(28) E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, **88**, 3929 (1966).

(29) J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972).

(30) M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 495 (1962).

(31) M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, **9**, 32 (1970).

(32) J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1246 (1972).

(33) W. D. Convey and T. L. Brown, *Inorg. Chem.*, **12**, 2823 (1973).

(34) In the strictest sense the σ-donor:π-acceptor ratio for $NH_2C_6H_{11}$ and NHC_5H_{10} cannot be defined due to the absence of π-acceptor character. However, the appearance of these ligands at this point in the series would indicate that the donation of electron density by the amines is less than the net donation of electron density by a phosphine, and we must therefore conclude that the σ-donor character of $NH_2C_6H_{11}$ and NHC_5H_{10} is less than that of PBu_3.

(35) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969).

(36) E. G. Finer and R. K. Harris, *Prog. Nucl. Magn. Reson. Spectrosc.*, **6**, 61 (1971).

(37) E. O. Fischer, E. Louis, W. Bathelt, E. Moser, and J. Muller, *J. Organomet. Chem.*, **14**, P9 (1968); and E. Moser and E. O. Fischer, *ibid.*, **15**, 157 (1968).

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(Cyclopentadienyl)dinitrosylcarbonylmolybdenum and -tungsten Cations and Related Complexes

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Reaction of $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ with $NOPF_6$ at −78° affords the reactive green $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ complexes in ~90% yields (M = Mo, W). These complexes undergo facile carbonyl substitution reactions with neutral (L) or anionic (X^-) Lewis bases to yield $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ and $(\eta^5\text{-}C_5H_5)M(NO)_2X$, respectively (L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$; X = Cl, Br, I). The $[(\eta^5\text{-}C_5H_5)Mo(NO)_2L]PF_6$ complexes were also prepared by direct reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$ with $NOPF_6$ and L. The carbonyl group in the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]^+$ cations is rapidly replaced by the coordinating solvents acetonitrile and acetone, in contrast to the behavior of the corresponding chromium cation and the related $[(\eta^5\text{-}C_5H_5)M'(CO)_2NO]^+$ cations (M' = Mn, Re).

Introduction

Numerous (cyclopentadienyl)dinitrosylchromium derivatives have been prepared since the initial synthesis[1] of the halides $(\eta^5\text{-}C_5H_5)Cr(NO)_2X$ (X = Cl, Br, I) almost 20 years ago. Such derivatives include the cation $[(\eta^5\text{-}C_5H_5)Cr(NO)_2CO]^+$,[2] the dimer $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$,[3] and compounds of the type $(\eta^5\text{-}C_5H_5)Cr(NO)_2Y$, which involve metathetical replacement of X by other one-electron ligands (Y = NCO,[4] CN,[5] NCSe,[5] SCF_3,[6] alkyl,[1,7] aryl[1]). In marked contrast the related chemistry of molybdenum and tungsten has remained largely unexplored.[8] This is particularly surprising in the case of molybdenum, for which there exists an extensive chemistry of monomeric and dimeric cyclopentadienyl *mono*nitrosyls.[8] In the course of work intended to expand this area we have now prepared molybdenum and tungsten derivatives of the types $(\eta^5\text{-}C_5H_5)M(NO)_2X$ (X = Cl, Br, I), $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$, and $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ (L = group 5A Lewis base), where M = Mo, W. Except for $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$,[9,10] no other (cyclopentadienyl)dinitrosylmolybdenum or -tungsten compounds were known prior to this work. Certain aspects of this work have been reported in a preliminary form.[11]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen using Schlenk-type apparatus. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were taken in capillaries sealed under nitrogen using a Thomas-Hoover melting point apparatus and are uncorrected. These data are summarized in Table I.

Materials. All solvents (reagent grade) were dried by appropriate methods and were saturated with nitrogen prior to use. Tungsten hexacarbonyl (Pressure Chemical Co.) and nitrosyl hexafluorophosphate (Ozark-Mahoning Co.) were purchased from the indicated commercial sources. Molybdenum hexacarbonyl was a generous gift from the Climax Molybdenum Co. Other chemicals were of reagent grade. $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$ was prepared by the method of Piper and Wilkinson.[1]

Spectra. Infrared spectra (Table II) were obtained on a Perkin-Elmer 180 spectrometer calibrated with carbon monoxide, polystyrene, and indene. Solution spectra were run in NaCl or KBr cells using dichloromethane as solvent. Mull spectra were recorded in Nujol between flat Irtran-2 plates. Mulls of the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ complexes were carefully prepared in a dry nitrogen-filled glove bag.

Proton NMR spectra (Table II) were recorded at 60 MHz on a JEOL C-60-H instrument using internal TMS as reference and chloroform-d_1 or acetone-d_6 as solvents. Mass spectra were obtained on a Perkin-Elmer Hitachi RMU-5 mass spectrometer at 70 eV with a chamber temperature of 200° and a sample temperature of 100–150°.

Preparation of $(\eta^5\text{-}C_5H_5)W(CO)_2NO$. This compound was prepared by a modification of the preparation reported[1] for the molybdenum derivative. A solution of $(\eta^5\text{-}C_5H_5)W(CO)_3H$, prepared from 50.5 g (143 mmol) of $W(CO)_6$ according to the published procedure,[12] and 34.1 g (159 mmol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ("Diazald") in ether (400 ml) was refluxed for 24 hr. Filtration, followed by removal of solvent, gave an orange crystalline residue which was chromatographed on a Florisil column (6 × 25 cm) using 5:1 hexane–dichloromethane. The broad orange band was collected and concentration of this solution on the rotary evaporator afforded 37.1 g of orange crystalline $(\eta^5\text{-}C_5H_5)W(CO)_2NO$ (77% yield based upon $W(CO)_6$), identified by infrared and NMR spectroscopy.[13]

Preparation of $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ (M = Mo, W). Solid $NOPF_6$ (5.90 g, 34.7 mmol) was added in several portions with stirring to a cooled (−78°) solution of $(\eta^5\text{-}C_5H_5)W(CO)_2NO$ (10.5 g, 31.4 mmol) in dichloromethane (70 ml) and acetonitrile (40 ml). A green precipitate immediately formed, accompanied by rapid gas evolution. The solution was stirred for an additional 30 min at −78° and then 400 ml of cold (−78°) ether was added to complete precipitation. Filtration gave $[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$ as a green powder (yield 13.9 g, 92%).

The molybdenum analog was prepared in comparable yield by a similar procedure involving $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$.

Preparation of $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ (M = Mo, W; L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$). (a) Solid $[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$ (1.35 g, 2.80 mmol) and PPh_3 (0.77 g, 2.93 mmol) were heated for 1 hr in refluxing dichloromethane. The solution was then filtered, heptane was added, and the resulting mixture was slowly concentrated on the rotary evaporator without external heating. Green crystalline $[(\eta^5\text{-}C_5H_5)W(NO)_2PPh_3]PF_6$ (1.49 g, 74%) was collected by filtration.

The other $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ complexes were prepared by

Table I. Analytical Data, Yields, and Melting Points

Complex[a]	Mp, °C	Yield, %	Elemental analyses, %							
			C		H		N		Other	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2CO]PF_6$		90	18.29	18.53	1.28	1.54	7.11	7.37		
$[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$		92	14.95	15.09	1.05	1.18	5.81	5.84		
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2PPh_3]PF_6$	180 dec	74[b]	43.97	44.08	3.21	3.21	4.46	4.16		
$[(\eta^5\text{-}C_5H_5)W(NO)_2PPh_3]PF_6$	153 dec	74[c]	38.57	38.24	2.81	2.50	3.91	3.56		
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2AsPh_3]PF_6$	205 dec	81[b]	41.09	41.09	2.99	3.10	4.17	3.97		
$[(\eta^5\text{-}C_5H_5)W(NO)_2AsPh_3]PF_6$	183 dec	65[c]	36.34	36.28	2.65	2.65	3.68	3.54		
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2SbPh_3]PF_6$	130 dec	74[b]	38.42	38.28	2.80	2.75	3.90	3.55		
$[(\eta^5\text{-}C_5H_5)W(NO)_2SbPh_3]PF_6$	148 dec	62[c]	34.23	34.37	2.50	2.48	3.47	3.36		
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2P(OMe)_3]PF_6$	65 dec	71[b]	19.61	19.66	2.88	2.86	5.71	5.14		
$[(\eta^5\text{-}C_5H_5)W(NO)_2P(OMe)_3]PF_6$	78 dec	75[c]	16.61	16.54	2.44	2.37	4.85	4.47		
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2P(OPh)_3]PF_6$	170 dec	80[b]	40.85	40.85	2.98	2.96	4.14	3.90		
$[(\eta^5\text{-}C_5H_5)W(NO)_2P(OPh)_3]PF_6$	100 dec	82[c]	36.15	35.72	2.64	2.50	3.67	3.56		
$(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$	110 dec[d]	80	23.41	23.45	1.96	1.94			Cl: 13.82	13.48
$(\eta^5\text{-}C_5H_5)W(NO)_2Cl$	127 dec	57	17.44	17.44	1.46	1.48	8.13	7.57	Cl: 10.29	9.90
$(\eta^5\text{-}C_5H_5)Mo(NO)_2Br$	112 dec	56	19.95	19.74	1.67	1.53	9.31	9.05	Br: 26.55	25.81
$(\eta^5\text{-}C_5H_5)W(NO)_2Br$	142 dec	75	15.44	15.41	1.30	1.19	7.20	7.10	Br: 20.55	20.48
$(\eta^5\text{-}C_5H_5)Mo(NO)_2I$	149 dec	67	17.26	17.28	1.45	1.43	8.05	7.93	I: 36.47	36.52
$(\eta^5\text{-}C_5H_5)W(NO)_2I$	158 dec	56	13.78	13.90	1.16	1.76	6.43	6.29	I: 29.12	29.10

[a] The $(\eta^5\text{-}C_5H_5)M(NO)_2I$ complexes (M = Mo, W) are olive green; all other complexes are green. [b] Method b. [c] Method a. [d] Literature mp 118°.[9]

Table II. Infrared and Proton NMR Data

Complex	ν_{NO},[a] cm^{-1}	Proton NMR[b]		
		$\tau(C_5H_5)$	τ(L)	J_{PH},[c] Hz
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2CO]PF_6$[d]	1826, 1736[f]			
$[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$[e]	1814, 1730[f]			
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2PPh_3]PF_6$	1792, 1710	3.62 d	2.37 m	1.1
$[(\eta^5\text{-}C_5H_5)W(NO)_2PPh_3]PF_6$	1770, 1696	3.46 d	2.35 m	1.1
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2AsPh_3]PF_6$	1792, 1712	3.51 s	2.40 m	
$[(\eta^5\text{-}C_5H_5)W(NO)_2AsPh_3]PF_6$	1771, 1697	3.36 s	2.35 m	
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2SbPh_3]PF_6$	1791, 1713	3.34 s	2.27 m	
$[(\eta^5\text{-}C_5H_5)W(NO)_2SbPh_3]PF_6$	1770, 1697	3.29 s	2.32 m	
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2P(OMe)_3]PF_6$[g]	1797, 1716	3.41 d	6.02 d	1.2
$[(\eta^5\text{-}C_5H_5)W(NO)_2P(OMe)_3]PF_6$[h]	1777, 1702	3.26 d	6.02 d	1.4
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2P(OPh)_3]PF_6$	1807, 1727	3.69 d	2.37 m	0.9
$[(\eta^5\text{-}C_5H_5)W(NO)_2P(OPh)_3]PF_6$	1788, 1712	3.59 d	2.45 m	1.1
$[(\eta^5\text{-}C_5H_5)Mo(NO)_2CH_3CN]PF_6$	1794, 1708			
$[(\eta^5\text{-}C_5H_5)W(NO)_2CH_3CN]PF_6$	1770, 1690			
$(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$[i]	1760, 1668	3.95 s[j]		
$(\eta^5\text{-}C_5H_5)W(NO)_2Cl$	1735, 1651	3.88 s[j]		
$(\eta^5\text{-}C_5H_5)Mo(NO)_2Br$	1763, 1672	3.92 s[j]		
$(\eta^5\text{-}C_5H_5)W(NO)_2Br$	1737, 1654	3.85 s[j]		
$(\eta^5\text{-}C_5H_5)Mo(NO)_2I$	1765, 1676	3.90 s[j]		
$(\eta^5\text{-}C_5H_5)W(NO)_2I$	1740, 1657	3.82 s[j]		

[a] CH_2Cl_2 solution unless otherwise noted. [b] Acetone-d_6 solution unless otherwise noted. Abbreviations: s, singlet; d, doublet; m, multiplet. [c] H on $(\eta^5\text{-}C_5H_5)$ ring. [d] ν_{CO} 2129 cm^{-1} (Nujol). [e] ν_{CO} 2116 cm^{-1} (Nujol). [f] Nujol mull. [g] $^3J_{POCH_3}$ = 12.7 Hz. [h] $^3J_{POCH_3}$ = 12.9 Hz. [i] Literature: ν_{NO} 1759, 1665 cm^{-1} (CH_2Cl_2); τ 3.84 ($CDCl_3$).[9] [j] Chloroform-d_1 solution.

the same method except that reactions involving $[(\eta^5\text{-}C_5H_5)Mo(NO)_2CO]PF_6$ were readily carried out at ambient temperature.

(b) Solid $NOPF_6$ (1.64 g, 9.38 mmol) was added in several portions to a stirred solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$ (2.29 g, 9.27 mmol) and PPh_3 (2.62 g, 10.0 mmol) in dichloromethane (50 ml). The reaction mixture was allowed to stir for 20 min and then excess ether was added to the resulting green solution. The green precipitate that formed was collected on filtration and was recrystallized from dichloromethane–heptane to give 4.30 g of green crystalline $[(\eta^5\text{-}C_5H_5)Mo(NO)_2PPh_3]PF_6$ (74% yield).

The other L ligands reacted in a similar fashion with $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$ and $NOPF_6$ to yield $[(\eta^5\text{-}C_5H_5)Mo(NO)_2L]PF_6$, but the corresponding tungsten derivatives could not be prepared from $(\eta^5\text{-}C_5H_5)W(CO)_2NO$ under the same conditions.

Preparation of $[(\eta^5\text{-}C_5H_5)M(NO)_2CH_3CN]PF_6$ (M = Mo, W). Solid $[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$ (35 mg, 0.073 mmol) was added to acetonitrile (5 ml). Vigorous gas evolution was observed and a green solution was formed. Excess solvent was removed in vacuo and the resulting green oil was washed with ether. Repeated attempts to crystallize this material were unsuccessful, but the complex was characterized by its infrared spectrum in the N–O stretching region and by its reactions.

The molybdenum analog was prepared by a similar procedure. Both complexes could also be prepared from the reaction of $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ with $NOPF_6$ at room temperature using acetonitrile as solvent.

Preparation of $(\eta^5\text{-}C_5H_5)M(NO)_2X$ (M = Mo, W; X = Cl, Br, I). Solid $[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$ (0.91 g, 1.90 mmol) was added at room temperature to a stirred slurry of NaBr (0.26 g, 2.50 mmol) in acetone (30 ml). The resulting green solution was stirred for 30 min and was evaporated to dryness in vacuo. The solid residue was extracted with dichloromethane and was filtered. Addition of heptane to the filtrate followed by concentration of the solution in vacuo afforded green crystals of $(\eta^5\text{-}C_5H_5)W(NO)_2Br$ (0.55 g, 75% yield).

The corresponding chloride and iodide were similarly prepared using the appropriate sodium halide. The molybdenum compounds $(\eta^5\text{-}C_5H_5)Mo(NO)_2X$ were synthesized from $[(\eta^5\text{-}C_5H_5)Mo(NO)_2CO]PF_6$ and KX by analogous procedures.

Results

Nitrosyl hexafluorophosphate, $NOPF_6$, readily reacts with $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ (M = Mo, W) in dichloromethane–acetonitrile at −78° to form the green ionic solids $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ in ~90% yield (eq 1). The insol-

$$(\eta^5\text{-}C_5H_5)M(CO)_2NO + NOPF_6 \xrightarrow[-78°]{CH_2Cl_2-CH_3CN} [(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6 + CO \quad (1)$$

ubility of these compounds in all but those solvents with which they react prevented recrystallization but satisfactory elemental analyses were obtained. It is particularly mandatory that all operations involving $[(\eta^5\text{-}C_5H_5)Mo(NO)_2CO]PF_6$ be carried out using Schlenk apparatus since the compound is extremely hygroscopic and is rapidly transformed into a viscous green mass in the presence of moist air. The tungsten analog is significantly less hygroscopic and can be handled in air for brief periods at room temperature without noticeable decomposition.

A characteristic feature of the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ complexes is the extreme lability of the carbonyl group. Thus although these complexes are insoluble in nonpolar solvents, ether, and dichloromethane, the coordinating solvents (S) acetonitrile and acetone rapidly displace carbon monoxide from $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ at room temperature to form dark green reactive solutions containing the $[(\eta^5\text{-}C_5H_5)M(NO)_2S]^+$ cations. The $[(\eta^5\text{-}C_5H_5)M(NO)_2CH_3CN]^+$ cations were also formed when $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ was allowed to react with $NOPF_6$ in acetonitrile solution at room temperature. Attempts to isolate solid PF_6^- salts of the $[(\eta^5\text{-}C_5H_5)M(NO)_2S]^+$ cations were unsuccessful, but infrared and reactivity studies (described below) support the proposed formulation. These cations are analogous to the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2S]^+$ cations which have been prepared and fully characterized as PF_6^- salts.[14]

The presence of a very labile carbonyl group in $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ makes these complexes convenient precursors for other (cyclopentadienyl)dinitrosylmolybdenum and -tungsten derivatives. Thus a slurry of $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ in dichloromethane reacted rapidly at room temperature (M = Mo) or under reflux (M = W) with various Lewis bases (L) to give good yields (60–80%) of the corresponding green $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ complexes (L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$)

$$[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6 + L \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6 + CO \quad (2)$$

The molybdenum complexes could be prepared more conveniently by direct reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$, $NOPF_6$, and L according to eq 3. Good yields (70–80%) were

$$(\eta^5\text{-}C_5H_5)Mo(CO)_2NO + NOPF_6 + L \xrightarrow[25°]{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Mo(NO)_2L]PF_6 + 2CO \quad (3)$$

obtained by this method, but attempts to prepare $[(\eta^5\text{-}C_5H_5)W(NO)_2L]PF_6$ complexes directly from $(\eta^5\text{-}C_5H_5)W(CO)_2NO$ under the same conditions were not successful. Similar substitution reactions involving $[(\eta^5\text{-}C_5H_5)Cr(NO)_2CO]PF_6$ have not been reported, although the $[(\eta^5\text{-}C_5H_5)Cr(NO)_2PPh_3]^+$ cation has been briefly mentioned in the literature.[15] This is perhaps surprising in view of the considerable attention[16] devoted to carbonyl substitution in the isoelectronic complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2NO]PF_6$.

The neutral halide complexes $(\eta^5\text{-}C_5H_5)M(NO)_2X$ (X = Cl, Br, I) were prepared by the facile reaction of $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ with sodium or potassium halides in acetone solution at 25° (eq 4). Recrystallization from dichloromethane–hexane afforded these compounds as green (X = Cl, Br) or olive green (X = I) crystalline solids in good yields (55–80%). Similar reaction conditions have been used to prepare the related (cyclopentadienyl)dicarbonyl halides of iron[17] and ruthenium,[18] e.g., $(\eta^5\text{-}C_5H_5)M'(CO)_2X$ (M' = Fe, Ru), from the appropriate $[(\eta^5\text{-}C_5H_5)M'(CO)_3]^+$ cation.

$$[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6 + M'X \xrightarrow[25°]{acetone} (\eta^5\text{-}C_5H_5)M(NO)_2X + M'PF_6 + CO \quad (4)$$
$$M' = Na, K$$

Formation of the halides, via eq 5, was also observed while

$$[(\eta^5\text{-}C_5H_5)M(NO)_2L']PF_6 + M'X \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)M(NO)_2X + M'PF_6 + L' \quad (5)$$
$$L' = L, CH_3CN; M'X = NaCl, KBr$$

recording solution infrared spectra of $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ and $[(\eta^5\text{-}C_5H_5)M(NO)_2CH_3CN]PF_6$ complexes in NaCl and KBr cells. Reaction with KBr was much more rapid than reaction with NaCl. Reaction 5 is also accelerated by the more polar solvent acetonitrile as illustrated by the infrared spectra of the $[(\eta^5\text{-}C_5H_5)M(NO)_2CH_3CN]PF_6$ complexes in this solvent. Spectra recorded immediately after introducing the acetonitrile solution into the infrared cell exhibit bands due only to $(\eta^5\text{-}C_5H_5)M(NO)_2X$. The compound $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$ has been previously prepared[9,10] by two routes, but the method used here appears to be more favorable in terms of both yield and convenience. The reported[9,10] instability of the chloride is also characteristic of the bromide and iodide. All three molybdenum halides gradually darken with apparent loss of nitric oxide even when stored in the freezer. The tungsten halides behave similarly. This behavior may be contrasted with the high thermal and oxidative stability of the related tris(1-pyrazolylborate) complexes $RB(pz)_3M(NO)_2Cl$ (M = Mo, W).[19]

Spectroscopic Properties. The spectroscopic properties (Table II) of the various complexes prepared in this work are fully consistent with the proposed structural formulations.

a. Infrared Spectra. The infrared spectra (Nujol mull) of the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ complexes show one carbonyl stretching band and two nitrosyl stretching bands. The infrared spectra of the $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ complexes exhibit two strong bands in the N–O stretching region. In both the molybdenum and tungsten series these frequencies appear to correlate with the generally acknowledged σ-donor and π-acceptor properties[20] of the L groups. In view of the relative electronic properties of CH_3CN,[20] the ν_{NO} band positions in the $[(\eta^5\text{-}C_5H_5)M(NO)_2CH_3CN]PF_6$ complexes are in accord with the proposed formulation. All $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ and $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ complexes also show a strong band in the 825–855-cm^{-1} region, characteristic of the PF_6^- anion.[21]

The neutral $(\eta^5\text{-}C_5H_5)M(NO)_2X$ halides show two strong ν_{NO} bands in their infrared spectra. Not surprisingly these bands are 30–50 cm^{-1} lower in energy than those in the cationic $[(\eta^5\text{-}C_5H_5)M(NO)_2L]^+$ species of the same metal. The slight increase in ν_{NO} with change in halogen, e.g., X = I > Br > Cl, has also been observed for the corresponding chromium halides[1] and for the $(\eta^5\text{-}C_5H_5)Re(CO)(NO)X$ halides,[22] which are isoelectronic with $(\eta^5\text{-}C_5H_5)W(NO)_2X$.

b. NMR Spectra. The proton NMR spectra of all complexes appear to be quite normal and in all cases correct integration is observed.

c. Mass Spectra. The mass spectra of all of the $(\eta^5\text{-}C_5H_5)M(NO)_2X$ halides exhibited a weak (M = Mo) or strong (M = W) molecular ion. Peaks corresponding to $C_5H_5M(NO)X^+$, $C_5H_5MX^+$, $C_3H_3MX^+$, and C_3M^+ were observed in moderate to high abundance for both series of compounds. The base peak for the molybdenum halides is due to $C_5H_5MoX^+$ in each case, while the base peak for the tungsten chloride and bromide corresponds to the appropriate $C_3H_3WX^+$ ion. For $(\eta^5\text{-}C_5H_5)W(NO)_2I$ this ion (X = I) is slightly less intense than the parent ion, which forms the base peak of the mass spectrum. In the molybdenum series peaks corresponding to $C_5H_5Mo(NO)X_2^+$ and $C_5H_5MoX_2^+$ were unambiguously assigned. The existence of these two ions

Table III. Infrared Data for Cyclopentadienylmetal Nitrosyl Carbonyl Complexes

Complex	ν_{CO}, cm^{-1}	ν_{NO}, cm^{-1}	Ref
$[(\eta^5\text{-}C_5H_5)Cr(NO)_2CO]PF_6$[a]	2137	1873, 1779	2
$[(\eta^5\text{-}C_5H_5)Mn(CO)_2NO]PF_6$[b]	2114, 2075	1852	26
$[(\eta^5\text{-}C_5H_5)Re(CO)_2NO]PF_6$[b]	2105, 2049	1815	26
$(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$[c]	2025, 1956	1716	30
$(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$[c]	2020, 1947	1689	30
$(\eta^5\text{-}C_5H_5)W(CO)_2NO$[c]	2011, 1934	1683	30

[a] Nujol mull. [b] Acetone solution. [c] Hexane solution.

suggests the partial formation of the $[(\eta^5\text{-}C_5H_5)Mo(NO)X_2]_2$ dimers[23] in the mass spectrometer. The presence of $C_5H_5Mo(NO)_2X^+$ ions in our spectra contrasts with the absence of these ions in the published[23,24] mass spectra of the halide dimers, indicating that decomposition of $(\eta^5\text{-}C_5H_5)Mo(NO)_2X$ is not complete.

Discussion

A comparison of the infrared spectral data in the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ series (M = Cr, Mo, W) indicates an appreciable decrease in ν_{NO} on going from chromium to molybdenum or tungsten (Tables II, III). A similar, though much less pronounced, trend is also observed for ν_{CO} in the series. These changes in ν_{NO} and ν_{CO} undoubtedly reflect changes in M–NO and M–CO back-bonding, since the destabilization of the metal *n*d levels with increasing *n* should result in an increase in the interaction of the metal dπ orbitals with the π^* orbitals of NO^+ and CO. In view of the fact that the π^* levels of NO^+ are lower in energy than those of CO, the M–NO interaction should be more sensitive to the change of metal than the M–CO interaction. However, a comparison of the relative change in ν_{NO} and ν_{CO} on going from chromium to molybdenum ($\Delta\nu_{NO} \approx 45$ cm^{-1}, $\Delta\nu_{CO} = 8$cm^{-1}) with the analogous parameters on going from molybdenum to tungsten ($\Delta\nu_{NO} \approx 9$ cm^{-1}, $\Delta\nu_{CO} = 13$cm^{-1}) illustrates that the overall π-acceptor ability of the dinitrosylcarbonyl unit, while large and variable, is not unrestricted. Similar conclusions can be drawn from ν_{NO} and ν_{CO} infrared data in related series, e.g., $[(\eta^5\text{-}C_5H_5)M'(CO)_2NO]PF_6$ (M' = Mn, Re) and $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ (M = Cr, Mo, W), as shown in Table III.

The extreme lability of the carbonyl group in the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ complexes (M = Mo, W), even toward coordinating solvents like acetone and acetonitrile, is in marked contrast to the behavior of the related $[(\eta^5\text{-}C_5H_5)M'(CO)_2NO]PF_6$ complexes (M' = Mn, Re), both of which can be recovered unchanged from these solvents.[22,25,26] It is interesting to note that the relative reactivities of the isoelectronic species $[(\eta^5\text{-}C_5H_5)W(NO)_2CO]^+$ and $[(\eta^5\text{-}C_5H_5)Re(CO)_2NO]^+$ are consistent with ν_{CO} and ν_{NO} infrared data for the two cations, although this is perhaps fortuitous. Thus ν_{CO} for the tungsten cation (2116 cm^{-1}) is significantly higher than ν_{CO}(av) for the rhenium cation (2071 cm^{-1}), suggesting a lower metal–carbon bond order in the former case. At the same time ν_{NO}(av) for the tungsten cation (1772 cm^{-1}) is considerably lower than ν_{NO} for the rhenium cation (1815 cm^{-1}). Whether these quite pronounced *ground-state* electronic effects can be correlated with qualitative and/or quantitative *rates* of CO substitution in the two cations is of course questionable since clearly there need not be any such relationship.[27] Nevertheless, the enhanced labilizing effect of NO^+ vs. CO has been demonstrated in carbonyl substitution reactions involving related systems.[28,29]

In this context it is also noteworthy that there is some qualitative evidence which indicates that the reactivity of the $[(\eta^5\text{-}C_5H_5)Cr(NO)_2CO]^+$ cation is signficantly lower than that of the analogous molybdenum and tungsten cations. For example, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2CO]PF_6$ is reported to be recrystallized from acetone solution.[2] This conclusion is also supported by our infrared spectral studies of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2CO]PF_6$ in acetonitrile solution.[30] Bands due to the parent cation (ν_{CO} = 2137, ν_{NO} = 1876, 1788 cm^{-1}) are initially observed prior to its complete conversion within 5–10 min to a mixture of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3CN]^+$ (ν_{NO} = 1847, 1745 cm^{-1}) and $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br^1$ (ν_{NO} = 1818, 1713 cm^{-1}), in contrast to the corresponding studies on the molybdenum and tungsten systems described above. The $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$ complex is formed by reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3CN]^+$ with the infrared cell windows (KBr). These observations and the observations concerning the relative ease of CO substitution in $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ (M = Mo, W) according to eq 2 thus indicate the following order of relative reactivity for the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]^+$ cations: M = Mo > W > Cr. The same order has been observed for the ease of CO replacement by PPh_3 in $(\eta^5\text{-}C_5H_5)M(CO)_2NO$.[29] The obvious lack of correlation between this reactivity order and C–O stretching frequencies in either the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ or $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ series (Tables II, III) again stresses that caution must be used in predicting *kinetic* effects from only *ground-state* measurements.[27]

Note Added in Proof. After this paper was accepted for publication an alternative preparation of $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Mo, W) and the synthesis of various alkyl and aryl derivatives, $(\eta^5\text{-}C_5H_5)M(NO)_2R$, were reported by Legzdins and coworkers.[31]

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Registry No. PPh_3, 603-35-0; $P(OMe)_3$, 121-45-9; $P(OPh)_3$, 101-02-0; CH_3CN, 75-05-8; $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$, 12128-13-1; $(\eta^5\text{-}C_5H_5)W(CO)_2NO$, 12128-14-2; $[(\eta^5\text{-}C_5H_5)Mo(NO)_2CO]PF_6$, 56403-92-0; $[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$, 53419-03-7; $[(\eta^5\text{-}C_5H_5)Mo(NO)_2PPh_3]PF_6$, 56403-94-2; $[(\eta^5\text{-}C_5H_5)W(NO)_2PPh_3]PF_6$, 53419-05-9; $[(\eta^5\text{-}C_5H_5)Mo(NO)_2AsPh_3]PF_6$, 56403-96-4; $[(\eta^5\text{-}C_5H_5)W(NO)_2AsPh_3]PF_6$, 53419-07-1; $[(\eta^5\text{-}C_5H_5)Mo(NO)_2SbPh_3]PF_6$, 56403-98-6; $[(\eta^5\text{-}C_5H_5)W(NO)_2SbPh_3]PF_6$, 53419-09-3; $[(\eta^5\text{-}C_5H_5)Mo(NO)_2P(OMe)_3]PF_6$, 56404-00-3; $[(\eta^5\text{-}C_5H_5)W(NO)_2P(OMe)_3]PF_6$, 53419-11-7; $[(\eta^5\text{-}C_5H_5)Mo(NO)_2P(OPh)_3]PF_6$, 56404-02-5; $[(\eta^5\text{-}C_5H_5)W(NO)_2P(OPh)_3]PF_6$, 53419-13-9; $[(\eta^5\text{-}C_5H_5)Mo(NO)_2CH_3CN]PF_6$, 56404-04-7; $[(\eta^5\text{-}C_5H_5)W(NO)_2CH_3CN]PF_6$, 56404-06-9; $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$, 12305-00-9; $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$, 53419-14-0; $(\eta^5\text{-}C_5H_5)Mo(NO)_2Br$, 56403-78-2; $(\eta^5\text{-}C_5H_5)W(NO)_2Br$, 53419-15-1; $(\eta^5\text{-}C_5H_5)Mo(NO)_2I$, 56403-79-3; $(\eta^5\text{-}C_5H_5)W(NO)_2I$, 53419-16-2; $NOPF_6$, 16921-91-8.

References and Notes

(1) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956); **3**, 104 (1956).

(2) E. O. Fischer and P. Kuzel, *Z. Anorg. Allg. Chem.*, **317**, 326 (1962).

(3) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

(4) M. A. Bush, G. A. Sim, G. R. Knox, M. Ahmad, and C. G. Robertson, *Chem. Commun.*, 74 (1969).

(5) M. A. Jennings and A. Wojcicki, *J. Organomet. Chem.*, **14**, 231 (1968).

(6) R. B. King and N. A. Welcman, *Inorg. Chem.*, **8**, 2540 (1969).

(7) J. A. Hanna and A. Wojcicki, *Inorg. Chim. Acta*, **9**, 55 (1974).

(8) (a) N. G. Connelly, *Inorg. Chim. Acta, Rev.*, **6**, 47 (1972), and references therein; (b) W. P. Griffith, *Adv. Organomet. Chem.*, **7**, 211 (1968); (c) B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, **7**, 277 (1966).

(9) R. B. King, *Inorg. Chem.*, **7**, 90 (1968).

(10) M. L. H. Green, T. R. Sanders, and R. N. Whiteley, *Z. Naturforsch. Teil B*, **23**, 106 (1968).

(11) R. P. Stewart, Jr., *J. Organomet. Chem.*, **70**, C8 (1974).

(12) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, N.Y., 1965, p 156.

(13) E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch. Teil B*, **10**, 598 (1955).

(14) (a) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966); (b) E. C. Johnson, T. J. Meyer, and N. Winterton, *ibid.*, **10**, 1673 (1971); (c) W. E. Williams and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1329 (1973).

(15) Reference 8c, p 348.

(16) (a) R. B. King and A. Efraty, *Inorg. Chem.*, **8**, 2374 (1969); (b) H. Brunner *Z. Anorg. Allg. Chem.*, **368**, 120 (1969); (c) T. A. James and J. A. McCleverty, *J. Chem. Soc. A*, 850 (1970).

(17) R. K. Kochar and R. Pettit, *J. Organomet. Chem.*, **6**, 272 (1966).

(18) A. E. Kruse and R. J. Angelici, *J. Organomet. Chem.*, **24**, 231 (1970).

(19) S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969).

(20) (a) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964); (b) W. A. G. Graham, *ibid.*, **7**, 315 (1968); (c) R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, **6**, 65 (1972).

(21) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1963, pp 114–119.

(22) R. P. Stewart and W. A. G. Graham, unpublished observations, 1972.

(23) (a) R. B. King, *Inorg. Chem.*, **6**, 30 (1967); (b) J. A. McCleverty and D. Seddon, *J. Chem. Soc., Dalton Trans.*, 2526 (1972).

(24) R. B. King, *Org. Mass Spectrom.*, **2**, 401 (1969).

(25) (a) R. B. King, ref 12, p 163; (b) N. G. Connelly and L. F. Dahl, *Chem. Commun.*, 880 (1970).

(26) E. O. Fischer and H. Strametz, *Z. Naturforsch. Teil B*, **23**, 278 (1968).

(27) For example see R. J. Angelici, *Organomet. Chem. Rev.*, **3**, 173 (1968).

(28) (a) W. Wawersik and F. Basolo, *J. Am. Chem. Soc.*, **89**, 4626 (1967); (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, N.Y., 1967, p 572; (c) E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, **88**, 3929 (1966).

(29) H. Brunner, *J. Organomet. Chem.*, **16**, 119 (1969).

(30) R. P. Stewart, unpublished results.

(31) P. Legzdins and J. T. Malito, *Inorg. Chem.*, **14**, 1875 (1975); J. K. Hoyano, P. Legzdins, and J. T. Malito, *J. Chem. Soc., Dalton Trans.*, 1022 (1975).

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Reactions of Metal Carbonyl Complexes. VII.[1] Kinetics and Mechanism of the Organosulfide Substitution Reactions of Some (η^5-Cyclopentadienyl)dicarbonyl(organosulfide)manganese(I) Complexes with Tertiary Phosphines and Phosphites[2]

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The organosulfide complexes η^5-$C_5H_5Mn(CO)_2(SR_2)$ (R = Me, Et, *n*-Pr, *n*-Bu, Ph, CH_2Ph) and η^5-$C_5H_5Mn(CO)_2$(THT) (THT = tetrahydrothiophene, C_4H_8S) undergo substitution of the organosulfide ligands with tertiary phosphines and phosphites (L) to form the η^5-$C_5H_5Mn(CO)_2L$ derivatives. The reaction rates in methylcyclohexane solution are first order in substrate, are independent of both the nature and the concentration of L, and increase with changes in the organosulfide ligand as $SMe_2 <$ THT $< SEt_2 < S(n\text{-Bu})_2 < S(n\text{-Pr})_2 < S(CH_2Ph)_2 << SPh_2$. An SN1 dissociative mechanism involving the rupture of the manganese–sulfur bonds as the rate-determining step is proposed. This mechanism is supported by the observed activation parameters and the small effect of solvent polarity on the rate of reaction of η^5-$C_5H_5Mn(CO)_2$(THT) with P(O-*n*-Bu)$_3$.

Introduction

Over the last 15 years, numerous transition metal carbonyl complexes containing organosulfide ligands have been synthesized, e.g., $Cr(CO)_3(C_4H_4S)$,[4] $Mo(CO)_5(SEt_2)$,[5] $W(CO)_4(MeSCH_2CH_2SMe)$,[6] and *fac*-$Mo(CO)_3(SMe_2)_3$.[7] Suprisingly, most of the research on them has been concerned with their spectroscopic properties[8] and little is known about the relative labilities of organosulfide ligands in such complexes. In fact, no kinetic studies appear to have been reported for organometallic carbonyls containing even simple monodentate organosulfide ligands such as SMe_2 and SPh_2. However, some kinetic data have been reported for substitution of the bidentate organosulfide ligands 2,5-dithiahexane ($MeSCH_2CH_2SMe$) and 2,2,7,7-tetramethyl-3,6-dithiaoctane [$MeC(Me)_2SCH_2CH_2SC(Me)_2Me$] (L-L), in *cis*-$M(CO)_4$(L-L) (M = Cr, Mo, W) by tertiary phosphites.[9,10]

In 1964, Strohmeier and Guttenberger[11] studied the photochemical reactions of η^5-$C_5H_5Mn(CO)_3$ with SEt_2 and SPh_2 and found that the monosubstituted derivatives η^5-$C_5H_5Mn(CO)_2(SEt_2)$ and η^5-$C_5H_5Mn(CO)_2(SPh_2)$ are produced. Moreover, the organosulfide ligands are apparently readily displaced by PPh_3 to form η^5-$C_5H_5Mn(CO)_2(PPh_3)$. As a first step in studying the potential of transition metal–carbonyl–organosulfide complexes for homogeneous catalysis, we have synthesized η^5-$C_5H_5Mn(CO)_2(SR_2)$ (R = Me, Et, *n*-Pr, *n*-Bu, Ph, CH_2Ph) and η^5-$C_5H_5Mn(CO)_2$(THT) (THT = tetrahydrothiophene, C_4H_8S) and studied the kinetics and mechanism of the organosulfide substitution reactions of these complexes with tertiary phosphines and phosphites (L) (eq 1).

$$\eta^5\text{-}C_5H_5Mn(CO)_2(\text{organosulfide}) + L \rightarrow \eta^5\text{-}C_5H_5Mn(CO)_2L + \text{organosulfide} \qquad (1)$$

In this paper, we report the results of our synthetic and kinetic investigation.

Experimental Section

Preparation and Purification of Materials. The organosulfide complexes η^5-$C_5H_5Mn(CO)_2(SR_2)$ (R = Me, Et, *n*-Pr, *n*-Bu, Ph, CH_2Ph) and η^5-$C_5H_5Mn(CO)_2$(THT) were prepared photochemically from η^5-$C_5H_5Mn(CO)_3$ (a gift from Ethyl Corp.) and the appropriate ligand according to the procedure reported by Strohmeier and Guttenberger[11] for the synthesis of the SEt_2 derivative.[12] Further details of two typical syntheses are given below.

(a) η^5-$C_5H_5Mn(CO)_2(SMe_2)$. (η^5-Cyclopentadienyl)tricarbonylmanganese(I) (2.0 g, 9.8 mmol) and excess SMe_2 (10 ml) were dissolved in deaerated *n*-hexane (200 ml) in a Pyrex photochemical reactor and this mixture was irradiated with a 100-W Hanovia uv lamp for 5 hr. The resulting yellow solution was filtered into a 250-ml Schlenk tube and the filtrate was concentrated under reduced pressure (0° (0.02 Torr)) to about 50 ml. After cooling of this solution to −78°, a yellow, crystalline product was obtained. The supernatant liquid was removed with a syringe and the yellow crystals were dried under vacuum (0° (0.04 Torr)) and then recrystallized from *n*-hexane solution at −78°.

(b) η^5-$C_5H_5Mn(CO)_2[S(CH_2Ph)_2]$. A deaerated *n*-hexane solution (200 ml) of η^5-$C_5H_5Mn(CO)_3$ (2.15 g, 11 mmol) and $S(CH_2Ph)_2$ (3.01 g, 14 mmol) was irradiated as described above for 5 hr. After solvent removal (25° (0.02 Torr)), any unreacted starting materials were removed by sublimation (55° (0.01 Torr)). The dark yellow residue was recrystallized from deaerated *n*-hexane solution at room temperature to give air-stable, yellow-brown needles.