Table III. Nickel Metal Catalyzed Hydrogenation of 2-Butyne

metal[a]	t, °C	% hydrogenation	product ratios[b,c]			
			I	II	III	IV
A	20	9.7	16	46	31	1.5
A	20	12.6	12	65	37	1.8
A	20	14.8	13	45	29	1.6
A	20	32.8	11	53	26	2.1
A	20	33.6	9	49	28	1.6
B	20	4.2	13	63	42	1.9
B	20	25.0	15	65	42	1.6
C	20	1.25	18	37	18	2.0
C	20	1.47	21	32	20	1.6
C	80	2.2	27	30	28	1.0
C	80	5.5	30	18	27	1.1

[a] Metal source: A, nickel from $Ni(COD)_2$; B, nickel from $Ni(COD)_2$ pretreated with CH_3NC; C, nickel from $Ni(NO_3)_2 \cdot 6H_2O$. [b] Uncertainties were estimated to be about 10% for these ratios. [c] Molar ratios of I, *cis*-2-butene to butane; II *cis*-2-butene to *trans*-2-butene; III, *cis*-2-butene to 1-butene; and IV, 1-butene to *trans*-2-butene.

°C for elution of the methylcyclopentane. The column was purged of 2-butyne at 100 °C.

Chromatographic separations of the gases from the competitive hydrogenation of 2-butyne and *cis*-2-pentene were effected with a 12 ft × 1/8 in. stainless-steel column of 5% dimethyl sulfolane on Chromosorb P connected in series to a 10 ft × 1/8 in. column of octane/Porasil C operating at 50 °C with a helium flow of 20 mL/min.

Peak areas were measured by the cut-and-weigh method and converted into mole percentage conversions by using the methylcyclopentane as an internal standard and establishing relative response factors for butane, *cis*-2-butene, and methylcyclopentane. The response factors of 1-butene and *trans*-2-butene were assumed to be the same as the response factor of *cis*-2-butene. Results were corrected for residual contaminants in the 2-butyne and methylcyclopentane. The results were very similar to those obtained for 2-butyne above; only small to trace amounts of pentane were detected.

Acknowledgment. Support of this research by the National Science Foundation and by the Foundation and the Academy of Sciences of the USSR in the Joint U.S.–U.S.S.R. Program in Chemical Catalysis (A.K.) is gratefully acknowledged.

Registry No. $Ni_4[C_6H_{11}NC]_7$, 73377-51-2; $Ni_4[CNC(CH_3)_3]_4(C_6H_5C_2C_6H_5)_3$, 60818-82-8; $Ni_4[CNC_6H_{11}]_4(C_6H_5C_2C_6H_5)_3$, 73296-55-6; $Ni_4[CNC(CH_3)_3]_4(p\text{-}CH_3C_6H_4C{\equiv}CC_6H_4CH_3\text{-}p)_3$, 73296-56-7; $Ni_4[CNC(CH_3)_3]_6(CNCH_3)$, 73377-49-8; $Ni_4[CNC(CH_3)_3]_6P(OCH_3)_3$, 73377-50-1; $Ni_4[CNC(CH_3)_3]_6$, 73377-48-7; $Ni(COD)_2$, 1295-35-8; $Ni_4[CNC(CH_3)_3]_7$, 60748-55-2; $Ni[CNC(CH_3)_3]_4$, 19068-11-2; 2-butyne, 503-17-3; 3-hexyne, 928-49-4; 1,3-hexadiene, 592-48-3; 2,4-hexadiene, 592-46-1; Ni, 7440-02-0.

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Organometallic Nitrosyl Chemistry. 12.[1] New Cyclopentadienylnitrosyl Complexes of Tungsten

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Treatment of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ with an equimolar amount of iodine in CH_2Cl_2 affords $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ in virtually quantitative yields. The dimer reacts with various Lewis bases, L (L = $P(OPh)_3$, PPh_3, $SbPh_3$, or CO), to give monomeric $(\eta^5\text{-}C_5H_5)W(NO)(I)_2L$ complexes; but the species with L = CO slowly decarbonylates in solution under ambient conditions and reverts to the original reactants. The L-containing compounds are also obtainable by the stoichiometric reaction of $(\eta^5\text{-}C_5H_5)W(CO)(NO)L$ with I_2. Reactions of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ in THF with $Tl(C_5H_5)$ or $Na(C_5H_5)$ in appropriate stoichiometries produce the novel complexes $(C_5H_5)_2W(NO)I$ and $(C_5H_5)_3W(NO)$, both of which are stereochemically nonrigid in solution at room temperature. Nitric oxide converts the dimer to the well-known $(\eta^5\text{-}C_5H_5)W(NO)_2I$ as the only nitrosyl product. The physical properties of all new complexes prepared are presented.

Introduction

We recently described the preparation and characteristic chemistry of $(\eta^5\text{-}C_5H_5)W(NO)_2H$.[2] Unlike related hydridocarbonyls which are Lowry–Brønsted acids in polar solvents, the hydridotungsten complex functions as a source of H^- in these solvents. This hydridic character is somewhat surprising since it is generally believed that the presence of electron-withdrawing ligands on the metal center enhances the acidic character of M–H bonds. In order to evaluate more fully the function of the NO groups, we decided to prepare other hydridonitrosyl complexes of tungsten and to investigate their physical and chemical properties. Unfortunately, very few convenient synthetic precursors of such complexes have been reported. However, considerably more work has been done with molybdenum systems; and, in particular, it has been shown that $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ can be converted to a variety of other cyclopentadienylmolybdenum nitrosyl derivatives.[3] Since an efficient preparation of the tungsten congener, $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$, has now been developed,[4] it seemed likely that we could utilize it as a general starting material in an analogous manner. In this paper we report conversions of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ to new cyclopentadienylnitrosyl complexes of tungsten, some of which are logical precursors of the ultimately desired hydridonitrosyl species.

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was confirmed by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures, distilled, and deaerated just prior to use. All manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared (IR) spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton magnetic resonance spectra were obtained on a Varian Associates T60 spectrometer or, with the assistance of Dr. S. O. Chan and Mrs. M. M. Tracey, on a Bruker WP-80 spec-

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[1] Part 11: Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B*, in press.

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Table I. Physical Properties of $(\eta^5\text{-}C_5H_5)W(NO)(I)_2L$ [L = $P(OPh)_3$, PPh_3, $SbPh_3$, or CO] Complexes

L	mp, °C (under N_2)	anal., %						IR	^{1}H NMR,[b] δ	
		C		H		N		ν(NO), cm^{-1}	C_5H_5	other
		calcd	found	calcd	found	calcd	found			
$P(OPh)_3$	140 dec	32.77	32.73	2.40	2.33	1.66	1.58	1651[a]	5.90 (5 H, d, $J_{^1H-^{31}P}$ = 3.0 Hz)	7.19 (15 H, b)
PPh_3	158 dec	34.74	34.79	2.54	2.48	1.76	1.79	1633[a]	5.91 (5 H, d, $J_{^1H-^{31}P}$ = 1.2 Hz)	7.54 (15 H, b)
$SbPh_3$	141 dec	31.16	31.09	1.58	1.60	2.26	2.26	1640[a]	6.00 (5 H, s)	7.50 (15 H, b)
CO								1694[c]		

[a] Nujol mull. [b] $CDCl_3$ solution. [c] CH_2Cl_2 solution; ν(CO) 2040 cm^{-1}.

trometer equipped with a Bruker B-VT-1000 variable-temperature probe. Tetramethylsilane was employed as an internal standard. The ^{13}C NMR spectra were recorded on a Varian Associates CFT-20 spectrometer with reference to the solvent used ($CDCl_3$), but all ^{13}C chemical shifts are reported in ppm downfield from Me_4Si [$\delta(Me_4Si) = \delta(CDCl_3\text{ internal}) + 76.9$]. Mass spectra were recorded at 70 eV on Atlas CH4B or Associated Electrical Industries MS902 spectrometers by using the direct-insertion method with the assistance of Dr. G. K. Eigendorf and Mr. J. W. Nip. Elemental analyses were performed by Mr. P. Borda of this department.

Reaction of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ with I_2. To a stirred, orange solution of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)^4$ (5.00 g, 14.9 mmol) in CH_2Cl_2 (100 mL) at room temperature was added solid iodine (3.79 g, 14.9 mmol). Vigorous gas evolution occurred immediately, and the reaction mixture became red-violet. The mixture was stirred for 0.5 h to ensure complete reaction and was then taken to dryness in vacuo. The remaining residue was recrystallized from CH_2Cl_2–hexanes to obtain purple-brown microcrystals (7.52 g, 94% yield) of analytically pure $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$, mp (under N_2) 120 °C dec.

Anal. Calcd for $C_{10}H_{10}N_2O_2I_4W_2$: C, 11.27; H, 0.95; N, 2.63. Found: C, 11.26; H, 0.88; N, 2.53. IR (CH_2Cl_2): ν(NO) 1652 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.15 (s).

Reactions of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ with Lewis Bases (L). These experiments were performed similarly, and the reaction with L = $P(OPh)_3$ is described as a representative example.

A stoichiometric amount of neat triphenyl phosphite (0.26 mL, 0.31 g, 1.0 mmol) was added to a stirred solution of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ (0.53 g, 0.50 mmol) in CH_2Cl_2 (50 mL) at ambient temperature. The color of the solution immediately changed to dark red. Hexanes (50 mL) were added, and the reaction mixture was slowly concentrated under reduced pressure to induce the precipitation of brown crystals of $(\eta^5\text{-}C_5H_5)W(NO)[P(OPh)_3]I_2$ (0.68 g, 81% yield).

The other, similarly colored complexes were isolated in yields of 78% (L = PPh_3) and 80% (L = $SbPh_3$). The physical properties of these compounds are summarized in Table I.

Reaction of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ with CO. Carbon monoxide was gently bubbled for 0.5 h through a CH_2Cl_2 solution (25 mL) containing 0.53 g (0.50 mmol) of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ at room temperature. At the end of this time, a solution infrared spectrum indicated ca. 90% conversion to $(\eta^5\text{-}C_5H_5)W(CO)(NO)I_2$ (ν(CO) 2040, ν(NO) 1694 cm^{-1}). However, continued treatment of the reaction mixture with CO did not consume any more of the dimeric reactant. The final mixture was taken to dryness in vacuo to recover $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ quantitatively.

Reaction of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ with NO. Prepurified nitric oxide was gently bubbled for 15 min through a solution of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ (0.53 g, 0.50 mmol) in CH_2Cl_2 (25 mL) at ambient temperature. Copious quantities of a brown precipitate formed during the course of the reaction. An infrared spectrum of the final supernatant liquid revealed that all the initial organometallic reactant had been consumed. The reaction mixture was then concentrated under reduced pressure to ca. 5 mL, and the resulting suspension was transferred to the top of a short (3 × 5 cm) Florisil column. Elution of the column with CH_2Cl_2 resulted in the development of a single, olive-green band which was collected. The eluate was taken to dryness in vacuo to obtain 0.12 g (28% yield based on W) of $(\eta^5\text{-}C_5H_5)W(NO)_2I$, which could be readily identified by its characteristic physical properties.[5] IR (CH_2Cl_2): ν(NO) 1657, 1740 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.10 (s). Mass spectrum: most intense parent ion *m/z* 436.

Table II. Mass Spectral Data for $(\eta^5\text{-}C_5H_5)W(CO)(NO)[P(OPh)_3]$[a]

m/z	rel abund	assign[b,c]
617	100	$(C_5H_5)W(CO)(NO)[P(OPh)_3]^+$
589	45	$(C_5H_5)W(NO)[P(OPh)_3]^+$
524	10	$(C_5H_5)W(CO)(NO)[P(OPh)_2]^+$
496	22	$(C_5H_5)W(NO)[P(OPh)_2]^+$
310	11	$P(OPh)_3^+$
217	44	$P(OPh)_2^+$

[a] Probe temperature ~185 °C. [b] The assignments involve the most abundant naturally occurring isotopes in each fragment. [c] The principal ions containing W are given. Ions arising from further fragmentation of $P(OPh)_3$ are also observed in the spectrum.

Reaction of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ with $P(OPh)_3$. A toluene solution (40 mL) containing $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ (1.43 g, 4.30 mmol) and triphenyl phosphite (1.13 mL, 1.33 g, 4.30 mmol) was stirred at reflux for 16 h. The reaction mixture was then permitted to cool to room temperature and was filtered through a short (3 × 5 cm) column of alumina (Woelm neutral, activity grade 1) supported on a medium porosity frit. The filtrate was taken to dryness under reduced pressure to obtain an orange solid. A small amount of unreacted $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ was removed from this solid by sublimation at 60 °C (5×10^{-3} mm) onto a water-cooled probe. The sublimation residue was recrystallized from CH_2Cl_2–hexanes to obtain 1.32 g (49% yield) of $(\eta^5\text{-}C_5H_5)W(CO)(NO)[P(OPh)_3]$ as a yellow-orange solid, mp (under N_2) 138 °C dec.

Anal. Calcd for $C_{24}H_{20}NO_5PW$: C, 46.70; H, 3.27; N, 2.27. Found: C, 46.99; H, 3.25; N, 2.29. IR (CH_2Cl_2): ν(CO) 1938, ν(NO) 1625 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.80 (s, 5 H), 7.15 (b, 15 H). Its mass spectrum is summarized in Table II.

Reaction of $(\eta^5\text{-}C_5H_5)W(CO)(NO)[P(OPh)_3]$ with I_2. To a stirred, orange solution of $(\eta^5\text{-}C_5H_5)W(CO)(NO)[P(OPh)_3]$ (0.62 g, 1.0 mmol) in CH_2Cl_2 (35 mL) was added solid iodine (0.25 g, 1.0 mmol). The reaction mixture immediately began to turn dark red, but it was stirred for 0.5 h at ambient temperature to ensure complete reaction. Addition of hexanes (35 mL) and slow concentration of the mixture under reduced pressure resulted in the crystallization of 0.67 g (79% yield) of analytically pure $(\eta^5\text{-}C_5H_5)W(NO)[P(OPh)_3]I_2$ (vide supra).

Reaction of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ with $Tl(C_5H_5)$. To a green solution of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ (0.42 g, 0.39 mmol) in THF (40 mL) was added solid $Tl(C_5H_5)$ (0.21 g, 0.78 mmol). The reaction mixture was stirred at room temperature for 1 h whereupon it gradually darkened to a deep red color, and a yellow precipitate formed. The mixture was then taken to dryness in vacuo, and the residue was extracted with CH_2Cl_2 (3 × 15 mL). The extracts were filtered through a Celite column (3 × 3 cm) supported on a medium-porosity frit, and the filtrate was concentrated under reduced pressure to ca. 5 mL. The addition of hexanes (60 mL) to this solution induced the precipitation of golden-brown, microcrystalline $(C_5H_5)_2W(NO)I$ (0.22 g, 60% yield), mp (under N_2) 127 °C dec.

Anal. Calcd for $C_{10}H_{10}NOIW$: C, 25.48; H, 2.12; N, 2.97; I, 26.96. Found: C, 25.13; H, 2.01; N, 3.13; I, 27.00. IR (CH_2Cl_2): ν(NO) 1622 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.16 (s). ^{13}C NMR ($CDCl_3$): δ 109.5 (s).

When $Na(C_5H_5)$ (0.78 mmol in 10 mL of THF) was employed instead of $Tl(C_5H_5)$ in the above reaction, the final organometallic product was isolated in comparable yield.

Reaction of $(C_5H_5)_2W(NO)I$ with $Tl(C_5H_5)$. Solid $Tl(C_5H_5)$ (0.27 g, 1.0 mmol) was added to a brown solution of $(C_5H_5)_2W(NO)I$ (0.47 g, 1.0 mmol) in THF (30 mL) at ambient temperature. The mixture

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(5) Stewart, R. P., Jr.; Moore, G. T. *Inorg. Chem.* **1975**, *14*, 2699–703.

was stirred for 1 h, during which time a yellow solid precipitated. The final reaction mixture was filtered through a column of Celite (3 × 5 cm) supported on a frit, and the deep red filtrate was taken to dryness in vacuo. The resulting residue was dissolved in benzene (8 mL), and the solution was transferred onto a short (3 × 5 cm) column of silica. Initial elution of the column with benzene developed a pale yellow band which was collected. Removal of solvent from this eluate under reduced pressure afforded a small amount of an air-sensitive, yellow solid whose identity remains to be ascertained. Further elution of the column with benzene–THF (3:1) resulted in the development of a single red band which was collected and taken to dryness in vacuo. Recrystallization of the tarry, red residue from CH_2Cl_2–hexanes produced brick-red microcrystals of $(C_5H_5)_3W(NO)$ (0.10 g, 24% yield), mp (in air) 85 °C dec.

Anal. Calcd for $C_{15}H_{15}NOW$: C, 44.01; H, 3.67; N, 3.42. Found: C, 43.71; H, 3.55; N, 3.45. IR (CH_2Cl_2): ν(NO) 1588 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.73 (s). ^{13}C NMR ($CDCl_3$): δ 110.6 (s).

Thallium and its compounds are extremely toxic and must be handled with care. $Na(C_5H_5)$ could be used in place of $Tl(C_5H_5)$ in this reaction without any detrimental effects.

Results and Discussion

The derivative chemistry of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ generally resembles that displayed by its molybdenum congener, but there are some notable differences. At room temperature in dichloromethane, the tungsten complex reacts rapidly and virtually quantitatively with an equimolar amount of iodine. Monitoring of the reaction by IR spectroscopy shows a disappearance of the characteristic absorptions due to the organometallic reactant (ν(CO) 2010, 1925 cm^{-1}; ν(NO) 1655 cm^{-1}) and the appearance of new absorptions in the carbonyl and nitrosyl regions (ν(CO) 2040 cm^{-1}; ν(NO) 1694 cm^{-1}). These observations are consistent with the replacement of one carbonyl ligand in the starting complex by two iodo ligands, i.e.

$$(\eta^5\text{-}C_5H_5)W(CO)_2(NO) + I_2 \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(CO)(NO)I_2 + CO \quad (1)$$

The carbonyldiiodonitrosyl complex thus formed is, however, unisolable. It decarbonylates in solution slowly under ambient conditions (but rapidly under reduced pressure) and oligomerizes to the final isolable complex, $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$.

$$2(\eta^5\text{-}C_5H_5)W(CO)(NO)I_2 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 + 2CO \quad (2)$$

The thermal instability of the product formed in reaction 1 is not unusual; the lability of carbonyl ligands appears to be an intrinsic property of transition-metal carbonyl nitrosyl halides.[6,7] During the analogous reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ with halogens to form $[(\eta^5\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Cl,[8] Br,[8] or I[9]), no such labile carbonyl species have been detected although they have been invoked as reaction intermediates.[9]

Table III. Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$[a]

m/z	rel abund	assignt[b,c]
812	2	$(C_5H_5)_2W_2(NO)_2I_2^+$
782	2	$(C_5H_5)_2W_2(NO)I_2^+$
533	98	$(C_5H_5)W(NO)I_2^+$
503	100	$(C_5H_5)WI_2^+$
438	10	WI_2^+
406	15	$(C_5H_5)W(NO)I^+$
376	79	$(C_5H_5)WI^+$
350	34	$(C_3H_3)WI^+$
311	3	WI^+
279	3	$(C_5H_5)W(NO)^+$
249	25	$(C_5H_5)W^+$
184	12	W^+

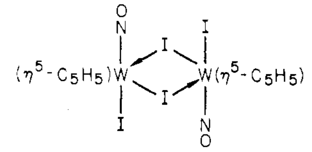
[a] Probe temperature ~135 °C. [b] See footnote *b* to Table II. [c] Only principal ions containing W are given.

Table IV. Mass Spectral Data for $(\eta^5\text{-}C_5H_5)W(NO)(I)_2[P(OPh)_3]$[a]

m/z	rel abund	assignt[b]
533	21	$(C_5H_5)W(NO)I_2^+$
503	19	$(C_5H_5)WI_2^+$
376	17	$(C_5H_5)WI^+$
350	10	$(C_3H_3)WI^+$
310	37	$P(OPh)_3^+$
217	100	$P(OPh)_2^+$

[a] Probe temperature ~145 °C. [b] See footnotes *b* and *c* to Table II.

Bis[$(\eta^5$-cyclopentadienyl)diiodonitrosyltungsten] is a purple-brown, diamagnetic solid which is freely soluble in THF and acetone, less soluble in benzene, CH_2Cl_2, and $CHCl_3$, and completely insoluble in hexanes. Its solutions are air sensitive, but the solid itself can be handled in air for short periods of time without the occurrence of noticeable decomposition. An IR spectrum of a CH_2Cl_2 solution of the complex exhibits a strong absorption at 1652 cm^{-1} attributable to a terminal nitrosyl ligand. The compound is best formulated as the iodo-bridged dimer



since a monomeric formulation would leave the tungsten atom with two electrons less than the favored 18-electron configuration. The dimeric nature of the complex is also suggested by its mass spectrum (Table III). Although a peak corresponding to the parent ion (m/z 1066) is not detectable, peaks due to ions containing two tungsten atoms (i.e., $(C_5H_5)_2W_2(NO)_2I_2^+$ and $(C_5H_5)_2W_2(NO)I_2^+$) are clearly identifiable by the correct W_2 isotope pattern. Nevertheless, the considerably greater relative abundances of the ions $(C_5H_5)W(NO)I_2^+$ and $(C_5H_5)WI_2^+$ indicate that the dimer is readily cleaved on vaporization or electron impact.[10]

The facile cleavage of the iodine bridges in $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ is also shown by its ready reactivity with a variety of Lewis bases, L, to form the monomeric complexes $(\eta^5\text{-}C_5H_5)W(NO)(I)_2L$ (eq 3). The products of reaction 3 are

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 + 2L \xrightarrow{CH_2Cl_2} 2(\eta^5\text{-}C_5H_5)W(NO)(I)_2L \quad (3)$$

$$L = PPh_3,\ P(OPh)_3,\ \text{or}\ SbPh_3$$

orange-brown, air-stable solids which are sparingly soluble in $CHCl_3$ and CH_2Cl_2 but even less soluble in benzene, THF, or acetone. Their IR spectra (Table I) display single nitrosyl-stretching absorptions in the range 1633–1659 cm^{-1} which are 30–60 cm^{-1} lower than that exhibited by $(\eta^5\text{-}C_5H_5)W(NO)(I)_2(CO)$. The decrease in ν(NO) as L varies in the order CO > $P(OPh)_3$ > PPh_3 is consistent with the documented

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(6) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1977**, *16*, 3173–8.

(7) Kolthammer, B. W. S.; Legzdins, P. *Inorg. Chem.* **1979**, *18*, 889–91.

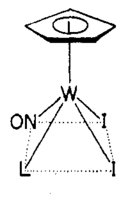
(8) McCleverty, J. A.; Seddon, D. *J. Chem. Soc., Dalton Trans.* **1972**, 2526–30.

(9) King, R. B. *Inorg. Chem.* **1967**, *6*, 30–4.

(10) Similar features have been observed in the low-resolution mass spectrum of $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$: King, R. B. *Org. Mass. Spectrom.* **1969**, *2*, 401–12.

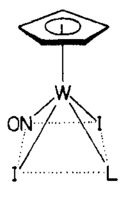
electron-donating and -accepting properties of these ligands.[11] The mass spectrum of $(\eta^5\text{-}C_5H_5)W(NO)(I)_2[P(OPh)_3]$ (Table IV) does not contain a parent-ion peak but does display a fragmentation pattern attributable to $(C_5H_5)W(NO)I_2^+$ and $P(OPh)_3^+$. Unfortunately, the analogous PPh_3 and $SbPh_3$ complexes are not sufficiently volatile to be analyzed in a similar manner by conventional electron-impact techniques.

If a "four-legged piano stool" geometry is assumed for the molecular structures of the $(\eta^5\text{-}C_5H_5)W(NO)(I)_2L$ complexes,[12] there exists the possibility of cis–trans geometrical isomerism for these species as illustrated in structures I and II.



cis

I



trans

II

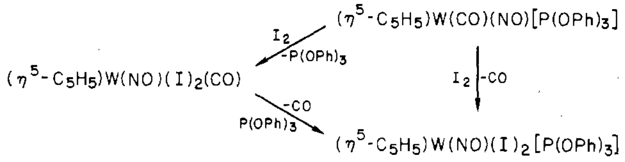
However, their spectral properties (Table I) suggest that only one isomer of each complex is formed in reaction 3. Thus, their ^1H NMR spectra consist of a single broad resonance due to the phenyl protons and a single sharp resonance assignable to the cyclopentadienyl protons, with coupling between the latter and the ^{31}P nucleus being observable when L = PPh_3 or $P(OPh)_3$. Furthermore, the proton-decoupled ^{13}C NMR spectrum of $(\eta^5\text{-}C_5H_5)W(NO)(I)_2[P(OPh)_3]$ in $CDCl_3$ displays a single C_5H_5 resonance at δ 101.36[13] and $P(OPh)_3$ signals [δ 121.03 (d, $J_{^{13}C-^{31}P} = 3.3$ Hz, C_2), δ 126.01 (s, C_4), δ 129.79 (s, C_3), δ 150.79 (d, $J_{^{13}C-^{31}P} = 12.3$ Hz, C_1)][13] which are also consistent with the presence of just one isomer. These properties contrast directly with those exhibited by $(\eta^5\text{-}C_5H_5)Mo(NO)(I)_2[P(OPh)_3]$ for which two isomers are detectable in solution by ^1H NMR spectroscopy.[9]

The $(\eta^5\text{-}C_5H_5)W(NO)(I)_2L$ complexes are also obtainable by another synthetic route originating with $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$. For instance, the L = $P(OPh)_3$ compound can be prepared in good yields by the consecutive reactions (4) and (5). The first of these (reaction 4) parallels the method

$$(\eta^5\text{-}C_5H_5)W(CO)_2(NO) + P(OPh)_3 \xrightarrow[\text{reflux}]{\text{toluene}} (\eta^5\text{-}C_5H_5)W(CO)(NO)[P(OPh)_3] + CO \quad (4)$$

$$(\eta^5\text{-}C_5H_5)W(CO)(NO)[P(OPh)_3] + I_2 \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)(I)_2[P(OPh)_3] + CO \quad (5)$$

described previously for the preparation of $(\eta^5\text{-}C_5H_5)W(CO)(NO)(PPh_3)$.[14] The second (reaction 5) can, in principle, proceed by either of the two routes depicted in (6). The iodine



(6)

could simply displace the CO ligand from the initial reactant to yield the final product directly. Alternatively, it could first displace the $P(OPh)_3$ group to form the labile carbonyl complex which, in turn, would lose the CO group and acquire the liberated $P(OPh)_3$, perhaps via $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$. However, no intermediates are detectable when reaction 5 is monitored by IR spectroscopy, thereby indicating that they are short-lived if they are indeed formed.

The iodine bridges of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ can also be cleaved by carbon monoxide, i.e.

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 + 2CO \xrightarrow{CH_2Cl_2} 2(\eta^5\text{-}C_5H_5)W(NO)(I)_2(CO) \quad (7)$$

This transformation is simply the reverse of reaction 2; and, as expected, the nonisolable product exhibits the same spectral properties as the product of reaction 1. Solution IR spectroscopy indicates that the maximum conversion in reaction 7 is ca. 90%. However, it is possible that the reaction does go to completion, but partial decarbonylation of the product occurs when a sample of the reaction mixture is removed from the CO atmosphere and is placed in the IR cell. Attempts to introduce alkenes or alkynes into the tungsten coordination sphere by reactions analogous to (3) and (7) have as yet been unsuccessful. For example, treatment of a CH_2Cl_2 solution of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ with diphenylethyne under ambient conditions results in no detectable consumption of the dimer. Nitric oxide, on the other hand, rapidly converts the dimer to the well-known $(\eta^5\text{-}C_5H_5)W(NO)_2I$ complex as the only nitrosyl-containing product (see eq 8).

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 \xrightarrow[CH_2Cl_2]{NO} (\eta^5\text{-}C_5H_5)W(NO)_2I \quad (8)$$

Reactions of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ in THF with thallium or sodium cyclopentadienide in appropriate stoichiometries afford the novel complexes $(C_5H_5)_2W(NO)I$ and $(C_5H_5)_3W(NO)$ (eq 9 and 10). Analogous conversions involving

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 + 2M(C_5H_5) \xrightarrow{THF} 2(C_5H_5)_2W(NO)I + 2MI \quad (9)$$

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 + 4M(C_5H_5) \xrightarrow{THF} 2(C_5H_5)_3W(NO) + 4MI \quad (10)$$

$$M = Tl \text{ or } Na$$

$[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$ can only be effected with $Tl(C_5H_5)$ since $Na(C_5H_5)$ is too reactive and fails to form any cyclopentadienyl derivatives.[15] IR monitoring of reactions 9 and 10 indicates that the iodide ligands of the organometallic reactant (which may be present as the solvated monomer $(\eta^5\text{-}C_5H_5)W(NO)I_2(THF)$, by analogy with reaction 7) are replaced sequentially; and indeed the transformations

$$(C_5H_5)_2W(NO)I + M(C_5H_5) \xrightarrow{THF} (C_5H_5)_3W(NO) + MI \quad (11)$$

$$M = Tl \text{ or } Na$$

can be performed independently.

Golden-brown $(C_5H_5)_2W(NO)I$ and brick red $(C_5H_5)_3W(NO)$ are diamagnetic, air-stable solids which are freely soluble in common organic solvents (except paraffin hydrocarbons) to give air-sensitive solutions. Their low-resolution mass spectra (Table V) confirm their monomeric natures and display fragmentation patterns corresponding to the stepwise loss of ligands from the metal center. Solutions of both complexes in CH_2Cl_2 exhibit single, strong absorptions in their IR spectra in the range normally associated with linearly bonded, terminal

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[11] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953–6.

[12] This is a reasonable assumption since it has recently been shown that the geometry of $(t\text{-}C_4H_9NC)_3W(CO)_2I_2$ closely approximates that of a 4:3 square-base, trigonal-cap "piano stool": Dreyer, E. B.; Lam, C. T.; Lippard, S. J. *Inorg. Chem.* **1979**, *18*, 1904–8.

[13] The assignments of these signals are based on the expected ^{13}C chemical shifts of the ligands: Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135–213.

[14] Brunner, H. *J. Organomet. Chem.* **1969**, *16*, 119–24.

[15] King, R. B. *Inorg. Chem.* **1968**, *7*, 90–4.

Table V. Mass Spectral Data for $(C_5H_5)_2W(NO)X$ (X = I or C_5H_5) Complexes

X = I[a]			X = C_5H_5[b]	
m/z	rel abund	assignt[c]	rel abund	*m/z*
471	21	$(C_5H_5)_2W(NO)X^+$	26	409
441	100	$(C_5H_5)_2WX^+$	14	379
344	0	$(C_5H_5)_2W(NO)^+$	44	344
314	85	$(C_5H_5)_2W^+$	100	314

[a] Probe temperature ~140 °C. [b] Probe temperature ~125 °C. [c] See footnotes *b* and *c* to Table *III*.

NO ligands, the respective $\nu(NO)$ values being 1622 and 1588 cm^{-1} for $(C_5H_5)_2W(NO)I$ and $(C_5H_5)_3W(NO)$.

The ^1H NMR spectrum of $(C_5H_5)_2W(NO)I$ in toluene-d_8 consists of a single, sharp resonance (δ 5.77 at 27 °C) in the temperature range −90 to +30 °C. Similar behavior has been reported previously for $(C_5H_5)_2Mo(NO)I$.[15,16] The variable-temperature ^1H NMR spectra of $(C_5H_5)_3W(NO)$ in toluene-d_8 resemble those displayed by its molybdenum congener.[17] Thus, the single, sharp resonance (δ 5.64 at 27 °C) due to all three rapidly interconverting cyclopentadienyl rings starts to broaden at ~0 °C. At about −40 °C, two new broad peaks begin to grow, indicating the presence of a slowly moving η^1-C_5H_5 ring. Between −40 °C and −80 °C, these two peaks sharpen considerably. The low-field resonance (δ 6.92 at −80 °C) shows some degree of coupling and may be attributed to the olefinic hydrogens, while the high-field resonance (δ 4.32 at −80 °C) can be assigned to the remaining hydrogen. (The low-field portion of the expected AA′BB′ spectrum is not observable because of masking by the solvent resonance.) The signal due to the other two cyclopentadienyl rings sharpens somewhat between −30 °C and −50 °C, but below −50 °C it collapses, and by −90 °C it has separated into two equally intense peaks (δ 4.82 and 5.57).

Both molecules $(C_5H_5)_2W(NO)X$ (X = I or η^1-C_5H_5) are thus probably stereochemically nonrigid in solution at room temperature, undergoing rearrangement processes which rapidly interconvert and equilibrate the cyclopentadienyl rings. To maintain an 18-electron valence configuration at the central metal, their instantaneous molecular structures may involve two C_5H_5 rings bonded in the same, grossly unsymmetrical manner as that found for $(C_5H_5)_3Mo(NO)$[18] and $(C_5H_5)_2Mo(NO)CH_3$[19] in the solid state. Alternatively, one ring may be bonded in a planar η^5 fashion and the other in a bent η^3 fashion in a manner analogous to that observed in the crystal structure of $(C_5H_5)_2W(CO)_2$.[20] A third, albeit less likely, structure would involve two planar η^5-C_5H_5 rings and a bent M–NO linkage. We have thus initiated a single-crystal X-ray diffraction study of $(C_5H_5)_3W(NO)$ with the hope of distinguishing between these three possibilities.

We have recently reported that $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ can be efficiently converted to the monomeric allylnitrosyl complex $(\eta^5\text{-}C_5H_5)W(NO)(\eta^3\text{-}C_3H_5)I$ by treatment with an equimolar amount of $Sn(C_3H_5)_4$[21] (see eq 12). The product complex

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 \xrightarrow[\text{THF}]{Sn(C_3H_5)_4} 2(\eta^5\text{-}C_5H_5)W(NO)(\eta^3\text{-}C_3H_5)I \quad (12)$$

contains a very asymmetric allyl ligand, a fact which is a manifestation of the electronic asymmetry at the metal center. It is quite probable that the factors responsible for the σ,π distortion of the η^3-C_3H_5 group in this compound are also operative in the $(C_5H_5)_2W(NO)X$ (X = I or η^1-C_5H_5) species described above.

Finally, in light of our earlier research with $(\eta^5\text{-}C_5H_5)W(NO)_2H$,[2] the logical precursors of hydridonitrosyl derivatives of tungsten are the various new iodonitrosyl complexes isolated during this work. Studies concerned with the reduction of these complexes by hydridic reagents are currently in progress.

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Registry No. $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$, 71341-43-0; $(\eta^5\text{-}C_5H_5)W(NO)[P(OPh)_3]I_2$, 73199-12-9; $(\eta^5\text{-}C_5H_5)W(NO)(PPh_3)I_2$, 73199-13-0; $(\eta^5\text{-}C_5H_5)W(NO)(SbPh_3)I_2$, 73199-14-1; $(\eta^5\text{-}C_5H_5)W(CO)(NO)I_2$, 73199-15-2; $(\eta^5\text{-}C_5H_5)W(NO)_2I$, 53419-16-2; $(\eta^5\text{-}C_5H_5)W(CO)(NO)[P(OPh)_3]$, 73199-16-3; $(C_5H_5)_2W(NO)I$, 73199-17-4; $(C_5H_5)_3W(NO)$, 73199-18-5; $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$, 33114-09-9.

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