using a subambient, programmable direct insertion probe. The fast reactions with Hg^{2+} were followed on a Durrum stopped-flow spectrophotometer. The absorbance vs. time data were either photographed and treated graphically or digitized and stored in a Biomation Transient Recorder for subsequent least-squares computer fitting.

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Registry No. I, 69493-83-0; II, 69493-84-1; 3,3′-bis(bromomethyl)diphenyl ether, 69484-03-3; poly[*m,m′*-oxybis(phenylmethylene)], 69484-06-6; poly[*m,m′*-oxybis(phenylmethylene)mercury(II)], 69484-07-7; 3,3′-oxybis(chloromercurimethylbenzene), 69484-04-4; $CH_3C_6H_4OC_6H_4CH_2Br$, 69484-05-5; Cr^{2+}, 22541-79-3; Hg^{2+}, 14302-87-5.

References and Notes

(1) Visiting faculty research participant, on leave from the Department of Chemistry, University of Neuchâtel, Neuchâtel, Switzerland.
(2) Anet, F. A. L.; LeBlanc, E. *J. Am. Chem. Soc.* **1957**, *79*, 2649.
(3) (a) Kochi, J. K.; Davis, D. D. *J. Am. Chem. Soc.* **1964**, *86*, 5264. (b) Kochi, J. K.; Buchanan, D. *J. Am. Chem. Soc.* **1965**, *87*, 853.
(4) Nohr, R. S.; Espenson J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.
(5) Espenson, J. H.; Leslie, J. P., II *J. Am. Chem. Soc.* **1974**, *96*, 1954.
(6) (a) Espenson, J. H.; Williams, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 1008. (b) Chang, J. C.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1974**, 233. (c) Espenson, J. H.; Samuels, G. J. *J. Organomet. Chem.* **1976**, *113*, 143.
(7) Leslie, J. P., II; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98* 4839.
(8) The green dipositive species has not been definitely identified although it appears to be $(H_2O)_5CrCl^{2+}$. The material can be rechromatographed and purified on Dowex 50W-X2 resin, 100–200 mesh, and has reproducible characteristics. Its absorption spectrum resembles that of a $(H_2O)_5CrX^{2+}$ complex with maxima at 608 nm (ϵ 16.7) and 427 (20.8), which agrees well with that reported for $CrCl^{2+}$: 607 (16.4), 428 (20.7) [Espenson, J. H.; Birk, J. P. *Inorg. Chem.* **1965**, *4*, 528]. Boiling slowly produces $Cr(H_2O)_6^{3+}$, as does base hydrolysis with carbonate ion followed by reacidification. The complex reacts *slowly* with mercury(II) ion forming $Cr(H_2O)_6^{3+}$ (the half-time is $\sim 7 \times 10^2$ s at 0.008 M Hg^{2+}, 0.25 M H^+), compared to 5.4×10^2 s for $CrCl^{2+}$. The chloro complex presumably arises from the small quantity of $CrCl^+$ in the solution of chromium(II) chloride.
(9) Compare the spectrum[4] of $(H_2O)_5CrCH_2C_6H_5^{2+}$ which shows very similar maxima: 356 (2200), 295 (6970), 273 (7670).
(10) Haupt, G. *J. Res. Natl. Bur. Stand.* **1952**, *48*, 414.
(11) Tomita, M. *Yakugaku Zasshi* **1937**, *57*, 391.
(12) Golden, J. H. *J. Chem. Soc.* **1961**, 1604.
(13) An extensive study of reactivity patterns of related difunctional compounds will be reported later [Pohl, M. C.; Espenson, J. H., unpublished work]. See also: Chipperfield, J. R. *J. Organomet. Chem.* **1977**, *137*, 355.
(14) Buckingham, D. A.; Francis, D. J.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2630.
(15) The rate constant for this reaction has not been determined but can be estimated from the values reported and the success of the Hammett correlation,[7] assuming it can be extended to meta substituents, which has not been tested.
(16) Buhts, R. E.; Chesney, D. K.; Handley, J. R.; Popp, F. D.; Smith, D. C. *Org. Prep. Proced. Int.* **1975**, *7*, 193.
(17) Bergmann, E. O.; Shahak, I.; Aizenshtat, X. *Tetrahedron Lett.* **1969**, 2007.
(18) Kägi, St.; Marty, W., unpublished work.
(19) The procedure for mild base hydrolysis was suggested to us by Dr. M. D. Johnson (private communication).

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Organometallic Nitrosyl Chemistry. 8.[1] Preparation and Characteristic Chemistry of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ and Its Group 6B Congeners

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The chloro compounds $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Mo, W, or Cr) react with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in toluene to form either the new hydrido complexes $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) or the known $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ complex. The hydridomolybdenum complex slowly decomposes at ambient temperature, but the thermally stable tungsten analogue can be isolated and fully characterized. $(\eta^5\text{-}C_5H_5)W(NO)_2H$ exhibits a ν_{M-H} at 1900 cm^{-1} in its infrared spectrum and a low-field hydride resonance at δ 2.27 in its ^1H NMR spectrum. Its characteristic chemistry is dominated by its tendency to function as a source of H^-. Hence, $(\eta^5\text{-}C_5H_5)W(NO)_2H$ is inert to $CHCl_3$, CCl_4, and $(C_2H_5)_3N$, but it reacts readily with anhydrous *p*-toluenesulfonic acid and trityl tetrafluoroborate (in CH_3CN) to yield $(\eta^5\text{-}C_5H_5)W(NO)_2OSO_2C_6H_4CH_3$ and $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]BF_4$, respectively. However, the hydridotungsten complex is not sufficiently hydridic to attack $Fe(CO)_5$, and it reacts with acidic hydridocarbonyls such as $HCo(CO)_4$ or $(\eta^5\text{-}C_5H_5)W(CO)_3H$ to afford products resulting from the scrambling of CO and NO ligands rather than bimetallic carbonyl nitrosyls.

Introduction

Organometallic carbonyl hydrides have received, and continue to receive, considerable attention by virtue of their utility in organic and organometallic syntheses.[2] In contrast, analogous nitrosyl complexes, even though being capable of existence in principle, remain virtually unknown. Indeed, the only such complex that has been isolated to date is $(\eta^5\text{-}C_5H_5)Re(CO)(NO)H$.[3] During our earlier work,[4,5] we developed preparative methods leading to chloronitrosyl compounds which are logical precursors of hydridonitrosyl species. In this paper we report the results of our attempts to convert some of these precursors, specifically the complexes $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Cr, Mo, or W),[6] to the desired hydridonitrosyls.

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 ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use, and all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared 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 with tetramethylsilane being employed as an internal standard. Mass spectra were recorded at 70 eV on Atlas CH4B or AEI MS902 spectrometers by using the direct-insertion method with the assistance of Dr. G. K. Eigendorf and Mr. J. W. Nip. Elemental analyses were carried out by Mr. P. Borda of this department.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$. To a green solution of $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$[6] (3.00 g, 8.71 mmol) in toluene (75 mL) at −78 °C was added dropwise with stirring a solution of $Na[AlH_2(OCH_2CH_2OCH_3)_2]$[7] (2.49 mL, 8.71 mmol) diluted to 20 mL with toluene. The reaction mixture changed immediately to dark green, and a brown solid precipitated. After all the aluminum reagent had been added, the reaction mixture was stirred for an additional 0.5 h to ensure complete reaction. Without being allowed to warm to room temperature, the mixture was quickly filtered through a short (3 × 5 cm) column of Florisil supported on a medium porosity frit. The bright green filtrate was taken to dryness in vacuo, and the residue was dissolved in 10 mL of dichloromethane. The resulting solution was transferred onto a 2 × 6 cm Florisil column. Elution of the column with dichloromethane resulted in the development of a single bright green band which was collected and taken to dryness under reduced pressure. Sublimation of the residue at ambient temperature (5×10^{-3} mm) onto a dry-ice-cooled probe afforded analytically pure (η^5-C_5H_5)W$(NO)_2$H (1.65 g, 61% yield).

Anal. Calcd for $C_5H_6WN_2O_2$: C, 19.37; H, 1.95; N, 9.04. Found: C, 19.58; H, 1.83; N, 8.91. IR (CH_2Cl_2): ν_{NO} 1718, 1632 cm^{-1}. Melting point (under N_2) 52 °C.

Reaction of (η^5-C_5H_5)W$(NO)_2$Cl with $NaBH_4$. The reaction of (η^5-C_5H_5)W$(NO)_2$Cl (1.00 g, 2.91 mmol) in tetrahydrofuran (25 mL) with solid $NaBH_4$ (0.11 g, 2.91 mmol) at ambient temperature for 1 h proceeded completely analogously to the previous transformation. The final reaction mixture was treated in an identical manner to obtain 0.12 g (13% yield) of (η^5-C_5H_5)W$(NO)_2$H.

Reaction of [(η^5-C_5H_5)W$(NO)_2$(CO)]PF_6 with $NaBD_4$. To a stirred green suspension of [(η^5-C_5H_5)W$(NO)_2$(CO)]PF_6[8] (2.40 g, 4.98 mmol) in tetrahydrofuran (60 mL) was added solid $NaBD_4$ (0.21 g, 5.02 mmol). The reaction mixture was stirred vigorously at room temperature for 0.5 h during which time it became red-brown. The solvent was then removed in vacuo, and the resulting residue was extracted with ~10 mL of dichloromethane. Chromatography of the dark green extracts on a 2 × 6 cm Florisil column with dichloromethane as eluant resulted in the development of a single bright green band that was eluted and collected. The eluate was taken to dryness in vacuo to obtain (η^5-C_5H_5)W$(NO)_2$D (0.36 g, 23% yield) which was identified by its infrared and mass spectra.

Reaction of (η^5-C_5H_5)Mo$(NO)_2$Cl with Na[AlH_2($OCH_2CH_2OCH_3$)$_2$]. To a stirred green solution of (η^5-C_5H_5)Mo$(NO)_2$Cl[6] (1.00 g, 3.89 mmol) in toluene (25 mL) at −78 °C was added dropwise a solution of Na[AlH_2($OCH_2CH_2OCH_3$)$_2$] (1.11 mL, 3.89 mmol) diluted to 10 mL with toluene. Immediately the reaction mixture developed a dark green coloration, and a red-brown precipitate formed. After all the aluminum reagent had been added, the mixture was stirred for an additional 0.5 h. It was then quickly filtered while cold through a short (3 × 5 cm) column of Florisil supported on a medium-porosity frit. The green filtrate was permitted to warm to room temperature and was titrated with a toluene solution of I_2 (~0.2 M) until the characteristic color of I_2 persisted. Volatile species were removed under reduced pressure, and the remaining residue was dissolved in ~5 mL of dichloromethane. Chromatography of this solution on a 2 × 6 cm Florisil column with dichloromethane as eluant resulted in the development of a single green band which was collected. The eluate was taken to dryness in vacuo to obtain green (η^5-C_5H_5)Mo$(NO)_2$I (0.29 g, 21% overall yield) which was identified by its characteristic physical properties.[8]

Reaction of (η^5-C_5H_5)Cr$(NO)_2$Cl with Na[AlH_2($OCH_2CH_2OCH_3$)$_2$]. A solution of Na[AlH_2($OCH_2CH_2OCH_3$)$_2$] (1.35 mL, 4.72 mmol) diluted to 10 mL with toluene was added dropwise at room temperature to a stirred, golden solution of (η^5-C_5H_5)Cr$(NO)_2$Cl[6] (0.80 g, 4.72 mmol) in toluene (25 mL). The reaction mixture became red, and a brown solid precipitated. After being stirred for an additional 0.5 h, the mixture was filtered through a Florisil column (3 × 4 cm) supported on a medium porosity frit. The filtrate was concentrated in vacuo to ~5 mL and was syringed onto a 3 × 4 cm column of alumina (Woelm neutral, activity grade 1). Elution of the column with benzene developed a single red band which was collected and taken to dryness under reduced pressure to obtain red-purple, microcrystalline [(η^5-C_5H_5)Cr$(NO)_2$]$_2$ (0.15 g, 22% yield), readily identifiable by its distinctive physical properties.[9]

Reactions of (η^5-C_5H_5)W$(NO)_2$H with I_2 and Br_2. To a green solution of (η^5-C_5H_5)W$(NO)_2$H (0.30 g, 0.97 mmol) in dichloromethane (25 mL) at room temperature was added dropwise with stirring a purple solution of I_2 (1.23 g, 0.49 mmol) in dichloromethane (15 mL). At once the reaction mixture turned dark green. The final solution was concentrated in vacuo to ~5 mL and was syringed onto a 2 × 6 cm Florisil column. Elution of the column with dichloromethane resulted in the development of a single green band which was collected. Solvent was removed from the eluate under reduced pressure to obtain (η^5-C_5H_5)W$(NO)_2$I (0.20 g, 47% yield) which was identified by its characteristic physical properties.[8]

A similar experiment performed by using Br_2 afforded the analogous (η^5-C_5H_5)W$(NO)_2$Br[8] in 48% yield.

Reaction of (η^5-C_5H_5)W$(NO)_2$H with p-$CH_3C_6H_4SO_3H$. To a stirred green solution of (η^5-C_5H_5)W$(NO)_2$H (0.31 g, 1.0 mmol) in tetrahydrofuran (30 mL) at room temperature was added solid, anhydrous *p*-toluenesulfonic acid (0.17 g, 1.0 mmol). The reaction mixture darkened while being stirred for 0.5 h before being taken to dryness in vacuo. The residue was dissolved in dichloromethane (30 mL) to obtain a blue-green solution. Addition of hexanes (60 mL) to this solution induced the deposition of a red-brown solid which was removed by filtration through a short (3 × 5 cm) column of Celite. Slow concentration of the filtrate under reduced pressure resulted in the crystallization of analytically pure, green (η^5-C_5H_5)W$(NO)_2OSO_2C_6H_4CH_3$ (0.35 g, 73% yield).

Anal. Calcd for $C_{12}H_{12}WN_2O_5S$: C, 30.01; H, 2.52; N, 5.84. Found: C, 29.75; H, 2.51; N, 5.66. IR (CH_2Cl_2): ν_{NO} 1737, 1650 cm^{-1}. Mp (under N_2) 120 °C dec. Mass spectrum: most intense parent ion *m/e* 480.

Reaction of (η^5-C_5H_5)W$(NO)_2$H with $(C_6H_5)_3CBF_4$. A yellow solution of $(C_6H_5)_3CBF_4$[10] (0.33 g, 1.0 mmol) in acetonitrile (5 mL) was added dropwise to a stirred solution of (η^5-C_5H_5)W$(NO)_2$H (0.31 g, 1.0 mmol) in acetonitrile (30 mL) at −10 °C. After complete mixing of the two solutions, an infrared spectrum of the resulting blue-green solution indicated [(η^5-C_5H_5)W$(NO)_2$(CH_3CN)]$^+$ to be the only nitrosyl-containing species present.[8] Upon addition of NaI (0.15 g, 1.0 mmol), the reaction mixture immediately became olive green. The reaction mixture was taken to dryness in vacuo, and the residue was dissolved in a minimum of dichloromethane (5 mL). Chromatography of this solution on Florisil with dichloromethane as eluant (vide supra) provided a green eluate which was concentrated in vacuo to 20 mL. The addition of hexanes (20 mL) and continued slow concentration of the solution resulted in the precipitation of olive green crystals of (η^5-C_5H_5)W$(NO)_2$I (0.25 g, 57% yield based on (η^5-C_5H_5)W$(NO)_2$H) which were collected by filtration.

The filtrate was taken to dryness in vacuo to leave a light green residue. This solid was dissolved in a minimum of benzene, and the solution was transferred to the top of a 3 × 4 cm column of alumina (activity grade 1). The column was washed with 100 mL of benzene to obtain a colorless eluate. Removal of solvent from the eluate under reduced pressure provided $(C_6H_5)_3CH$ (0.15 g, 61% yield) which was identified by comparison of its physical properties with those of an authentic sample.

The above experiment was repeated by using (η^5-C_5H_5)W$(NO)_2$D to obtain comparable yields of $(C_6H_5)_3CD$ which was identified mass spectrometrically.

Reaction of (η^5-C_5H_5)W$(NO)_2$H with $HCo(CO)_4$. To a pale yellow solution of $HCo(CO)_4$ [prepared from $Co_2(CO)_8$ (0.34 g, 1.0 mmol) in tetrahydrofuran (50 mL)[11]] cooled to −78 °C was added dropwise with stirring a solution of (η^5-C_5H_5)W$(NO)_2$H (0.62 g, 2.0 mmol) in tetrahydrofuran (50 mL). After the addition was complete, the reaction mixture was permitted to warm slowly to room temperature whereupon its color changed gradually to red-brown. The mixture was stirred at ambient temperature for an additional 16 h to ensure complete reaction, and it was then filtered through a short (3 × 4 cm) column of Celite. Concentration of the filtrate under reduced pressure resulted in the removal of solvent and an orange-red, volatile compound which was not isolated but was identified as $Co(CO)_3(NO)$ by a solution infrared spectrum.[12] After removal of all volatile species, the remaining orange-brown residue was sublimed at room temperature (5×10^{-3} mm) onto a dry-ice-cooled probe to obtain orange (η^5-C_5H_5)W$(CO)_2$(NO)[6] (0.25 g, 37% yield based on W).

Reaction of (η^5-C_5H_5)W$(NO)_2$H with (η^5-C_5H_5)W$(CO)_3$H. To a green solution of (η^5-C_5H_5)W$(NO)_2$H (0.31 g, 1.0 mmol) in tetrahydrofuran (30 mL) was added solid, yellow (η^5-C_5H_5)W$(CO)_3$H[13] (0.33 g, 1.0 mmol), and the resulting solution was stirred at room temperature for 48 h. During this time, the reaction mixture became red, and a considerable amount of a brown precipitate formed. The solvent was removed from the mixture in vacuo, and the residue was dissolved in dichloromethane (5 mL). The red solution was then chromatographed on a 2 × 5 cm Florisil column with dichloromethane as eluant to obtain a single red band which was collected and taken to dryness in vacuo. Sublimation of the residue at room temperature onto a dry-ice-cooled probe afforded orange (η^5-C_5H_5)W$(CO)_2$(NO)[6] (0.14 g, 0.42 mmol). The red solid remaining in the sublimer was

Table I. Spectral Properties of New Complexes

	Infrared,[a] cm^{-1}		Proton NMR, δ	
complex	ν_{NO}	other	C_5H_5	other
$(\eta^5\text{-}C_5H_5)W(NO)_2H$	1718 s, 1632 s	1900 w [ν(W-H)]	5.05[b]	2.77 s (1 H)
$(\eta^5\text{-}C_5H_5)W(NO)_2D$	1718 s, 1632 s	1372 w [ν(W-D)]	5.05[b]	
$(\eta^5\text{-}C_5H_5)W(NO)_2\text{-}OSO_2C_6H_4CH_3$	1737 s, 1650 s		6.15[c]	2.70 s (3 H), 7.41 m (4 H)
$[(\eta^5\text{-}C_5H_5)W(NO)_2\text{-}(CH_3CN)]BF_4$	1770 s, 1690 s			
$(\eta^5\text{-}C_5H_5)Mo(NO)_2H$	1732 s, 1642 s[d]			

[a] In CH_2Cl_2 unless otherwise indicated. [b] In C_6D_6. [c] In $CDCl_3$. [d] In toluene.

found to be $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$[14] (0.09 g, 0.14 mmol). Both products were identified by their characteristic physical properties.

Results and Discussion

Reduction of $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Cr, Mo, or W) Complexes. King and Bisnette first reported in 1963 that the reduction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with $NaBH_4$ in a two-phase water–benzene system affords $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ in 5% yield.[15] A plausible first step of this reaction may well involve the formation of the thermally unstable hydridochromium complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2H$, which subsequently dimerizes to the observed product with concomitant expulsion of hydrogen.[16] However, there have been no reports since that time concerning the isolation of this hydride or its molybdenum and tungsten analogues.

We have found that the complexes $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) can best be prepared by treatment of the respective $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ precursors with the gentle reducing agent sodium dihydridobis(2-methoxyethoxy)aluminate,[7] in toluene at −78 °C

$$(\eta^5\text{-}C_5H_5)M(NO)_2Cl \xrightarrow[\text{toluene, -78 °C}]{Na[AlH_2(OCH_2CH_2OCH_3)_2]} (\eta^5\text{-}C_5H_5)M(NO)_2H \quad (1)$$

$$M = \text{Mo or W}$$

Monitoring of the progress of reaction 1 by infrared spectroscopy indicates that the optimum stoichiometric ratio of reactants is 1:1. It also shows that an aluminohydride adduct[17] with $(\eta^5\text{-}C_5H_5)M(NO)_2$ is not formed, but the exact nature of the aluminum byproduct remains to be ascertained.

The thermally stable complex $(\eta^5\text{-}C_5H_5)W(NO)_2H$ can be readily obtained in 61% yield from reaction 1, but the molybdenum congener has so far defied all attempts at isolation. Bright green toluene solutions containing $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$ slowly deposit a red-brown solid when stirred at ambient temperature in a prepurified nitrogen atmosphere, the decomposition being complete after ~3 days. The rate of decomposition of the hydrido complex is markedly enhanced by removal of the solvent in vacuo, a procedure which only affords the red-brown solid. This solid does not dissolve in any common organic solvents, and its infrared spectrum (Nujol mull) is devoid of any absorptions attributable to a coordinated nitrosyl group. Nevertheless, spectroscopic (Table I) and chemical (vide infra) properties of the green toluene solutions are completely consistent with the presence of $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$.

Not surprisingly, reduction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in toluene at room temperature does produce $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ in 22% yield

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl \xrightarrow[\text{toluene}]{Na[AlH_2(OCH_2CH_2OCH_3)_2]} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \quad (2)$$

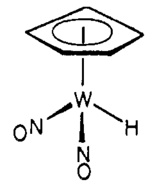
Reaction 2 does not occur at −78 °C. We could not find any direct physical evidence for the existence of the elusive $(\eta^5\text{-}C_5H_5)Cr(NO)_2H$ species at either temperature. However, by analogy with the molybdenum and tungsten systems, we believe that reaction 2 probably does proceed via this hydridochromium complex which must be very thermally unstable. The observed increase in thermal stability of the $(\eta^5\text{-}C_5H_5)M(NO)_2H$ compounds from the first to the third transition series thus parallels the well-known behavior of the analogous $(\eta^5\text{-}C_5H_5)M(CO)_3H$ complexes for which the thermal and oxidative stabilities also increase in the order Cr < Mo < W.[16]

Conversions 1 and 2 can also be effected in tetrahydrofuran with $NaBH_4$ as the reducing agent, but the yields of the desired products are much lower. For instance, $(\eta^5\text{-}C_5H_5)W(NO)_2H$ is obtainable in only 13% yield in this manner. However, it has been found[18] that this hydrido complex can be formed, albeit in only 23% yield, by reaction 3. When $NaBD_4$ is

$$[(\eta^5\text{-}C_5H_5)W(NO)_2(CO)]PF_6 \xrightarrow[\text{THF}]{NaBH_4} (\eta^5\text{-}C_5H_5)W(NO)_2H \quad (3)$$

employed as the reducing agent, reaction 3 represents a convenient synthetic route to the deuteride, $(\eta^5\text{-}C_5H_5)W(NO)_2D$.

Physical Properties of $(\eta^5\text{-}C_5H_5)W(NO)_2H$. The complex is a bright green, diamagnetic solid (mp 52 °C) which can be handled in air for short periods of time without the occurrence of noticeable decomposition. It is freely soluble in common organic solvents, but only sparingly soluble in paraffin hydrocarbons, to give air-sensitive green solutions, and it sublimes readily at room temperature (5×10^{-3} mm) onto a dry-ice-cooled probe. Its spectral properties (Table I) are consistent with the compound having the molecular structure



Thus, an infrared spectrum of a dichloromethane solution of the complex exhibits two strong absorptions at 1718 and 1632 cm^{-1} attributable to the terminal nitrosyl ligands. These bands are at frequencies slightly lower than the corresponding absorptions of the $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ precursor.[4] Furthermore, there is a broad, weak band at 1900 cm^{-1} assignable as the terminally bonded W–H stretching absorption. In accord with this assignment is the fact that the infrared spectrum of $(\eta^5\text{-}C_5H_5)W(NO)_2D$ in CH_2Cl_2 does not exhibit this band but does show a weak absorption at 1372 cm^{-1} assignable to a terminal W–D group. As expected, the observed shift, ν_{MH}/ν_{MD}, is 1.38 since ν_{MH} and ν_{NO} are not appreciably mixed in the hydrido derivative.

The ^1H NMR spectrum of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ in C_6D_6 consists of a sharp resonance at δ 5.05 and a slightly broader resonance at δ 2.77 of relative intensity 5:1. The former signal is characteristic of a η^5-cyclopentadienyl ring. The latter we assign to a hydrogen atom bonded directly to the tungsten center since it does not appear in the ^1H NMR spectrum of $(\eta^5\text{-}C_5H_5)W(NO)_2D$ recorded under identical conditions (Table I). We do not, however, observe any ^{183}W–H coupling even though such coupling has been detected for the related $(\eta^5\text{-}C_5H_5)W(CO)_3H$ complex.[19] The occurrence of the hydride resonance at relatively low field is somewhat anomalous since these resonances are usually observed at high fields, typically in the range δ −5 to −20.[2] For example, $(\eta^5\text{-}C_5H_5)Re(CO)(NO)H$ displays a broad signal at δ −8.2 due to the hydride ligand.[3] A low-field resonance is not unknown for

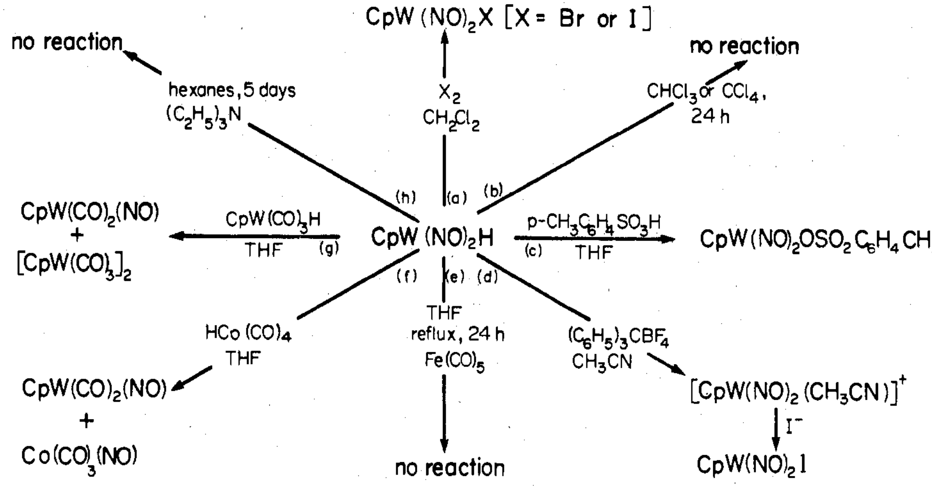


Figure 1. The characteristic chemistry of $CpW(NO)_2H$ [Cp = η^5-C_5H_5].

transition-metal hydrides, but to date it has been characteristic only of some bis(cyclopentadienyl)hydrido complexes of titanium, zirconium,[20] and niobium.[21]

The high-resolution mass spectrum of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ exhibits a fragmentation pattern similar to that displayed by $(\eta^5\text{-}C_5H_5)W(NO)_2CH_3$[22] under identical conditions. Peaks attributable to the parent ion and ions corresponding to the stepwise loss of the nitrosyl ligands are observable in both cases, but ions resulting from cleavage and rearrangement of the cyclopentadienyl ring appear to be much more abundant in the spectrum of $(\eta^5\text{-}C_5H_5)W(NO)_2H$. Unfortunately, overlapping of some medium to strong intensity peaks in the lower mass range makes unambiguous assignments difficult, especially in the light of the polyisotopic nature of tungsten.

The Chemical Reactivity of $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W). When compared with metal carbonyl hydrides to which they are formally related, the $(\eta^5\text{-}C_5H_5)M(NO)_2H$ complexes display both similarities and very striking differences in their chemical reactivity, as evidenced by the reactions of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ summarized in Figure 1. For instance, even though carbonyl hydrides of general formula $(\eta^5\text{-}C_5H_5)M(CO)_xH$ (x = 3 for M = Cr, Mo, or W;[16] x = 2 for M = Fe[23] or Ru[24]) can all be decomposed thermally or oxidatively to yield the corresponding dimers, $[(\eta^5\text{-}C_5H_5)M(CO)_x]_2$; the green $(\eta^5\text{-}C_5H_5)M(NO)_2H$ species only decompose to red-brown, nitrosyl-free solids when subjected to the same experimental conditions. Moreover, $(\eta^5\text{-}C_5H_5)W(NO)_2H$ does not react with halocarbons such as $CHCl_3$ or CCl_4 at ambient temperature although such a reaction is often employed to establish the presence of a metal–hydrogen bond.[2] However, like numerous carbonyl hydrides, $(\eta^5\text{-}C_5H_5)W(NO)_2H$ does react directly with halogens to afford the respective halo derivatives in reasonable yields. A similar conversion enabled us to identify chemically $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$ as the product formed in reaction 1:

$$(\eta^5\text{-}C_5H_5)Mo(NO)_2H \text{ (not isolated)} \xrightarrow[\text{toluene}]{I_2} (\eta^5\text{-}C_5H_5)Mo(NO)_2I \quad (4)$$

The most significant difference between $(\eta^5\text{-}C_5H_5)W(NO)_2H$ and most neutral carbonyl hydrides is evident in its acid–base behavior. Many hydridocarbonyls are Lowry–Brønsted acids in polar solvents,[2] but the hydridotungsten complex functions as a source of H^- in these solvents. This fact is clearly demonstrated by its reaction with anhydrous *p*-toluenesulfonic acid to yield the new *p*-toluenesulfonato complex under conditions which leave $(\eta^5\text{-}C_5H_5)W(CO)_3H$ unaltered. Consistent with this view of W(δ+)–H(δ–) bond polarity is the failure of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ to react with $(C_2H_5)_3N$ and its reaction with the well-known hydride abstractor triphenylcarbenium tetrafluoroborate in acetonitrile to afford $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]BF_4$ and $(C_6H_5)_3CH$. The organic product can be isolated in 61% yield, but the organometallic complex is obtained as an oil which cannot be readily purified. However, it can be identified by comparison of its infrared spectrum (ν_{NO} at 1770 and 1690 cm^{-1} in CH_2Cl_2) with that exhibited by $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]PF_6$ and by its reaction with NaI to form $(\eta^5\text{-}C_5H_5)W(NO)_2I$.[8] As expected, similar treatment of $(\eta^5\text{-}C_5H_5)W(NO)_2D$ with $(C_6H_5)_3CBF_4$ provides $(C_6H_5)_3CD$ in comparable yields.

The hydridic character of the tungsten hydride is 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.[2] Nevertheless, the chemistry of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ resembles that typically exhibited by transition-metal tertiary phosphine hydride complexes which also are not acidic in solution and will not form sodium salts analogous to those of the carbonyl hydrides.[2] It thus appears that the nitrosyl ligands in $(\eta^5\text{-}C_5H_5)W(NO)_2H$ are not particularly effective as π acids in removing electron density from tungsten. Consistent with this view is the fact that several cations of the type $[(\eta^5\text{-}C_5H_5)W(NO)_2L]^+$ (L = neutral Lewis base) are known,[8] but the anion $[(\eta^5\text{-}C_5H_5)W(NO)_2]^-$ has yet to be characterized (cf. reaction (h) in Figure 1). In order to evaluate more fully the function of the NO groups, we have initiated a study to determine the effect of varying the other ligands attached to the metal on the physical and chemical properties of hydridonitrosyl complexes of tungsten.

In light of the observed hydridic behavior of $(\eta^5\text{-}C_5H_5)W(NO)_2H$, it is not unreasonable to expect that it will react with acidic hydridocarbonyl complexes to form bimetallic carbonyl nitrosyl products. However, we have yet to isolate these types of products from such reactions. Thus, when $(\eta^5\text{-}C_5H_5)W(NO)_2H$ is treated with equimolar amounts of $HCo(CO)_4$ or $(\eta^5\text{-}C_5H_5)W(CO)_3H$, the only carbonyl- and nitrosyl-containing products formed result from scrambling of the two ligands among the metal centers, possibly via a bimetallic intermediate. A similar redistribution of ligands has been recently observed to occur during reactions of $Ni(NO)[P(C_6H_5)_3]_2X$ (X = Cl, Br, or I) with carbonylmetalate anions such as $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$.[25]

Finally, it is known that strong hydride donors attack electrophiles such as metal carbonyls to produce formyl complexes.[26] However, $(\eta^5\text{-}C_5H_5)W(NO)_2H$ is not sufficiently hydridic to react in this manner with $Fe(CO)_5$ in refluxing tetrahydrofuran. The W–H bond in the complex also does not undergo simple addition reactions with unsymmetrical olefins such as bromostyrene. The $(\eta^5\text{-}C_5H_5)W(NO)_2H$ is consumed during this latter reaction, but no organometallic nitrosyl products are formed. Further studies in this regard are currently in progress.

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Registry No. $(\eta^5\text{-}C_5H_5)W(NO)_2H$, 69532-01-0; $(\eta^5\text{-}C_5H_5)W(NO)_2D$, 69532-02-1; $(\eta^5\text{-}C_5H_5)W(NO)_2OSO_2C_6H_4CH_3$, 69532-03-2; $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]BF_4$, 69532-04-3; $(\eta^5\text{-}C_5H_5)Mo(NO)_2H$, 69532-05-4; $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$, 53419-14-0; $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$, 12305-00-9; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $[(\eta^5\text{-}C_5H_5)W(NO)_2(CO)]PF_6$, 53419-03-7; $Na[AlH_2(OCH_2CH_2OCH_3)_2]$, 22722-98-1; $(C_6H_5)_3CBF_4$, 341-02-6; $HCo(CO)_4$, 16842-03-8; $(\eta^5\text{-}C_5H_5)W(CO)_3H$, 12128-26-6.

References and Notes

(1) Part 7: Kolthammer, B. W. S.; Legzdins, P. *Inorg. Chem.*, in press.

(2) See for example: (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231, and references cited therein. (b) Schunn, R. A. In "The Hydrogen Series"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; Vol 1, pp 203–69.

(3) Stewart, R. P., Jr.; Okamoto, N.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, C32.

(4) Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1975**, *14*, 1875.

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

(6) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.

(7) Purchased from the Aldrich Chemical Co. as a 70% benzene solution under the trade name Red-al.

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

(9) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Synth.*, **1979**, *19*, 208.

(10) Olah, G. A.; Svoboda, J. J.; Olah, J. A. *Synthesis* **1972**, 544.

(11) (a) Gilmont, P.; Blanchard, A. A. *Inorg. Synth.* **1946**, *2*, 238. (b) Edgell, W. F.; Lyford, J. *Inorg. Chem.* **1970**, *9*, 1932.

(12) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, pp 168–69.

(13) Reference 12, pp 156–58.

(14) Barnett, K. W.; Slocum, D. W. *J. Organomet. Chem.* **1972**, *44*, 1.

(15) King, R. B.; Bisnette, M. B. *J. Am. Chem. Soc.* **1963**, *85*, 2527; *Inorg. Chem.* **1964**, *3*, 791.

(16) Cf. the thermal dimerization of $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$: Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(17) For the first such adduct to be characterized see: McNeese, T. J.; Wreford, S. S.; Foxman, B. M. *J. Chem. Soc., Chem. Commun.* **1978**, 500.

(18) The general features of H^- attack on nitrosyl cations will be discussed in a future publication.

(19) Faller, J. W.; Anderson, A. S.; Chen, C. *J. Chem. Soc. D* **1969**, 719.

(20) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136, and references contained therein.

(21) Labinger, J. A. *Adv. Chem. Ser.* **1978**, *No. 167*, 11.

(22) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1022.

(23) Green, M. L. H.; Street, C. N.; Wilkinson, G. *Z. Naturforsch., B* **1959**, *14*, 1595.

(24) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133.

(25) Braunstein, P.; Dehand, J.; Munchenbach, B. *J. Organomet. Chem.* **1977**, *124*, 71.

(26) Gladysz, J. A.; Tam. W. *J. Am. Chem. Soc.* **1978**, *100*, 2545, and references contained therein.

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Quantitative Data on Some Oxidative Addition Reactions and on the Lewis Basicity of $Ir^I[(C_6H_5)_3P]_2(CO)Cl$

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A hydrogen-bonding interaction involving a d^8 transition-metal donor is reported and the enthalpy of adduct formation determined. This data coupled with the enthalpy of formation of the SO_2 adduct permits a tentative characterization of this donor in terms of the *E* and *C* model. The donor is contrasted with organic donors. Average metal–halogen bond energies for the Ir(III)–Br and Ir(III)–I bonds in the oxidative addition product of the titled compound are reported.

Introduction

The lone pair of electrons on d^8 rhodium(I) and iridium(I) complexes has given rise to some novel reaction types and to some interesting catalytic systems for small-molecule activation.[1-3] The basicity and nucleophilicity of these Lewis bases are very unusual when compared to those of typical organic donors. Accordingly, considerable effort[1,4-8] has been expended in an attempt to obtain quantitative information to characterize the reactivity of these systems and to provide a theoretical understanding of the reactivity. In this article, we report the first data involving hydrogen bonding to this type of lone pair in $Ir[(C_6H_5)_3P]_2(CO)Cl$ and describe the thermodynamics of a displacement-type reaction that permits a reevaluation of the enthalpy of formation of the SO_2 adduct. The enthalpy of the reaction of this complex with $(CN)_2C{=}C(CN)_2$, I_2, and Br_2 is also reported.

The hydrogen-bonding interaction has a low equilibrium constant and a low enthalpy. A previously described[10,15] GLC technique permits the accurate determination of this enthalpy. A direct determination of the enthalpy of formation of the SO_2 adduct has also been made by using the GLC technique.

Experimental Section

Materials. Chlorocarbonylbis(triphenylphosphine)iridium(I) (t-Ir) and chlorocarbonylbis(tritolylphosphine)iridium(I) (t-Ir′) were prepared by the method of Vrieze et al.[11] Anal. Calcd for $IrCl(CO)[P(C_6H_5)_3]_2$: C, 56.96; H, 3.88; Cl, 4.54. Found: C, 56.96; H, 3.82; Cl, 4.81. Calcd for $IrCl(CO)[P(CH_3C_6H_4)_3]_2$: C, 59.74; H, 4.90; Cl, 4.10. Found: C, 60.00; H, 4.99; Cl, 3.94. 3,3′-Dimethylbiphenyl was prepared by using the method of Kornblum,[12] the clear, colorless distillate boiling at 119 °C at 3 torr being retained. Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.31; H, 7.71. PCR Inc. 2,2,2-trifluoroethanol (TFE) and Baker Analyzed Reagent benzene were dried over Linde 4A molecular sieves for at least 24 h prior to use. Linde technical grade sulfur dioxide was used as received. The solid support for GLC work was Johns-Manville Chromosorb W, 60–80 mesh, which was acid washed and DMCS treated. Iodine was purified as previously described.

Calorimetry. The basic calorimeter, the procedure for performing the experiments, and analysis of data have been described elsewhere.[13,14] Prior to preparation of the solutions, the solvent was degassed with nitrogen. All solutions were handled in a nitrogen-filled glovebag. The sulfur dioxide adduct of Ir was prepared by saturating the solution for 30 min to ensure complete reaction. The solution was then transferred to the calorimeter and resaturated with a fast