were made with solutions of the tungsten and molybdenum species using the Cary 60 as modified by the Cary Division of Varian Instruments to accommodate a Varian superconducting magnet, employing a magnetic field of 44 kG. Samples and pure solvent were studied in 1- and 2-cm Supracil cells. Only spectral observations made for dynode voltages <400 V were considered as reliable. Spectra are base line corrected for solvent and cell absorptions.

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Registry No. $Na_3[W(CN)_8]$, 52239-56-2; $K_3[W(CN)_8]$, 18347-84-7; $[(n\text{-}Bu)_4N]_3[W(CN)_8]$, 52239-57-3; $K_4[W(CN)_8]$, 17475-73-9; $K_4[Mo(CN)_8]$, 17456-18-7; $Ag_3[W(CN)_8]$, 52239-58-4.

(25) Note Added in Proof. The spectrum recently reported as that of tetra-*n*-propylammonium octacyanotungstate(IV)[5d] is very similar to the spectra reported earlier for other salts of the tungstate(V) ion.[8] In fact, the tetra-*n*-propylammonium octacyanotungstate(V) salt has been isolated in our laboratory [C. J. Donahue, unpublished results] using the synthetic procedure[5d] for the "IV" salt. Apparently the octacyanotungstate(IV) ion is more susceptible to oxidation than the corresponding molybdenum complex; *e.g.*, the tungsten ion readily oxidizes in aqueous acid [A. Samotus and B. Kosowicz-Czajkowska, *Rocz. Chem.*, 45, 1623 (1971)].

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A Fourier Transform Carbon-13 Nuclear Magnetic Resonance Study of Thiocarbonyl and Other π-$(C_5H_5)M(CO)_2L$ Derivatives of Iron and Manganese

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^{13}C nmr spectra have been obtained for a series of complexes of the types π-$(C_5H_5)Cr(CO)_3^-$, π-$(C_5H_5)Mn(CO)_2L$ (L = CS, CO, $P(OPh)_3$, $P(OCH_3)_3$, PPh_3, PBu_3, $C_5H_{10}NH$, C_8H_{14}), and π-$(C_5H_5)Fe(CO)_2L^+$ (L = CS, CO, PPh_3, NH_3). The observed carbonyl chemical shift data are in agreement with a previously suggested hypothesis of increasingly deshielded carbonyl resonances with increasing transition metal → carbonyl π back-donation and suggest that the CS ligand is a significantly better π acceptor than CO in π-$(C_5H_5)Mn(CO)_2(CS)$. The thiocarbonyl in π-$(C_5H_5)Mn(CO)_2(CS)$ exhibits the most intensely deshielded carbon resonance yet reported. This would appear to indicate the localization of a substantial positive charge on the thiocarbonyl carbon atom, in close similarity to that suggested previously for the carbene carbon in $(CO)_5CrC(OCH_3)CH_3$.

Introduction

The characterization of transition metal–carbonyl complexes[1,2] preceded the first reports of analogous thiocarbonyl complexes by over 75 years.[3] While only a limited number of thiocarbonyl derivatives have been synthesized to date, their ubiquitous nature has been demonstrated by the characterization of complexes containing Rh,[3-6] Ir,[7-9] Ru,[10,11] Co,[12] Fe,[13,14] Mn,[15,16] Cr, Mo, and W,[17] and Ni, Pd, Pt, and Os.[18]

The relative scarcity of thiocarbonyl complexes does not arise from an inherent instability, but rather from synthetic complications. Thiocarbonyl complexes have been obtained *via* two synthetic schemes (eq 1 and 2) and thus depend either

$$\begin{aligned}&\pi\text{-}(C_5H_5)Fe(CO)_2^- + ClC(S)OR \rightarrow \pi\text{-}(C_5H_5)Fe(CO)_2C(S)OR\\&\pi\text{-}(C_5H_5)Fe(CO)_2C(S)OR + HCl \rightarrow \pi\text{-}(C_5H_5)Fe(CO)_2(CS)^+\end{aligned}\qquad(1)$$

$$\begin{aligned}&(Ph_3P)_3RhCl + CS_2 \rightarrow (Ph_3P)_2RhCl(\pi\text{-}CS_2)\\&(Ph_3P)_2RhCl(\pi\text{-}CS_2) + PPh_3 \rightarrow (Ph_3P)_2RhCl(CS) + S{=}PPh_3\end{aligned}\qquad(2)$$

upon the nucleophilicity of the starting material toward a derivative of thiophosgene or the relative stability of a transition metal-π-CS_2 intermediate.

Substantial evidence suggests that the CS ligand is a better π acceptor toward transition metals than its CO analog. Baird and Wilkinson[3] have argued that the absence of oxidative addition of HCl to $(Ph_3P)_2RhCl(CS)$ and the instability of this complex in the presence of $HgCl_2$ suggest the importance of a $(Ph_3P)_2ClRh^{\delta+}{=}C{=}S^{\delta-}$ resonance structure. This formulation is in accord with the crystallographic data of De Boer, *et al.*,[4] who found that the Rh-C bond length in $(Ph_3P)_2RhCl(CS)$ is 0.1 Å shorter than in $(Ph_3P)_2RhCl(CO)$, while the C–S bond length is only 0.018 Å shorter than the C=S bond length in CS_2. Yagupsky and Wilkinson[7] and Mays and Stefanini[9] have noted a reluctance of Ir-CS complexes to undergo oxidative addition with H_2 under conditions where their Ir-CO analogs undergo rapid reaction, and they have invoked an increased π acidity of the CS ligand to explain

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Table I. Infrared Stretching Frequencies (cm^{-1}) and Force Constants (mdyn/Å) for the Carbonyl Mode in π-$(C_5H_5)Mn(CO)_2L$ Derivatives

L	$\nu_s^{CS_2}$	$\nu_a^{CS_2}$	$k_{CO}^{CS_2}$	$\nu_s^{CHCl_3}$	$\nu_a^{CHCl_3}$	$k_{CO}^{CHCl_3}$
CS	2007	1955	15.86	2010	1954	15.88
CO	2024	1939	15.64[a]	2025	1920	15.45
$P(OPh)_3$	1963	1900	15.08[a]	1962	1894	15.02
C_8H_{14}	1956	1893	14.97[a]	1955	1887	14.92
$P(OCH_3)_3$	1949	1884	14.84	1950	1880	14.82
PPh_3	1934	1874	14.65[a]	1934	1864	14.58
PBu_3	1929	1863	14.53[a]	1925	1852	14.42
$C_5H_{10}NH$	1920	1840	14.29[a]	1917	1832	14.20

[a] Data taken from W. P. Anderson, T. B. Brill, A. R. Schoenberg, and C. W. Stanger, Jr., *J. Organometal. Chem.*, **44**, 161 (1972).

these results. Cotton-Kraihanzel force constant calculations on π-$(C_5H_5)M(CO)_2L$ complexes (L = CS, CO; M = Fe^+, Mn^0) are also consistent with the formulation of the CS ligand as a good π acceptor[13] (see Table I).

Conversely, Busetto, *et al.*,[19] have observed preferential attack of nucleophilic reagents such as CH_3O^-, N_3^-, and RNH_2 at the CS ligand in π-$(C_5H_5)Fe(CO)_2(CS)^+$ which occurs at a rate substantially faster than for the analogous π-$(C_5H_5)Fe(CO)_3^+$ complex. In the absence of an unknown stabilization of the transition state for the CS complex, this would indicate an increased electrophilic character for the CS carbon atom, which is inconsistent with the results discussed above. An explanation of this behavior might arise from the comparison of SCF-MO calculations for CS[20] and CO[21] which suggest a higher energy for the 7σ donor orbital on CS than for the 5σ orbital on CO and a lower energy for the $3\pi^*$ orbitals on CS than for the $2\pi^*$ orbitals on CO, thereby implying an increase in both the σ-donor and π-acceptor abilities for the CS ligand.

Recent studies of a series of π-$(C_6H_5X)Cr(CO)_3$ derivatives have suggested that the ^{13}C nmr carbonyl chemical shifts are a linear measure of the extent of transition metal → carbonyl π back-donation in these complexes.[22] We report here a systematic study of the ^{13}C nmr spectra of a series of π-$(C_5H_5)M(CO)_2L$ derivatives (L = CS, CO, PPh_3, PBu_3, $P(OPh)_3$, $P(OCH_3)_3$, $C_5H_{10}NH$, NH_3, C_8H_{14}; M = Cr^-, Mn^0, Fe^+), undertaken to develop further the proposed relationship between ^{13}C nmr carbonyl chemical shifts and the carbonyl π acidity. The results of this study are then applied to a consideration of the transition metal-thiocarbonyl bond.

Experimental Section

Materials. $Cr(CO)_6$ and $[\pi\text{-}(C_5H_5)Fe(CO)_2]_2$ were purchased from the Pressure Chemical Co. A sample of π-$(C_5H_5)Mn(CO)_3$ was generously provided by the Ethyl Corp. Samples of $[\pi\text{-}(C_5H_5)Fe(CO)_2(CS)]PF_6$ and π-$(C_5H_5)Mn(CO)_2(CS)$ were obtained from Dr. R. J. Angelici and Dr. I. S. Butler.

$[\pi\text{-}(C_5H_5)Cr(CO)_3]Na$ was synthesized by the method of Piper and Wilkinson[23] and characterized by infrared spectroscopy.

$[\pi\text{-}(C_5H_5)Fe(CO)_2L]PF_6$ derivatives, L = NH_3[24] and PPh_3,[25] were synthesized *via* literature methods. $[\pi\text{-}(C_5H_5)Fe(CO)_3]PF_6$ was synthesized independently by the methods of Busetto and Angelici[26] and Reimann and Singleton.[27] π-$(C_5H_5)Mn(CO)_2L$ derivatives, L = C_8H_{14},[28] $P(OPh)_3$,[29] PPh_3,[29] PBu_3,[30] $P(OCH_3)_3$, and NHC_5H_{10},[31] were synthesized *via* the photolysis of π-$(C_5H_5)Mn(CO)_3$ with a high-pressure Hg lamp in either benzene or hexane solution in the presence of a slight excess of the respective ligand. The C_8H_{14}, PPh_3, $P(OPh)_3$, and NHC_5H_{10} derivatives were recrystallized from benzene-hexane and characterized by infrared spectroscopy and microanalysis. The PBu_3 and $P(OCH_3)_3$ derivatives were obtained as viscous oils, purified by sublimation of unreacted π-$(C_5H_5)Mn(CO)_3$, and then characterized by infrared spectroscopy and mass spectroscopy.

Instrumentation. ^{13}C nmr spectra were obtained in deuteriochloroform, deuterioacetone, or tetrahydrofuran solution on a Varian Associates XL-100-FT spectrometer operating at 25.16 MHz. Deuteriobenzene was added to tetrahydrofuran solutions to provide an internal deuterium lock. The ^{13}C nmr chemical shifts were measured relative to the internal solvent resonance and are reported in ppm *downfield* from TMS using the conversions

$$\delta_{TMS} = \delta_{CDCl_3} - 76.98 \text{ ppm}$$

$$\delta_{TMS} = \delta_{(CD_3)_2CO} - 29.66 \text{ ppm}$$

$$\delta_{TMS} = \delta_{THF\,\{C(2,5)\}} - 68.05 \text{ ppm}$$

Infrared spectra were obtained in cyclohexane, carbon disulfide, and chloroform solution on a Beckman IR-12 spectrometer calibrated below 2000 cm^{-1} with ambient water vapor. A 10-fold ordinate expansion was used with a 20 cm^{-1}/min scan speed.

Microanalytic data were obtained in the microanalysis laboratory of the School of Chemical Sciences, University of Illinois.

Results and Discussion

Previous reports of the ^{13}C nmr spectra of transition metal carbonyl complexes of manganese have suggested that the carbonyl resonances cannot be observed in the absence of shiftless relaxation reagents such as tris(acetylacetonato)-chromium(III) due to coupling with the $^5/_2$-spin ^{55}Mn nucleus undergoing rapid quadrupole relaxation.[32,33]. Figure 1 shows the proton-coupled ^{13}C nmr spectrum of π-$(C_5H_5)Mn(CO)_3$ in deuteriochloroform. We note that allowing sufficient time for relaxation of the carbonyl resonance between pulses yields high-resolution spectra of derivatives of the type π-$(C_5H_5)Mn(CO)_2L$ in the absence of paramagnetic relaxation reagents.

Darensbourg and Brown[34,35] have shown that changes in the magnitude of carbonyl mode stretching frequencies for transition metal carbonyl complexes may be brought about by changes in either the σ-donor or π-acceptor character of the carbonyl ligand. Rather than pursuing a dubious separation of the σ and π contributions to the force constant,

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Table II. ^{13}C Nmr Chemical Shifts (ppm) and $^2J_{^{13}C^{31}P}$ Coupling Constants (Hz) in π-$(C_5H_5)M(CO)_2L$ Derivatives

Complex	C_5H_5	CO	CS	$^2J_{^{13}C^{31}P}$	Solvent
π-$(C_5H_5)Cr(CO)_3Na$	-81.87^a	-246.7_5			THF-C_6D_6
π-$(C_5H_5)Mn(CO)_2(CS)$	-85.7_1	-224.0	-442.6		$CDCl_3$
π-$(C_5H_5)Mn(CO)_2(CS)$	-86.0	-224.5	-442.9		Acetone-d_6
π-$(C_5H_5)Mn(CO)_3$	-82.6_9	-225.1			$CDCl_3$
π-$(C_5H_5)Mn(CO)_2[P(OPh)_3]$	-81.1_1	-228.8		36	$CDCl_3$
π-$(C_5H_5)Mn(CO)_2[P(OCH_3)_3]$	-80.9_4	-229.5		34	$CDCl_3$
π-$(C_5H_5)Mn(CO)_2(PBu_3)$	-79.0_0	-231.1		26	$CDCl_3$
π-$(C_5H_5)Mn(CO)_2(PPh_3)$	-82.4_0	-232.8		23	$CDCl_3$
π-$(C_5H_5)Mn(CO)_2(C_8H_{14})$	-83.9_0	-234.5			$CDCl_3$
π-$(C_5H_5)Mn(CO)_2(NHC_5H_{10})$	-81.9_4	-236.2			$CDCl_3$
π-$(C_5H_5)Fe(CO)_3PF_6$	-90.8_1	-202.9_8			Acetone-d_6
π-$(C_5H_5)Fe(CO)_2(CS)PF_6$	-92.1_6	-203.3_2	-307.9_0		Acetone-d_6
π-$(C_5H_5)Fe(CO)_2(PPh_3)PF_6$	-90.8_1	-210.5_3		24	Acetone-d_6
π-$(C_5H_5)Fe(CO)_2(NH_3)PF_6$	-86.7_0	-211.7_6			Acetone-d_6

[a] Chemical shifts in ppm *downfield* from TMS; Mn–CO chemical shifts ±0.1 ppm; all other chemical shifts ±0.06 ppm.

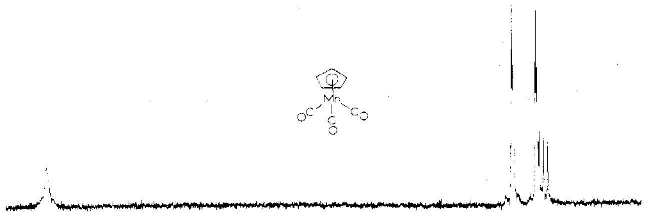

Figure 1. Proton-*coupled* Fourier transform ^{13}C nmr spectrum of π-$(C_5H_5)Mn(CO)_3$ in deuteriochloroform, with 1000 scans, a 10-sec pulse delay between scans, and a flip angle of 45°. Resonance assignments and chemical shifts (in ppm downfield from TMS): CO, −225.1; C_5H_5, -82.6_9. The three small peaks at high field arise from the $CDCl_3$ solvent.

Darensbourg and Darensbourg[36] have argued that the magnitude of the stretching force constant is directly proportional to the positive character of the carbonyl carbon atom. One might therefore suggest that the order of increasing electron density on the carbonyl carbon for a series of π-$(C_5H_5)Mn(CO)_2L$ derivatives (see Table I) is $CS < CO < P(OPh)_3 < C_8H_{14} < P(OCH_3)_3 < PPh_3 < PBu_3 < C_5H_{10}NH$.[37]

This postulate has led several authors to investigate the nature of the correlation between ^{13}C nmr carbonyl chemical shifts and infrared stretching frequencies or force constants. While a gratifyingly high linear correlation has been observed for several classes of closely related derivatives,[22,38,39] this correlation has been questioned when applied to a broad range of derivatives.[40] The ^{13}C nmr carbonyl chemical shift data for a series of π-$(C_5H_5)M(CO)_2L$ derivatives ($M = Cr^-$, Mn^0, Fe^+) are presented in Table II. Figure 2 shows a plot of the carbonyl chemical shifts for π-$(C_5H_5)Mn(CO)_2L$ complexes *vs.* the infrared stretching force constants calculated *via* the Cotton-Kraihanzel approximations[41] assuming idealized C_{2v} symmetry. As noted previously[22] the sign of this correlation is opposite to that expected on the basis of the Darensbourg-Brown model and a dependence of the carbonyl chemical shift upon electron density at the carbonyl carbon atom. We have argued[22] that the observed correlation is consistent with the hypothesis of increasingly deshielded carbonyl resonances with increasing transition metal → carbonyl π back-donation. Thus the data presented in Table II for the isoelectronic π-$(C_5H_5)M(CO)_3$ complexes suggest an increase in transition metal → carbonyl π back-donation with increasing negative charge on the complex in accord with infrared data[26,42] and the results of SCF-MO calculations on the isoelectronic $M(CO)_6$ complexes ($M = V^-, Cr^0, Mn^+$).[43]

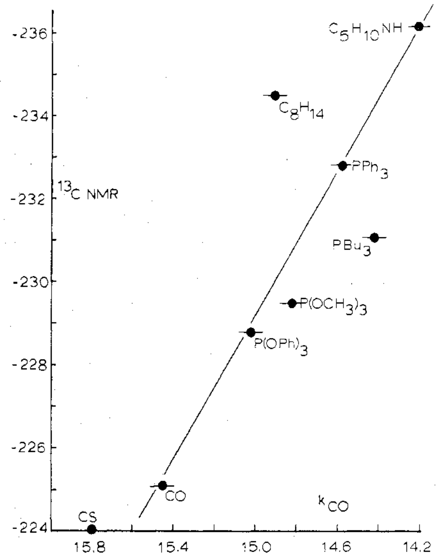

Figure 2. Plot of the ^{13}C nmr carbonyl chemical shifts in ppm downfield from TMS *vs.* the infrared stretching force constants in mdyn/Å for π-$(C_5H_5)Mn(CO)_2L$ derivatives. Relative error bars for k_{CO} of ±0.06 mdyn/Å are included. The relative error in carbonyl chemical shift is approximated by the size of the circle.

Deviations from a linear correlation in Figure 2 may arise from several complications. First, while it has been suggested that comparisons of infrared and ^{13}C nmr data be restricted to a common solvent,[40] the use of chloroform leads to broadened infrared absorption bands with a concomitant decrease in the accuracy of the stretching force constants. Second, the force constants were calculated using an approximate theory with an assumed C_{2v} symmetry instead of the more exact C_s symmetry. Third, infrared stretching force constants have been shown to be proportional to changes in either the σ basicity or π acidity of the carbonyl ligand, whereas the ^{13}C nmr carbonyl chemical shifts appear to be proportional to changes in the extent of transition metal → carbonyl π back-donation alone.[22]

Transition metal → carbonyl π back-donation increases with increasing electron density on the transition metal. The

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^{13}C nmr carbonyl chemical shift should thus be proportional to the electron density on the transition metal and therefore should be a good measure of the relative σ basicity/π acidity of ligands in substituted metal carbonyl complexes. The data in Table II suggest that the order of increasing electron density at the transition metal in π-$(C_5H_5)Mn(CO)_2L$ derivatives is $CS < CO < P(OPh)_3 < P(OCH_3)_3 < PBu_3 < PPh_3 < C_8H_{14} < C_5H_{10}NH$. The relative order $CO < P(OPh)_3 < P(OCH_3)_3 < PPh_3 < C_5H_{10}NH$ is in excellent agreement with the well-established increase in the σ-donor/π-acceptor ratios of these ligands.

Studies of $LW(CO)_5$ complexes have shown an increase in the $^1J_{^{183}W^{31}P}$ nuclear spin-spin coupling constant in the order $PBu_3 < PPh_3 < P(OCH_3)_3 < P(OPh)_3$,[44] the order of increasing withdrawal of electron density from the phosphorus by the X substituent.[45] The Pople-Santry[46] expression for directly bound coupling constants predicts an increase in this coupling constant with an increased effective nuclear charge due to the withdrawal of electron density from the phosphorus atom.[47] We might therefore suggest that this coupling constant is proportional to the basicity of the phosphorus ligand. The data presented in Table II show an increase in the $^2J_{^{13}C^{31}P}$ coupling constants in the order $PPh_3 < PBu_3 < P(OCH_3)_3 < P(OPh)_3$, indicative of a stronger σ basicity for PPh_3 than for PBu_3 in π-$(C_5H_5)Mn(CO)_2L$ complexes. A similar correlation has been observed in $LMo(CO)_5$ derivatives between the cis $^2J_{^{13}C^{31}P}$ coupling constants and the cis-carbonyl chemical shifts,[48] which suggests a stronger σ basicity for PBu_3 than for PPh_3 in this system. We can thus predict the correct order of carbonyl chemical shifts in π-$(C_5H_5)Mn(CO)_2L$ complexes as $CO > P(OPh)_3 > P(OCH_3)_3 > PBu_3 > PPh_3 > C_5H_{10}NH$.

The close similarity between the carbonyl chemical shifts for the cyclooctene (C_8H_{14}) and piperidine ($C_5H_{10}NH$) derivatives is indicative of extensive donation of electron density from the olefin to the transition metal. The *shielding* of the carbonyl resonance in π-$(C_5H_5)Mn(CO)_2(CS)$ relative to π-$(C_5H_5)Mn(CO)_3$ is indicative of a decrease in electron density at the transition metal in the CS complex which might arise from an increased π acidity of the CS ligand.

The reduced range of carbonyl chemical shifts for π-$(C_5H_5)Fe(CO)_2L^+$ relative to π-$(C_5H_5)Mn(CO)_2L$ derivatives is in agreement with a decrease in transition metal → carbonyl π back-donation in the positively charged complex. The data in Table II suggest that PPh_3 cannot compete with two strong π-acceptor CO ligands toward a weak π-donor Fe^+ complex as well as it can toward the stronger π-donor Mn^0 complex.

Demarco, Doddrell, and Wenkert[49] have observed a deshielding of the C(2) carbon resonance in thiocamphor of 54.3 ppm relative to the C(2) carbon resonance in camphor. They have argued that this deshielding is inconsistent with either the relative electronegativities or dipole moments for C=S and C=O but is in agreement with the known decrease in the energy of the $n \rightarrow \pi^*$ transition upon replacement of C=O with C=S[50,51] and with the expression for the paramagnetic screening tensor derived by Karplus and Pople.[52] Kalinowski and Kessler[53] have noted a fairly constant deshielding of thiocarbonyls by 25-30 ppm relative to their carbonyl analogs in $R_2C{=}X$ derivatives (X = O, S), which they suggest is due to the change in ΔE. In π-$(C_5H_5)Mn(CO)_2(CS)$ the thiocarbonyl resonance is over 218 ppm downfield from the carbonyl resonance. While a portion of this chemical shift difference is to be expected from changes in ΔE, the magnitude of this effect is reminiscent of the 135-ppm difference between the chemical shifts of the carbene and carbonyl resonances in $(CO)_5CrC(OCH_3)CH_3$.[39] The observed thiocarbonyl chemical shift might therefore be best understood in terms of a $-{}^{\delta+}C{=}S^{\delta-}$ resonance structure which is stabilized by transition metal-thiocarbonyl π back-donation. This hypothesis is in agreement with studies of the Raman spectra of thiocarbonyl complexes which suggest a significant dipole moment for the thiocarbonyl ligand.[54]

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Registry No. π-$(C_5H_5)Cr(CO)_3Na$, 12203-12-2; π-$(C_5H_5)Mn(CO)_2(CS)$, 51804-24-1; π-$(C_5H_5)Mn(CO)_3$, 12079-65-1; π-$(C_5H_5)Mn(CO)_2[P(OPh)_3]$, 12278-56-7; π-$(C_5H_5)Mn(CO)_2[P(OCH_3)_3]$, 34922-82-2; π-$(C_5H_5)Mn(CO)_2(PBu_3)$, 12277-85-9; π-$(C_5H_5)Mn(CO)_2(PPh_3)$, 12100-41-3; π-$(C_5H_5)Mn(CO)_2(C_8H_{14})$, 12088-20-9; π-$(C_5H_5)Mn(CO)_2(NHC_5H_{10})$, 38497-86-8; π-$(C_5H_5)Fe(CO)_3PF_6$, 34738-62-0; π-$(C_5H_5)Fe(CO)_2(CS)PF_6$, 34738-61-9; π-$(C_5H_5)Fe(CO)_2(PPh_3)PF_6$, 12100-39-9; π-$(C_5H_5)Fe(CO)_2(NH_3)PF_6$, 52225-44-2; ^{13}C, 14762-74-4.

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