5$, mp 125°. *Anal.* Calcd for $C_{32}H_{20}F_5WO_3As$: C, 47.62; H, 2.50; F, 11.78; mol wt, 806. Found: C, 48.20; H, 2.82; F, 12.24; mol wt, 862.

Attempted Reactions of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]_2{}^+PF_6{}^-$ and $C_5H_5W(CO)_2[(C_6H_5)_3P]_2{}^+PF_6{}^-$ with Pentafluorophenyllithium.—The bis-substituted derivatives, $C_5H_5Mo(CO)_2[(C_6H_5)_3P]_2{}^+PF_6{}^-$ and $C_5H_5W(CO)_2[(C_6H_5)_3P]_2{}^+PF_6{}^-$, were treated in the usual manner with pentafluorophenyllithium, but no reaction was observed even when stirred at room temperature for up to 8 hr. The molybdenum compound also did not react in glyme. It is possible that these reactions were inhibited by the low solubility of these compounds in the solvents used.

Reaction of $C_5H_5Mo(CO)_4{}^+PF_6{}^-$ and C_6H_5Li.—Phenyllithium (3.6 mmoles) was added to a slurry of $C_5H_5Mo(CO)_4{}^+PF_6{}^-$ (1 g, 2.4 mmoles) in 50 ml of tetrahydrofuran at room temperature. Reaction was immediate; stirring was continued for 3 hr. The solvent was removed and the residue was dissolved in benzene (50 ml). The benzene solution was filtered, leaving behind some insoluble decomposition product. Addition of hexane to the benzene filtrate gave purple crystals of the dimer $[C_5H_5Mo(CO)_3]_2$ (0.1 g, 33% yield).

Reaction of $C_5H_5W(CO)_4{}^+PF_6{}^-$ and C_6H_5Li.—Phenyllithium (3 mmoles) was added to a slurry of $C_5H_5W(CO)_4{}^+PF_6{}^-$ in 50 ml of tetrahydrofuran and the mixture was stirred for 3 hr. The solvent was removed and the residue was dissolved in benzene, filtered (which left a considerable amount of decomposition product), and chromatographed on alumina. The single red band which eluted with benzene gave 0.05 g (7.5% yield) of the dimeric $[C_5H_5W(CO)_3]_2$.

Reaction of $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ and C_6H_5Li.—Phenyllithium (2.3 mmoles) was added to a slurry of $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ (1 g, 1.35 mmoles) in 50 ml of tetrahydrofuran and the mixture was stirred for 3 hr at room temperature. Removal of the solvent, dissolution in benzene, filtration, and chromatography on alumina with benzene as eluent gave a purple-red band whose infrared spectrum indicated a mixture of $[C_5H_5Mo(CO)_3]_2$ and its monotriphenylphosphine-substituted derivative[1] (0.25 g). No phenyl-substituted derivative was found.

Reaction of $CpW(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ and C_6H_5Li.—The reaction was carried out in a fashion similar to that of the molybdenum analog. There was primarily decomposition, but a small red band did elute from the chromatography. The infrared spectrum indicates that this is mostly $[C_5H_5W(CO)_3]_2$ with a small amount of the triphenylphosphine-substituted derivative.

Reaction of $C_5H_5W(CO)_4{}^+PF_6{}^-$ and $NaBH_4$.—Freshly distilled tetrahydrofuran (50 ml) was placed in a 150-ml three-necked flask equipped with a nitrogen inlet, a magnetic stirrer, a pressure-equalizing dropping funnel, and a rubber septum inlet. Nitrogen was bubbled through the solvent for 15 min to ensure that it was free of air. Then $C_5H_5W(CO)_4{}^+PF_6{}^-$ (2 g, 3.95 mmoles) and $NaBH_4$ (0.45 g, 11.85 mmoles) were added as solids through a fast stream of nitrogen and the reaction mixture was stirred for 3 hr at 0°. Deaerated water (50 ml) was added dropwise over a period of 1 hr while the temperature was maintained at 0°. The product was extracted from the aqueous solution with pentane in the following manner. In turn, each of three 30-ml portions of the pentane was syringed into the reaction flask. The mixture was then stirred vigorously for 10 min with the magnetic stirrer held at the interface of the two solvents. The pentane layer was syringed out of the flask and into a closed flask containing 50 ml of deaerated water under nitrogen. After the three portions had been added to the flask, the pentane–water mixture was shaken well and then allowed to settle. The pentane layer was syringed into a second flask containing water where the washing procedure was repeated and then into a closed flask containing anhydrous sodium sulfate under nitrogen. The dried pentane solution was now syringed into a three-necked flask equipped with rubber septum, nitrogen inlet, vacuum outlet, and sublimation probe. The pentane was removed with an aspirator vacuum, leaving a dark residue. At 55° and 0.4 mm a total of 0.5 g (37.8% yield) of $C_5H_5W(CO)_3H$ sublimed to the ice-cooled probe, mp (sealed capillary) 64–66° (lit.[20] 66–67°). The infrared (CS_2 solution) corresponds to that reported for this compound. Treatment with CCl_4 gives a quantitative yield of $C_5H_5W(CO)_3Cl$.

Reaction of $C_5H_5Mo(CO)_4{}^+PF_6{}^-$ and $NaBH_4$.—Solid $C_5H_5Mo(CO)_4{}^+PF_6{}^-$ (10 g, 2.39 mmoles) and $NaBH_4$ (0.17 g, 4.4 mmoles) were allowed to react and were worked up in the same way as already described for the corresponding tungsten compound. The resulting cyclopentadienylmolybdenum tricarbonyl hydride sublimed at 50° and 0.2 mm pressure, mp (sealed capillary) 50–51° dec (lit.[20] 50–52°). The yield was 0.05 g (8.5%). The extreme air sensitivity of the product was probably responsible for the small yield.

Reaction of $C_5H_5W(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ and $NaBH_4$.—A slurry of $C_5H_5W(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ (1.5 g, 2.06 mmoles) and $NaBH_4$ (0.23 g, 6.2 mmoles) was stirred in tetrahydrofuran for 1 hr at 0° and for an additional 16 hr at room temperature. The mixture was filtered and the yellow-orange filtrate was evaporated to dryness. The yellow residue was then extracted with small portions of benzene (50 ml total) until no color remained. Hexane was added to the clear extract, and the product was crystallized at −10° to give 0.83 g (69% yield) of a yellow crystalline compound which was shown to be the known[1] methyl derivative, $C_5H_5W(CO)_2[(C_6H_5)_3P]CH_3$. The product was purified by chromatography on alumina with benzene as eluent and recrystallized from benzene–hexane. *Anal.* Calcd for $C_{26}H_{23}WO_2P$: C, 53.63; H, 3.98; P, 5.32; mol wt, 582. Found: C, 55.08; H, 4.22; P, 5.21; mol wt, 573.

Infrared and proton nmr spectra and the melting point (185°) were in agreement with values for the known compound.[1]

Reaction of $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ and $NaBH_4$.—The reaction of $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6{}^-$ (1.0 g, 1.35 mmoles) and $NaBH_4$ (0.2 g, 5.3 mmoles) was carried out in a fashion identical with that of the corresponding tungsten analog, with the reaction time being 1 hr at 0° and 1 hr at room temperature. Chromatography on aluminum (1:1 benzene–hexane) gave a yellow band followed by a light red band. The latter gave only a trace of oil and was not identified. The yellow band was crystallized at −10° to give 0.2 g (26.5% yield) of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]CH_3$, which was identified by comparison of its infrared spectrum to that of an authentic sample.[1] The product begins to melt at 158° and then decomposes at 163–166°. The same behavior is shown by an authentic sample and by a mixture of the two.

Attempted Reactions of $C_5H_5M(CO)_2[(C_6H_5)_3P]_2{}^+PF_6{}^-$ (M = Mo, W) and $NaBH_4$.—Several attempts were made to cause the bis-substituted triphenylphosphine derivatives, $C_5H_5M(CO)_2[(C_6H_5)_3P]_2{}^+PF_6{}^-$ (M = Mo, W), to react with $NaBH_4$. At room temperature there was no reaction for either compound in tetrahydrofuran. At reflux both compounds reacted, but the unstable products could not be isolated and identified.

Discussion

The results here indicate that the mode of nucleophilic attack on a metal carbonyl cation is highly dependent on the metal in question. With cyclopentadienylmolybdenum and -tungsten carbonyl cations there is no evidence to suggest substitution of the attacking group R^- on the C_5H_5 ring, though for other systems such as $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+$ this is the primary reaction observed to occur. Clearly then, any attempt to systematize these nucleophilic reactions must initially involve a classification based on the metal and its coordination geometry.

In addition it is clear that some of the initial reactions attempted here were not as conclusive as was originally hoped, because the over-all yield of carbonyl-containing products represented only a small fraction of the starting material. The route by which decomposition occurs remains only as speculation.

The reactions of $C_5H_5Fe(CO)_3{}^+$ and $C_5H_5Fe(CO)_2L^+$ (L = $(C_6H_5)_3P$, py, acetonitrile) with pentafluorophenyllithium can be considered first. Prior to this work, the borohydride reaction with $C_5H_5Fe(CO)_3{}^+$ and $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+$ giving $C_5H_5Fe(CO)_2H$ and $C_5H_6Fe(CO)_2[(C_6H_5)_3P]$, respectively, had been reported,[9] so we had reason to suspect that similar variations in behavior could be expected with other nucleophilic reagents. This proved to be the case though, in fact, some complications were evident on careful examination.

The reactions of $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+$ with the nucleophilic reagents pentafluorophenyllithium, phenyllithium, and $NaBH_4$ occur primarily by a single pathway involving attack at the C_5H_5 ring to give the *exo*-1-substituted cyclopentadiene complex (Figure 1). Only with phenyllithium did an alternate reaction lead to a second product; here a small amount of $C_5H_5Fe(CO)_2C_6H_5$ was found. The *exo*-substituted cyclopentadiene complexes are formed in relatively high yield. Stereospecific attack to give the *exo* isomer was anticipated in these reactions. All other reactions that are known to occur with substitution on a π-bonded hydrocarbon ring appear to proceed to this configuration. Those complexes of substituted cyclopentadiene ligands derived from this type of reaction, for which X-ray crystallography has established a structure, have been found to be *exo* isomers.[21,22]

The proton nmr spectra of the substituted cyclopentadiene complexes show three resonances near τ 5.0, 6.0, and 7.4, of relative intensity 2:1:2, due to the protons on the C_5H_5R ring. The lack of more than three resonances is strong evidence that only a single isomer is present. The chemical shifts of each proton do not conclusively suggest the proposed stereochemistry; however, a reasonable assignment of these resonances to H_α and H_β and to the proton on the substi-

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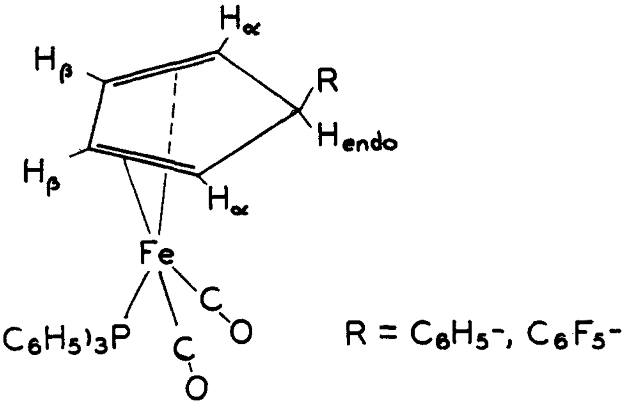

Figure 1.—Structure of *exo*-(1-R)$C_5H_5Fe(CO)_2[(C_6H_5)_3P]$.

tuted carbon can be made by comparison with data for similar known compounds. Thus C_5H_5R complexes of cobalt and rhodium[23] and of iron[9] all show H_β resonances near τ 5.0, and H_α resonances occur near τ 6.7 (Rh) and 7.1–7.6 (Co and Fe). By analogy we have made the assignments of the τ 5.0 and 7.4 resonances to H_β and H_α, respectively, in the compounds described here, and hence the peak at τ 6.0 remains to be assigned to a proton of the 1-carbon in the C_5H_5R ring.

Strongest support for the *exo* configuration comes from comparisons of infrared data for analogous compounds. Each of the *exo*-substituted cyclopentadiene compounds has a single sharp C–H stretching frequency near 2950 cm^{-1} which is believed to be characteristic of the *endo*-C–H group.[9,21,23] Moreover, the infrared spectra of the known cyclopentadiene–metal complexes possess a second C–H stretch near 2750 cm^{-1} as well as the ~2950-cm^{-1} peak. If an assignment of the 2950-cm^{-1} peak to the *endo*-C–H is correct here, then the 2750-cm^{-1} peak would be due to the *exo*-C–H; one observes the absence of this latter peak in all *exo*-substituted cyclopentadiene–metal derivatives. This indicates (though not conclusively) the lack of *exo*-C–H group in the molecule.

The formation of *exo*-(1-aryl)$C_5H_5Fe(CO)_2[(C_6H_5)_3P]$ as the primary reaction product is interesting because it is likely that the compounds $C_5H_5Fe(CO)[(C_6H_5)_3P]COR$, which would be formed by an alternate mode of reaction, would have a stable existence. The compound for which R = CH_3 in that formula is a highly stable entity.[14] It may be that the pathway of this reaction is determined entirely by mechanistic considerations. There may be considerable reluctance of the complex to undergo an attack directly on the carbonyl because of steric hindrance due to the large phosphine ligand. In addition, subtle electronic changes associated with replacement of carbon monoxide by triphenylphosphine would render the terminal carbonyls more electron rich (*cf.* the CO stretching frequencies) and thus less amenable to attack.

The reaction of the cation $C_5H_5Fe(CO)_3^+$ with C_6F_5Li proved rather more complex. Three different products were isolated from this reaction; the over-all yield of these accounts for only about 30% of the starting material however. It appears that three independent pathways are important here. The two most important are reaction at a carbonyl, to give the pentafluorobenzoyl derivative, and reaction at the metal with displacement of a carbonyl. These occur to the extent of about 17 and 12%, respectively, as judged by the yield of the reaction. The possibility that the C_6F_5 derivative takes up carbon monoxide to give the C_6F_5CO compound, or the reverse of this reaction, is less likely since under the conditions of the reaction these products can be shown not to be interconvertible.

The third product to be characterized from the reaction was found in very small quantity. It was derived from substitution on the C_5H_5 ring. The reaction rate here must be at least competitive with the rates of other reaction types; moreover it appears that there would be no possible interconversion of this product and the others in the reaction. This then would support the conclusions of Pettit, *et al.*, regarding related hydride-transfer reactions.[24]

The results on this system suggest that C_6F_5Li as a nucleophilic reagent is rather unselective in its mode of reaction.

The reaction of phenyllithium with the $C_5H_5Fe(CO)_3^+$ cation leads primarily to reduction. A good yield of the reduction products $[C_5H_5Fe(CO)_2]_2$ and biphenyl was isolated. Reactions of $C_5H_5Fe(CO)_2L^+$ (L = py, CH_3CN) with C_6F_5Li give small amounts of $[C_5H_5Fe(CO)_2]_2$ and $C_5H_5Fe(CO)_2C_6H_5$, the latter arising from ligand displacement.

The low yield of volatile carbonyl-containing products of some of these reactions is a definite problem. In these reducing systems one might expect perhaps a large yield of $[C_5H_5Fe(CO)_2]_2$, if other products are lacking. We speculate that the low yields may be due to further reaction of products with the reactive lithium reagents, with the products of these reactions then degrading in air, reacting with the solvents, or failing to elute on chromatography. This would support our previous conclusion regarding the unselective nature of these reagents. Fischer and Maasbol[25] have shown that such reactions are possible and have reported the products of such reactions with the group VI hexacarbonyls.

Reactions of pentafluorophenyllithium and the cations $C_5H_5M(CO)_4^+$, $C_5H_5M(CO)_3[(C_6H_5)_3P]^+$ (M = Mo, W), and $C_5H_5W(CO)_3[(C_6H_5)_3As]^+$ follow a single path only. From each reaction the product observed is a pentafluorobenzoyl–metal compound, indicating attack at a carbonyl ligand to be the primary reaction route. The products were isolated in relatively good yields in all cases.

Reactions of the above cations with phenyllithium led only to reduction products, $[C_5H_5M(CO)_3]_2$, $(C_5H_5M)_2(CO)_5[(C_6H_5)_3P]$,[1] and biphenyl, consistent with the results observed in the iron systems. The

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yields of these reactions were relatively low. No isolable products of reactions of $C_5H_5M(CO)_2[(C_6H_5)_3P]_2^+$ cations could be obtained.

Reactions of $NaBH_4$ with $C_5H_5M(CO)_4^+$ and $C_5H_5M(CO)_3[(C_6H_5)_3P]^+$ were undertaken to see first if the results paralleled those analogous reactions with pentafluorophenyllithium. These reactions proved to be quite unexpected however. The formation of $C_5H_5M(CO)_3H$ from the former reaction is consistent with formation of $C_5H_5Fe(CO)_2H$[9] from the reaction between $NaBH_4$ and $C_5H_5Fe(CO)_3^+$. Whether the reaction involves displacement of a carbon monoxide unit by the incoming ligand or initial formation of a formyl derivative $C_5H_5M(CO)_3CHO$ cannot be determined with certainty. Initial attack at a carbonyl would be analogous to the pentafluorophenyllithium reaction and the resulting formyl derivative would undoubtedly be unstable with respect to loss of carbon monoxide and formation of the hydride. The reaction does appear to be a high-yield reaction, limited only by experimental difficulties associated with the air sensitivity of the hydride.

The reaction of $C_5H_5M(CO)_3[(C_6H_5)_3P]^+$ and $NaBH_4$ proved to be quite unexpected, however, and led to high yields of the compounds $C_5H_5M(CO)_2[(C_6H_5)_3P]CH_3$. Relatively mild conditions were required in this reaction. The methyl group can only be visualized to arise from reduction of a carbonyl group. This behavior is certainly without precedent in this field. A mechanism which we believe best explains this result is detailed in Figure 2. Step 1, hydride attack on a carbonyl, is a reasonable postulate, since the other nucleophilic reactions that we have investigated with this cation proceed in this manner. The stability of the formyl derivative (B) to decarbonylation must be significant, however. Reduction of the ketonic carbonyl in B must proceed completely before decarbonylation can occur. It seems likely that the presence of the phosphine ligand is rather important in stabilizing this intermediate to decarbonylation.

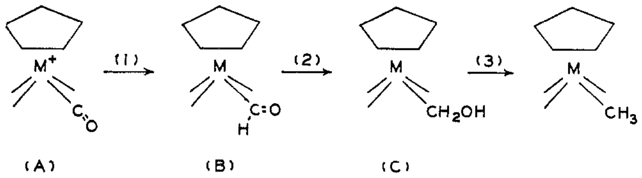

Figure 2.—Proposed mechanism for the reduction of $C_5H_5M(CO)_3L^+$ to $C_5H_5M(CO)_2LCH_3$. (The terminal carbonyl groups and the phosphine ligand are omitted for clarity.)

It should be observed that reactions involving acyl carbonyl groups are somewhat rare. There is no mention of derivative chemistry of such groups, nor have any reductions been described. However such groups have been reported to be susceptible to nucleophilic attack in some instances, the reactions accompanied by degradation.[26,27]

One can regard intermediate C from the reduction step as a derivative of a hydroxymethyl–metal compound. Recent studies by Pettit and Jolly[28] of substituted methyl–metal compounds suggest that such substituents may be rather labile owing perhaps to resonant interactions such as

$$M{-}CH_2{-}X \longleftrightarrow M^+{=}CH_2\ X^-$$

Hence we would expect hydride displacement of the OH^- group to be rather facile.

We are now engaged in studies by which we hope to elucidate further the scope of this type of reaction.

Acknowledgment.—We are pleased to acknowledge support of this work through National Science Foundation Grants GP 4667 and GP 5966.

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