

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602**Organonitrogen Derivatives of Metal Carbonyls. 10. Cyclopentadienylmetal Dicarboxyl Ketoximate Derivatives of Molybdenum and Tungsten^{1,2}**R. B. KING and K. N. CHEN³

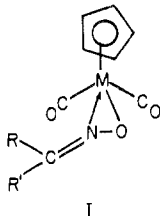
Received November 23, 1976

AIC60852H

Compounds of the type $RR'CNOM(CO)_2C_5H_5$ ($M = Mo$ and W ; $R' = CH_3$, $R = CH_3$, $CH=CH_2$, $CH=C(CH_3)_2$, and $(CH_2)_2CH=CH_2$; $R + R' = (CH_2)_5$) can be prepared by the following three methods: (1) reaction of $RR'C=NOSn(CH_3)_3$ with $C_5H_5M(CO)_3Cl$; (2) reaction of $RR'C=NOLi$ with $C_5H_5M(CO)_3Cl$; (3) reaction of $RR'C=NOH$ with $C_5H_5M(CO)_3Cl$ in the presence of pyridine. Ultraviolet irradiation is necessary for the syntheses of the tungsten compounds but not for their molybdenum analogues. The proton and carbon-13 NMR spectra of the ten $RR'CNOM(CO)_2C_5H_5$ derivatives are described and discussed.

Introduction

In 1974 the reaction of $NaMo(CO)_3C_5H_5$ with 2-bromo-2-nitrosopropane was reported⁴ to give a volatile purple solid of stoichiometry $(CH_3)_2CNOMo(CO)_2C_5H_5$, apparently containing a novel neutral three-electron donor R_2CNO ligand. The structure of this complex was unclear from the chemical and spectroscopic studies. However, subsequent x-ray crystallography studies by Doedens and Khare^{5,6} indicated that this complex had structure I ($M = Mo$; $R = R' = CH_3$) in which the nitrogen and oxygen atoms but not the carbon atom of the R_2CNO ligand was bonded to the molybdenum atom.



The preparation of $(CH_3)_2CNOMo(CO)_2C_5H_5$ from $NaMo(CO)_3C_5H_5$ and 2-bromo-2-nitrosopropane has several disadvantages. It proceeds in relatively low yield (~11%). In addition the required 2-bromo-2-nitrosopropane is an unstable, explosive reagent that is somewhat inconvenient to handle. Finally, attempts to use this method for the preparation of the analogous tungsten compounds were unsuccessful.

A close examination of structure I ($M = Mo$; $R = R' = CH_3$) suggests that the R_2CNO ligand may be regarded as derived from the corresponding ketoxime $R_2C=NOH$ by deprotonation. This suggested the possibility of developing more efficient and convenient methods for the preparation of complexes of the structure I from ketoximes. This paper describes several new methods for preparing these complexes.

Experimental Section

Microanalyses (Table I) were performed by the Atlantic Microanalytical Laboratory, Atlanta, Ga. Molecular weight determinations (Table I) were determined in benzene solution using a Mechrolab Model 301 vapor pressure osmometer located in the laboratory of Professor G. E. Boyd at the University of Georgia. Melting points (Table I) were taken in capillaries and are uncorrected.

Infrared spectra (Table I) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 257 spectrometer with grating optics. Proton NMR spectra (Table II) were recorded on a Perkin-Elmer Hitachi R-20 spectrometer or Varian T-60 spectrometer at 60 MHz. Carbon-13 NMR spectra (Table II) were recorded on a Jeolco PFT-100 spectrometer operating at 25.035 MHz with proton noise decoupling and a deuterium lock using a 6 to 10 s repetition rate. Both the proton and carbon-13 NMR spectra were run in $CDCl_3$ solutions using tetramethylsilane as an internal standard. In the carbon-13 NMR spectra chromium(III) acetylacetonate was added in ~0.15% concentration as a shiftless relaxation reagent to facilitate observation of the metal carbonyl resonances.

Dichloromethane and diethyl ether were freshly distilled over phosphorus pentoxide and calcium hydride, respectively. Pyridine

was dried over solid potassium hydroxide and then freshly distilled over barium oxide. Solvents were saturated with nitrogen before use in organometallic experiments.

Reagents. Acetone and cyclohexanone oximes were commercial samples. The unsaturated ketones were converted to their oximes by treatment with hydroxylammonium chloride in aqueous ethanol or tetrahydrofuran using solid calcium carbonate to neutralize the liberated acid. They were isolated by ether extraction, purified by vacuum distillation, and identified by their proton NMR spectra.

The cyclopentadienylmetal tricarbonyl chlorides, $C_5H_5M(CO)_3Cl$ ($M = Mo$ and W), were prepared on a 0.1 mol scale by an adaptation of the standard published method.⁸ The metal hexacarbonyls were allowed to react with sodium cyclopentadienide in boiling tetrahydrofuran for several hours to give solutions of $NaM(CO)_3C_5H_5$. These solutions were treated with glacial acetic acid at 0 °C followed by excess carbon tetrachloride. After stirring the resulting mixture for 2 h at room temperature, solvent was removed at ~25 °C (40 mm). The residue was extracted with acetone. Evaporation of the acetone extracts followed by chromatography on a large Florisil column in dichloromethane solution and crystallization from a mixture of dichloromethane and hexane gave the red crystalline $C_5H_5M(CO)_3Cl$ in up to 80% yields based on $M(CO)_6$.

O-Trimethylstannyl Oximes. (a) $(CH_3)_2C=NOSn(CH_3)_3$. The $(CH_3)_2C=NOSn(CH_3)_3$ was prepared by the procedure of Harrison and Zuckerman.⁷ It was purified by vacuum distillation (bp 56–58 °C (0.01 mm) [lit.⁹ bp 58 °C (0.01 mm)]) and identified by its proton NMR spectrum.

(b) $(CH_3)_2C=CHC(CH_3)=NOSn(CH_3)_3$. A solution of 11.3 g (100 mmol) of mesityl oxide oxime in 100 ml of diethyl ether and 100 ml of petroleum ether was treated at 0 °C with 62.6 mL of 1.5 M *n*-butyllithium in hexane (94 mmol). After warming to room temperature the resulting $(CH_3)_2C=CHC(CH_3)=NOLi$ was treated with a solution of 19.6 g (104 mmol) of trimethyltin chloride in 200 mL of diethyl ether. After boiling under reflux for 5 h solvent was removed at 25 mm. Fractional vacuum distillation gave 12.8 g (47% yield) of colorless liquid $(CH_3)_2C=CHC(CH_3)=NOSn(CH_3)_3$, bp 48–50 °C (0.15 mm). Anal. Calcd. for $C_9H_{19}NOSn$: C, 39.1; H, 6.9; N, 5.1. Found: C, 39.0; H, 6.8; N, 5.0. Proton NMR spectrum: resonances at τ 4.49 (broad singlet), 8.10 (singlet), 8.17 (singlet), 8.23 (singlet), and 9.52 (singlet) of approximate relative intensities 1:3:3:3:9, respectively.

(c) $H_2C=CH(CH_2)_2C(CH_3)=NOSn(CH_3)_3$. A solution of 5.7 g (50 mmol) of allylacetone oxime in 250 mL of diethyl ether was treated with 25 mL of 2.5 M *n*-butyllithium in hexane (62.5 mmol). The resulting lithium reagent was treated with a solution of 9.5 g (50 mmol) of trimethyltin chloride in 100 mL of diethyl ether. After boiling under reflux for 2 h, the resulting mixture was filtered. Removal of solvent at ~25 mm followed by fractional vacuum distillation gave 9.5 g (69% yield) of liquid $H_2C=CH(CH_2)_2C(CH_3)=NOSn(CH_3)_3$, bp 35–36 °C (0.2 mm). Anal. Calcd. for $C_9H_{19}NOSn$: C, 39.1; H, 6.9; N, 5.1. Found: C, 39.0; H, 7.0; N, 4.9. Proton NMR spectrum: resonances at τ 4.1 (broad multiplet), 4.9 (multiplet), 7.7 (multiplet), 8.15 (doublet, ~1.5 Hz separation), and 9.58 (singlet) of approximate relative intensities 1:2:4:3:9, respectively.

Preparation of the $R_2CNOMo(CO)_2C_5H_5$ Derivatives. (a) From the *O*-Trimethylstannyl oximes and $C_5H_5Mo(CO)_3Cl$. A mixture of 5 to 10 mmol of $C_5H_5Mo(CO)_3Cl$, an excess of the *O*-trimethylstannyl oxime (mole ratio Sn/Mo 1.1 to 1.4), and 200 to 300 mL of diethyl ether was boiled under reflux for 24 to 36 h. The resulting

Table I. Preparation and Properties of RR'CNOM(CO)₂C₅H₅ Derivatives

Compd ^a	Color	Mp, °C	Yield, % ^b	Anal.					
				% C	% H	% N	Mol wt	IR ν(CO), cm ⁻¹	
Molybdenum derivatives									
Me ₂ CNOMo(CO) ₂ Cp	Purple	100-101 dec	80 (Sn), 51 (Li), 69 (Py)	Calcd	41.5	3.8	4.8	289	1944 (s), 1840 (s)
(CH ₂) ₅ CNOMo(CO) ₂ Cp	Purple	78-79 dec	64 (Li), 67 (Py)	Found	41.3	3.9	4.9	278	1950 (s), 1835 (s)
(CH ₂ =CH)(Me)CNOMo(CO) ₂ Cp	Purple	104 dec	43 (Li), 5 (Py)	Calcd	47.4	4.6	4.3	329	1948 (s), 1849 (s)
(Me ₂ C=CH)(Me)CNOMo(CO) ₂ Cp	Purple	97-98 dec	75 (Sn), 74 (Li)	Found	47.6	4.6	4.2	334	1945 (s), 1853 (s)
CH ₂ =CH(CH ₂) ₂ C(Me)NOMo(CO) ₂ Cp	Purple	79-80 dec	61 (Sn), 70 (Li), 45 (Py)	Calcd	47.4	4.6	4.3	329	1940 (s), 1828 (s)
				Found	47.2	4.5	4.3	319	
Tungsten derivatives									
Me ₂ CNOW(CO) ₂ Cp	Purple	113 dec	41 (Sn), 45 (Li), 30 (Py)	Calcd	31.8	2.9	3.7	377	1925 (s), 1815 (s)
(CH ₂) ₅ CNOW(CO) ₂ Cp	Purple	92-93 dec	30 (Sn), 48 (Li)	Found	31.6	3.0	3.7	344	1935 (s), 1811 (s)
(CH ₂ =CH)(Me)CNOW(CO) ₂ Cp	Deep red	115 dec	25 (Li)	Calcd	37.2	3.6	3.4	417	1932 (s), 1830 (s)
(Me ₂ C=CH)(Me)CNOW(CO) ₂ Cp	Deep red	89-90 dec	36 (Li)	Found	37.2	3.7	3.3	383	1940 (s), 1841 (s)
CH ₂ =CH(CH ₂) ₂ C(Me)NOW(CO) ₂ Cp	Purple	69-70 dec	20 (Sn), 43 (Li)	Calcd	37.2	3.6	3.4	417	1924 (s), 1807 (s)
				Found	36.0	3.5	3.1	391	

^a Me = methyl, Cp = cyclopentadienyl. ^b In each case the preparative method for which the yield is given is indicated as follows: Sn = reaction of the *O*-trimethylstannyloxime with C₅H₅M(CO)₃Cl (methods a in the Experimental Section); Li = reaction of the lithium oximate with C₅H₅M(CO)₃Cl (methods b in the Experimental Section); Py = reaction of the oxime with C₅H₅M(CO)₃Cl in the presence of pyridine (methods c in the Experimental Section).

Table II. NMR Spectra of RR'CNOM(CO)₂C₅H₅ Derivatives

Compd ^a	Proton NMR ^b , τ				¹³ CNMR, δ					
	C ₅ H ₅	>C=CH	CH ₂	CH ₃	CO	R ₂ CNO	C ₅ H ₅	Olefinic C	CH ₂ ^c	CH ₃
Me ₂ CNOMo(CO) ₂ Cp	4.42 s			7.90 s, 7.97 s	229.0, 223.0	148.6	96.8			20.7 19.4
Me ₂ CNOW(CO) ₂ Cp	4.23 s			7.84 s, 7.93 s	237.0, 230.7	149.0	95.8			20.7 19.4
(CH ₂) ₅ CNOMo(CO) ₂ Cp	4.37 s		7.38 br 7.73 br 8.41 br		228.8, 223.2	153.7	96.7		31.6 (1), 30.3 (1) 26.6 (1), 25.7 (2)	
(CH ₂) ₅ CNOW(CO) ₂ Cp	3.98 s		7.20 br 7.52 br 8.29 br		235.9, 230.6	154.3	95.8		31.4, 30.1 26.5, 25.8 25.5	
(CH ₂ =CH)(Me)CNO-Mo(CO) ₂ Cp	4.23 s	3.35 dd 4.47 dd		7.73 s	229.6, 223.8	149.5	96.9	132.2 119.2		13.9
(CH ₂ =CH)(Me)CNOW(CO) ₂ Cp	3.98 s	3.27 dd ~4.26 m		7.64 s	237.2, 231.6	149.2	95.9	131.7 120.3		13.8
(Me ₂ C=CH)(Me)CNOMo(CO) ₂ Cp	4.42 s	4.15 s		7.69 s, 8.10 s 8.16 s	229.2, 223.3	149.5	96.8	141.3 120.6		28.2, 20.5 19.0
(Me ₂ C=CH)(Me)CNOW(CO) ₂ Cp	4.24 s	4.15 s		7.62 s, 8.07 s 8.11 s	236.3, 230.7	149.4	95.9	142.7 120.2		28.1, 20.6 18.8
CH ₂ =CH(CH ₂) ₂ C(Me)NOMo(CO) ₂ Cp	4.28 s	~4.95 m	~7.6 m	7.84 s	229.1, 222.6	151.1	96.8	136.4 116.0	34.4 30.7	17.7
CH ₂ =CH(CH ₂) ₂ C(Me)NOW(CO) ₂ Cp	4.03 s	4.74 br 4.98 br	~7.5 m	7.74 s	236.2, 230.1	151.4	95.9	136.4 116.1	34.2 30.6	17.7

^a Me = methyl, Cp = cyclopentadienyl. ^b s = singlet, dd = double doublet, m = ill-defined multiplet, br = broad. ^c Relative intensities are given in parentheses.

deep purple reaction mixture was filtered. Solvent was removed from the filtrate at ~25 °C (40 mm). The residue was chromatographed on a 2 × 50 cm Florisil column in dichloromethane solution. In some cases a relatively weak red-violet band of [C₅H₅Mo(CO)₃]₂ first appeared. After eluting this band with dichloromethane, the intense violet band of the product was eluted with dichloromethane. The product was isolated by evaporation of the eluate followed by a low-temperature crystallization from a mixture of dichloromethane and hexane. In the case of CH₂=CH(CH₂)₂C(CH₃)NOMo(CO)₂C₅H₅, further chromatography on Florisil in diethyl ether solution was used to obtain an analytically pure product.

(b) From the Lithium Oximate and C₅H₅Mo(CO)₃Cl. A solution of 10 to 20 mmol of the ketoxime in 200 mL of diethyl ether was treated at room temperature with a 20% excess of a 2.5 M *n*-butyllithium solution in hexane. After stirring for 30 min to 1 h at room temperature, the resulting lithium oximate was treated with 5 to 10

mmol of C₅H₅Mo(CO)₃Cl (mole ratio of lithium oximate to C₅H₅Mo(CO)₃Cl ~2:1) in 250 mL of diethyl ether. The reaction mixture was stirred for several hours (5 to 36) at room temperature and then filtered. Solvent was removed from the filtrate at ~25 °C (40 mm). The residue was chromatographed on a 2 × 50 cm Florisil column in dichloromethane solution. After eluting [C₅H₅Mo(CO)₃]₂ with dichloromethane, the major purple band of the product was eluted with dichloromethane. After evaporation of the eluates, the resulting products were purified by low-temperature crystallizations from mixtures of dichloromethane and hexane. In some experiments the products were purified further by chromatography on Florisil in diethyl ether solution and crystallizations from mixtures of diethyl ether and hexane.

(c) From the Oxime and C₅H₅Mo(CO)₃Cl in the Presence of Pyridine. A solution of 20 mmol of the ketoxime in 85 mL of pyridine was heated with 1.4 g (5 mmol) of C₅H₅Mo(CO)₃Cl to 70 °C for

6 h. Pyridine was then removed at $\sim 25^\circ\text{C}$ (0.1 mm). The residue was chromatographed on a 2×50 cm Florisil column in dichloromethane solution. After eluting the first small band of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ with dichloromethane, the major purple band of the $\text{R}_2\text{CNOMo}(\text{CO})_2\text{C}_5\text{H}_5$ derivative was eluted with dichloromethane. This product was isolated by evaporation of this eluate followed by crystallization from mixtures of dichloromethane and hexane.

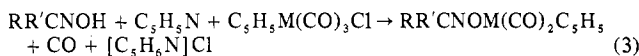
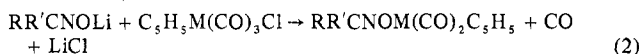
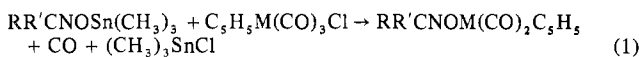
Preparation of the $\text{R}_2\text{CNOW}(\text{CO})_2\text{C}_5\text{H}_5$ Derivatives. (a) **From the *O*-Trimethylstannyloximes and $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$.** A mixture of 5 to 10 mmol of $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$, an excess of the *O*-trimethylstannyloxime (mole ratio Sn/W = 1.2 to 1.5), and 250 to 350 mL of diethyl ether was exposed for 1 h at room temperature to the ultraviolet irradiation from a 450 W mercury lamp in a water-cooled Pyrex immersion well. Solvent was removed from the filtered reaction mixture at $\sim 25^\circ\text{C}$ (40 mm). The residue was chromatographed on a 2×50 cm Florisil column in dichloromethane solution. The strong purple band of the product was eluted with dichloromethane and crystallized from a mixture of dichloromethane and hexane at low temperatures to give the $\text{R}_2\text{CNOW}(\text{CO})_2\text{C}_5\text{H}_5$ derivative. In the case of $\text{CH}_2=\text{C}(\text{H})(\text{CH}_2)_2\text{C}(\text{CH}_3)\text{NOW}(\text{CO})_2\text{C}_5\text{H}_5$ the product was purified further by chromatography on a Florisil column in diethyl ether solution.

(b) **From the Lithium Oximate and $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$.** A solution of 15 mmol of the ketoxime in 400 mL of diethyl ether was stirred with 17.5 mmol of *n*-butyllithium for 30 min at room temperature. The resulting mixture was treated with 3.7 g (10 mmol) of $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ and then irradiated for 1 h at room temperature with a 450 W ultraviolet lamp in a water-cooled Pyrex immersion well. Solvent was removed from the filtered reaction mixture at $\sim 25^\circ\text{C}$ (40 mm). The residue was chromatographed on a 2×50 cm Florisil column prepared in diethyl ether. The dark red band of the product was eluted with diethyl ether. Evaporation of the eluate at $\sim 25^\circ\text{C}$ (40 mm) gave the crude $\text{R}_2\text{NCOW}(\text{CO})_2\text{C}_5\text{H}_5$ derivative. This product was purified further by low-temperature crystallization from mixtures of dichloromethane and hexane and, if necessary, by chromatography on Florisil in diethyl ether solution.

(c) **From the Oxime and $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$ in the Presence of Pyridine.** A mixture of 2.0 g (27.4 mmol) of acetone oxime, 0.92 g (2.5 mmol) of $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$, and 170 mL of pyridine was irradiated for 48 h with a 100 W ultraviolet lamp. Pyridine was removed from the filtered reaction mixture at $\sim 25^\circ\text{C}$ (0.1 mm). The black residue was chromatographed on a 2×50 cm Florisil column in dichloromethane solution. The major purple band was eluted with dichloromethane. Evaporation of this eluate followed by crystallization from a mixture of dichloromethane and hexane gave $(\text{CH}_3)_2\text{CNOW}(\text{CO})_2\text{C}_5\text{H}_5$.

Results and Discussion

The following three methods were used to prepare the $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives:



The lithium oximates required for the second method were readily obtained by treatment of the ketoxime with *n*-butyllithium. The *O*-trimethylstannyloximes required for the first method were prepared by reactions of the lithium oximates with trimethyltin chloride using a general procedure reported by Harrison and Zuckerman.⁹ The *O*-trimethylstannyloximes are moisture-sensitive distillable liquids. The previously unreported *O*-trimethylstannyloximes derived from mesityl oxide and allylacetone were characterized by their elemental analyses (C, H, N) and proton NMR spectra.

The reactions of the *O*-trimethylstannyloximes (eq 1) and the lithium oximates (eq 2) with $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ proceed readily at or near room temperature. However, the reactions of the oximes with $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ in the presence of pyridine (eq 3) required somewhat elevated temperatures ($\sim 70^\circ\text{C}$) in order to proceed to completion at a reasonable rate. The corresponding reactions with $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$

require ultraviolet irradiation to form significant quantities of the corresponding $\text{RR}'\text{CNOW}(\text{CO})_2\text{C}_5\text{H}_5$ derivative. This appears to be another of the many examples of the greater stability of tungsten-carbon bonds relative to corresponding molybdenum-carbon bonds¹⁰ which makes more vigorous reaction conditions necessary for removal of carbonyl groups. No evidence was obtained in any of the preparations of the dicarbonyls $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ for the formation of intermediate tricarbonyls $\text{RR}'\text{CNOM}(\text{CO})_3\text{C}_5\text{H}_5$ in which the $\text{RR}'\text{CNO}$ unit is attached to the metal only through a metal-oxygen bond.

The $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives form dark red to violet solids. The molybdenum derivatives $\text{RR}'\text{CNOMo}(\text{CO})_2\text{C}_5\text{H}_5$ ($\text{R} = \text{R}' = \text{CH}_3$; $\text{R} = (\text{CH}_3)_2\text{C}=\text{CH}$, $\text{R}' = \text{CH}_3$; $\text{R} = \text{CH}_2=\text{CHCH}_2\text{CH}_2$, $\text{R}' = \text{CH}_3$) can be purified by sublimation at $70\text{--}80^\circ\text{C}$ (0.01 mm) with some decomposition. The tungsten derivatives $\text{RR}'\text{CNOW}(\text{CO})_2\text{C}_5\text{H}_5$ also sublime under vacuum, but only with extensive decomposition.

The $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives are stable to air in the solid state over a period of hours but begin to show signs of decomposition during more prolonged exposure to air. Solutions of the $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives rapidly decompose upon exposure to air and therefore must be handled in an inert atmosphere. However, a tetrahydrofuran solution of $(\text{CH}_3)_2\text{CNOMo}(\text{CO})_2\text{C}_5\text{H}_5$ is stable to carbon monoxide at 25°C (1 atm) indicating that the three-membered nitrogen-oxygen-molybdenum ring is resistant to carbon monoxide insertion.

All of the physical and spectroscopic properties of the $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives are consistent with structures of the type I analogous to the structure found by x-ray crystallography^{5,6} for $(\text{CH}_3)_2\text{CNOMo}(\text{CO})_2\text{C}_5\text{H}_5$. Molecular weights of all ten compounds in benzene solution indicate monomeric formulations. The infrared spectra of the $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives all exhibit two $\nu(\text{CO})$ frequencies like other $\text{C}_5\text{H}_5\text{M}(\text{CO})_2\text{T}$ derivatives. The nonequivalence of the two carbonyl groups in the $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives as required by structure I is indicated by the observation of two metal carbonyl resonances in the carbon-13 NMR spectra at δ 229 and 223 for the molybdenum derivatives and at δ 236 and 230 for the tungsten derivatives.

The NMR data also indicate the nonequivalence of the R and R' positions in the $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives as required by structure I. Thus in the $(\text{CH}_3)_2\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives (I: $\text{R} = \text{R}' = \text{CH}_3$; $\text{M} = \text{Mo}$ and W) both the proton and carbon-13 NMR spectra exhibit two methyl resonances. Similarly, the carbon-13 NMR spectra of the $(\text{CH}_3)_2\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives (I: $\text{M} = \text{Mo}$ and W ; $\text{R} + \text{R}' = -(\text{CH}_2)_5-$) derived from cyclohexanone indicate nonequivalence of all five CH_2 groups showing that the two sides of the cyclohexane ring in these complexes are different.

We investigated the preparation of some $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives from the unsaturated ketones, methyl vinyl ketone, mesityl oxide, and allylacetone in order to see whether these compounds can be decarbonylated to monocarbonyls of the stoichiometry $\text{RR}'\text{CNOM}(\text{CO})\text{C}_5\text{H}_5$ in which the carbon-carbon double bond of the R or R' group is bonded to the molybdenum or tungsten atom. However, attempted heating or ultraviolet irradiation of the $\text{RR}'\text{CNOM}(\text{CO})_2\text{C}_5\text{H}_5$ derivatives with unsaturated R or R' groups gave no evidence for the formation of any stable monocarbonyls. Apparently, the carbon-carbon double bonds in these unsaturated ketone derivatives are not suitably situated to bond to the metal atoms with retention of the metal-oxygen-nitrogen ring system.

We also investigated reactions of $(\text{CH}_3)_2\text{C}=\text{NOSn}(\text{CH}_3)_3$ with other transition metal complexes in attempts to convert them to $(\text{CH}_3)_2\text{CNO}$ metal derivatives. Reaction of this tin

derivative with $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Br}$ or Cl) gave only $(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$.¹¹ Reaction of $(\text{CH}_3)_2\text{C}=\text{NOSn}(\text{CH}_3)_3$ with $\text{C}_5\text{H}_5\text{Mo}(\text{NO})_2\text{Cl}$ in diethyl ether gave an unidentified yellow solid suggested by its NMR spectrum to contain $(\text{CH}_3)_3\text{Sn}$ groups but neither C_5H_5 nor $(\text{CH}_3)_2\text{C}$ groups. Reaction of $(\text{CH}_3)_2\text{C}=\text{NOSn}(\text{CH}_3)_3$ with $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ in boiling benzene gave only $(\text{CH}_3)_3\text{SnFe}(\text{CO})_2\text{C}_5\text{H}_5$.¹² No tractable products were obtained from reactions of $(\text{CH}_3)_2\text{C}=\text{NOSn}(\text{CH}_3)_3$ with $\text{Fe}_2(\text{CO})_9$ or $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$ in ethereal solvents at or near room temperature. These observations suggest that the range of transition metal systems to which $(\text{CH}_3)_2\text{C}=\text{NOSn}(\text{CH}_3)_3$ can transfer $(\text{CH}_3)_2\text{CNO}$ groups is extremely limited and that in some cases this tin reagent instead transfers $(\text{CH}_3)_3\text{Sn}$ or possibly $(\text{CH}_3)_3\text{SnO}$ units to the transition metal system.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant CHE-75-19974. We are also indebted to M and T Chemical Co. for generous gifts of trimethyltin chloride.

Registry No. $\text{Me}_2\text{CNOMo}(\text{CO})_2\text{Cp}$, 61491-36-9; $(\text{CH}_2)_5\text{CNOMo}(\text{CO})_2\text{Cp}$, 61813-21-6; $(\text{CH}_2=\text{CH})(\text{Me})\text{CNOMo}(\text{CO})_2\text{Cp}$, 61813-22-7; $(\text{Me}_2\text{C}=\text{CH})(\text{Me})\text{CNOMo}(\text{CO})_2\text{Cp}$, 61813-23-8; $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{Me})\text{NOMo}(\text{CO})_2\text{Cp}$, 61813-24-9;

$\text{Me}_2\text{CNOW}(\text{CO})_2\text{Cp}$, 61813-25-0; $(\text{CH}_2)_5\text{CNOW}(\text{CO})_2\text{Cp}$, 61813-26-1; $(\text{CH}_2=\text{CH})(\text{Me})\text{CNOW}(\text{CO})_2\text{Cp}$, 61813-27-2; $(\text{Me}_2\text{C}=\text{CH})(\text{Me})\text{CNOW}(\text{CO})_2\text{Cp}$, 61813-28-3; $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{Me})\text{NOW}(\text{CO})_2\text{Cp}$, 61813-29-4; $(\text{CH}_3)_2\text{C}=\text{NOSn}(\text{CH}_3)_3$, 25092-71-1; $(\text{CH}_3)_2\text{C}=\text{CHC}(\text{CH}_3)=\text{NOSn}(\text{CH}_3)_3$, 61812-49-5; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)=\text{NOSn}(\text{CH}_3)_3$, 61812-50-8; $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$, 12128-23-3; $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{Cl}$, 12128-24-4; mesityl oxide oxime, 2158-24-9; trimethyltin chloride, 1066-45-1; allylacetone oxime, 59239-06-4; ¹³C, 14762-74-4.

References and Notes

- (1) For part 9 of this series see: R. B. King and C. A. Harmon, *Inorg. Chem.*, **15**, 879 (1976).
- (2) Portions of this work were presented at the 28th Southeast Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., October 1976, Abstracts, paper No. 360.
- (3) Postdoctoral research associate, 1975-1977.
- (4) R. B. King and W. M. Douglas, *Inorg. Chem.*, **13**, 1339 (1974).
- (5) G. P. Khare and R. J. Doedens, paper presented at the 170th National Meeting of the American Chemical Society, Chicago, Ill., August 1975, Abstracts, paper No. INOR 67.
- (6) G. P. Khare and R. J. Doedens, submitted for publication.
- (7) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Am. Chem. Soc.*, **94**, 2550 (1972).
- (8) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).
- (9) P. G. Harrison and J. J. Zuckerman, *Inorg. Chem.*, **9**, 175 (1970).
- (10) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).
- (11) H. C. Clark and J. H. Tsai, *Inorg. Chem.*, **5**, 1407 (1966).
- (12) R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 1510 (1968).

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Electrochemical Studies on $[\text{Mn}(\text{CNR})_6]^+$ Complexes

P. M. TREICHEL* and H. J. MUEH

Received September 20, 1976

AIC607074

The $E_{1/2}$ values for the processes $[\text{MnL}_6]^+ \rightleftharpoons [\text{MnL}_6]^{2+} + e^-$ and $[\text{MnL}_6]^{2+} \rightleftharpoons [\text{MnL}_6]^{3+} + e^-$ ($\text{L} =$ eleven aryl and four alkyl isocyanides) in dichloromethane were determined by cyclic voltammetry. The alkyl isocyanide complexes are easier to oxidize than the aryl isocyanide complexes in keeping with the better donor strength of these ligands. For the complexes of the aryl isocyanides there is substantial variation of $E_{1/2}$ values. A good correlation between $E_{1/2}$ values for complexes of meta- and para-substituted phenyl isocyanides and Hammett σ values is obtained.

Manganese(I) complexes of organic isocyanides $[\text{Mn}(\text{CNR})_6]^+$ are known¹ to react with oxidizing agents such as HNO_3 giving the manganese(II) species $[\text{Mn}(\text{CNR})_6]^{2+}$. The reverse reaction is effected by reducing agents including the free ligand itself; hence the synthesis of $[\text{Mn}(\text{CNR})_6]^+$ complexes from reactions of an isocyanide and a manganese(II) salt is often encountered. Recently, electrochemical studies have been reported for $[\text{Mn}(\text{CNR})_6]^+$ complexes. By using both dichloromethane² and acetonitrile,³ $E_{1/2}$ values were obtained by cyclic voltammetry for two one-electron oxidation processes: $[\text{Mn}(\text{CNR})_6]^+ \rightleftharpoons [\text{Mn}(\text{CNR})_6]^{2+} + e^-$; $[\text{Mn}(\text{CNR})_6]^{2+} \rightleftharpoons [\text{Mn}(\text{CNR})_6]^{3+} + e^-$. The first oxidation is chemically reversible, with anodic and cathodic currents being equal. The second process is not, a consequence of decomposition of the unstable manganese(III) species.

In the earlier work^{2,3} differences in the ease of oxidation of complexes of different ligands were noted. The $E_{1/2}$ value for the complex $[\text{Mn}(\text{CNCH}_3)_6]\text{PF}_6$ was found to be 0.38 V vs. SCE (in acetonitrile). Complexes of several aryl isocyanides, $[\text{Mn}(\text{CNR})_6]\text{PF}_6$ ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$, $p\text{-ClC}_6\text{H}_4$) had $E_{1/2}$ values between 0.68 and 0.95 V vs. SCE, indicating that oxidation is more difficult. A simple interpretation was accorded this observation, based on the relative donor abilities of alkyl and aryl isocyanides established some time ago by infrared studies.⁴ In complexes of aryl isocyanides there is more negative charge withdrawal from the metal by π bonding due to extended conjugation into the aryl ring. The

extent of negative charge buildup on the metal center influences the energies of the HOMO (primarily metal d_{xy} , d_{xz} , d_{yz}) in the complex. In turn there is a direct correlation between HOMO energy and $E_{1/2}$ value.⁵

Variation with R of $E_{1/2}$ values for isoelectronic $\text{Cr}(\text{CNR})_6$ complexes ($\text{R} =$ aryl) was also noted in the earlier work.² Lack of alkyl isocyanide complexes of chromium(0) did not allow their inclusion in that study.

Work by McCleverty and co-workers⁶ has further defined differences between isocyanide ligands in a series of complexes $\text{M}(\text{CO})_{6-x}(\text{CNR})_x$ ($x = 1-3$; $\text{M} = \text{Cr}, \text{Mo}$; $\text{R} = \text{CH}_3$, CH_2CH_3 , $\text{CH}(\text{CH}_3)_2$, C_6H_{11} , $\text{C}(\text{CH}_3)_3$, $p\text{-CH}_3\text{C}_6\text{H}_4$, C_6H_5 , $p\text{-ClC}_6\text{H}_4$); infrared, ultraviolet, NMR, and mass spectroscopic data and electrochemical measurements were used to assess the effect of varying R and x in these systems. The electrochemical measurements showed that for the alkyl isocyanide complexes there are no significant differences in $E_{1/2}$ values, suggesting that alkyl isocyanide ligands are electronically alike. Among the aryl isocyanide complexes, which had higher $E_{1/2}$ values, there was a marked difference in $E_{1/2}$ values between species of the same stoichiometry; this was attributed to the inductive and/or mesomeric effects of aryl ring substituent group.

This work was carried out to extend consideration over a wider range of isocyanides, encompassing both the more commonly used alkyl isocyanides and also a wider range of substituted phenyl isocyanides. A linear free energy correlation