The orientation of the ring-tilt openings and/or the flexibility of the molecules appear to affect the rate of dihydrogen evolution. Since both geometrical effects have some control over the ability of the protons on the irons to approach each other, protonation of the iron atoms is apparently an essential part of the mechanism. It can be inferred from the electrochemical behavior of the system that the first protonation is fast. Only at the highest acidities is it possible to affirm that the elimination of dihydrogen is the rate-determining step. At lower acidities, the second protonation may be comparably slow.

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New Organometallic Hydrido Nitrosyl Complexes of Tungsten[1,2]

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Treatment of dark purple $[CpW(NO)I_2]_2$ (Cp = η^5-C_5H_5) with 1 or 2 equiv of $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ in CH_2Cl_2–C_6H_6 affords green $[CpW(NO)IH]_2$ or orange $[CpW(NO)H_2]_2$, respectively, both products being isolable as analytically pure solids. Addition of PR_3 (R = Me, Ph, OMe or OPh) to any of the bimetallic nitrosyl complexes results in formation of the corresponding monometallic derivatives. Hence, $[CpW(NO)I_2]_2$ is converted into brown $CpW(NO)I_2(PR_3)$, $[CpW(NO)IH]_2$ transforms into orange $CpW(NO)IH(PR_3)$, and $[CpW(NO)H_2]_2$ ultimately yields orange $CpW(NO)H_2(PR_3)$. The latter compounds are formed via the intermediate complexes $[CpW(NO)H(PR_3)]_2$, which can be isolated from C_6H_6 as purple microcrystals when R = OPh. The monomeric diiodo nitrosyl complexes may also be converted to their hydrido nitrosyl analogues by reaction with $Na[H_2Al(OCH_2CH_2OCH_3)_2]$. All new compounds synthesized have been characterized by conventional spectroscopic techniques, particularly ^1H NMR spectroscopy. The physical properties of the dimeric hydride complexes indicate that they all contain bridging hydride ligands and that they are best formulated as $[CpW(NO)]_2(\mu\text{-}I)_2(\mu\text{-}H)_2$, $[CpW(NO)H]_2(\mu\text{-}H)_2$, and $[CpW(NO)(PR_3)]_2(\mu\text{-}H)_2$. Plausible molecular structures for these compounds and their monomeric derivatives are proposed.

Introduction

Current interest in the synthesis, characterization, and properties of organotransition-metal hydride complexes continues unabated, primarily because many important stoichiometric and catalytic chemical conversions have been demonstrated to involve metal-hydrogen linkages at key stages.[4] In this regard, however, relatively little is known presently about how the physical and chemical properties of such linkages are affected by the presence of NO ligands in the metal's coordination sphere. This state of affairs simply reflects the paucity of well-defined organometallic hydrido nitrosyl complexes. The first report of such a species appeared in 1972 when Graham and coworkers communicated the existence of CpRe(CO)(NO)H (Cp = η^5-C_5H_5).[5] Since that time, only this compound,[6] its PPh_3 derivative,[7] $CpW(NO)_2H$,[8] $HFe(CO)_2(NO)(PPh)_3$,[9] and $HFe(CO)(NO)(PPh_3)_2$[9] have been studied in any detail. Consequently, we have recently been endeavoring to develop synthetic routes to other members of this class of compounds.

As part of a previous study,[10] we succeeded in synthesizing $CpW(NO)IH[P(OPh)_3]$ and $[CpW(NO)IH]_2$, but in only 9% yield and of poor quality, respectively. We have now improved upon and extended this earlier work, and in this paper we wish to report superior preparations and characterizations of these two compounds as well as several other related hydrido nitrosyl complexes of tungsten.

Experimental Section

All manipulations were performed so as to maintain all chemicals under an atmosphere of prepurified dinitrogen either on the bench using conventional techniques for the manipulation of air-sensitive compounds[11] or in a Vacuum Atmospheres Corp. Dri-Lab Model HE-43-2 drybox. 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, melting point determinations, and/or other suitable methods. Melting points were taken in capillaries by using

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Table I. Analytical and Infrared Data for the Complexes

		analytical data									IR data (CH_2Cl_2)	
		C		H		N		other				
complex	mp, °C (dec)	calcd	found	calcd	found	calcd	found		calcd	found	ν_{NO}, cm^{-1}	ν_{WH}, cm^{-1}
$CpW(NO)I_2[P(OPh)_3]$[14]											1663	
$CpW(NO)I_2[P(OMe)_3]$	178	14.63	14.58	2.15	2.18	2.13	2.12	I	38.64	38.49	1653	
$CpW(NO)I_2(PPh_3)$[14]											1646	
$CpW(NO)I_2(PMe_3)$	160	15.78	15.70	2.32	2.28	2.30	2.28	I	41.69	41.55	1638	
$CpW(NO)IH[P(OPh)_3]$	112	38.52	38.46	2.95	2.93	1.95	1.94				1643	1883
$CpW(NO)IH[P(OMe)_3]$	103	18.08	18.19	2.82	2.88	2.64	2.58	I	23.92	23.71	1629	1923
								O	12.05	12.17		
$CpW(NO)IH(PPh_3)$	142	41.26	41.20	3.14	3.18	2.09	2.15				1615	?[a]
$CpW(NO)IH(PMe_3)$	101	19.90	19.80	3.13	3.24	2.90	2.85				1613 (isomer A)	1931
		19.90	19.86	3.13	3.00	2.90	2.85	I	26.28	26.40	1609 (A + B)	1929, 1898
$[CpW(NO)I_2]_2$[14]											1655	
$[CpW(NO)IH]_2$	174	14.74	14.91	1.47	1.51	3.44	3.40	I	31.20	30.95	1646	not observed
$[CpW(NO)H_2]_2$	130	21.37	21.44	2.51	2.46	4.99	4.93	O	5.69	6.00	1599	1906
$[CpW(NO)H\{P(OPh)_3\}]_2$	85	46.80	46.64	3.59	3.63	2.37	2.36				1578	not observed
$CpW(NO)H_2[P(OPh)_3]$	91	46.72	46.55	3.75	3.84	2.37	2.50				1607	1863

[a] The ν_{WH} for $CpW(NO)IH(PPh_3)$ cannot be unequivocally assigned as there are several bands in the appropriate spectral regions.

a Gallenkamp Melting Point apparatus and are uncorrected. All solvents were dried by standard procedures,[12] distilled, and deaerated with N_2 just prior to use. Unless specified otherwise, the chemical reactions described below were effected at ambient temperatures.

Infrared spectra were recorded on a Perkin-Elmer 598 spectrophotometer (calibrated with the 1601-cm^{-1} band of polystyrene film) or on a Nicolet 5DX FT-IR instrument (internally calibrated with a He/Ne laser). Proton magnetic resonance spectra were obtained on a Bruker WP-80, WH-400, or Nicolet-Oxford H-270 spectrometer with reference to the deuterium signal of the solvent employed. All ^1H chemical shifts are reported in parts per million downfield from Me_4Si. ^{31}P NMR spectra were recorded at 40.5 MHz on a Varian Associates XL-100 spectrometer or at 32.38 MHz on a Bruker WP-80 instrument using deuterium as the internal lock. The observed resonances were referenced to external $P(OMe)_3$ which was considered to have a chemical shift of + 141 ppm downfield from 85% H_3PO_4.[13] Mrs. M. T. Austria, Ms. M. A. Heldman, Ms. L. K. Darge, and Dr. S. O. Chan assisted in obtaining the NMR data.

Mass spectra were recorded at 70 eV on an Atlas CH4B or a Kratos MS50 spectrometer using the direct-insertion method with the assistance of Dr. G. K. Eigendorf, Mr. J. W. Nip, and Mr. M. A. Lapawa. The GC–MS samples were run on a Varian Vista 6000 gas chromatograph interfaced with a Nermag R10-10 quadrupole mass spectrometer using the conditions specified below with the assistance of Ms. C. M. Moxham. Gas chromatographic analyses were carried out on a Perkin-Elmer Sigma 4B instrument employing the experimental conditions described below. Elemental analyses were performed by Mr. P. Borda of this department.

Preparation of $CpW(NO)I_2L$ (L = $P(OMe)_3$ or PMe_3). These compounds were prepared by treating $[CpW(NO)I_2]_2$ in CH_2Cl_2 with 2 equiv of L in the manner described previously[14] for L = $P(OPh)_3$ or PPh_3. Both complexes were isolated as brown crystals in yields of 87%.

The analytical, IR, and ^1H NMR data for these and the other complexes synthesized during this work are collected in Tables I and II.

Preparation of $[CpW(NO)IH]_2$. A vigorously stirred mixture of $[CpW(NO)I_2]_2$[14] (3.00 g, 2.82 mmol), CH_2Cl_2 (25 mL), and benzene (150 mL) was heated gently to effect solubilization of the organometallic reagent. Once a clear, yellow-brown solution had formed, the mixture was cooled to room temperature with a water bath. Then, before precipitation of $[CpW(NO)I_2]_2$ could occur, 0.85 mL (2.9 mmol) of a 3.4 M solution of $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ in toluene[15] was rapidly added. The reaction mixture immediately became dark green in color, and copious quantities of a very fine, brown precipitate formed. This mixture was then filtered as rapidly as possible through a 3 × 4 cm column of Celite supported on a medium-porosity glass frit, and the column was washed with benzene (2 × 15 mL). The volume of the combined filtrates was reduced in vacuo to 10–15 mL, an operation which induced the formation of intensely colored, dark green microcrystals. The crystalline precipitate was collected by filtration, washed with benzene (3 × 5 mL), and dried under vacuum (5 × 10^{-3} mm) to obtain 0.80 g (35% yield) of analytically pure $[CpW(NO)IH]_2$.

Preparation of $CpW(NO)IHL$ (L = $P(OPh)_3$, $P(OMe)_3$, or PPh_3). These experiments were performed similarly, and the reaction with L = $P(OPh)_3$ is described as a representative example.

To the dark green filtrate containing $[CpW(NO)IH]_2$ (vide supra) was added by syringe 1.0 mL (1.2 g, 3.8 mmol) of neat $P(OPh)_3$. After being stirred for a few minutes, the resulting solution became orange. The final solution was concentrated under reduced pressure to 10 mL and then transferred by syringe to the top of a Florisil column (2 × 8 cm) made up in benzene. Elution of the column with benzene resulted in the development of a single, orange-yellow band which was collected. Volatiles were removed from the eluate in vacuo, and the resulting oil was further purified by crystallization from CH_2Cl_2–hexanes to obtain 1.74 g (43% yield based on original $[CpW(NO)I_2]_2$) of pure $CpW(NO)IH[P(OPh)_3]$ as orange microcrystals.

The other, similarly colored complexes were isolated in yields of 42% (L = $P(OMe)_3$) and 40% (L = PPh_3).

Reaction of $CpW(NO)I_2[P(OPh)_3]$ with $Na[H_2Al(OCH_2CH_2OCH_3)_2]$. A stirred benzene suspension (50 mL) of $CpW(NO)I_2[P(OPh)_3]$[14] (1.0 g, 1.2 mmol) was treated with 0.35 mL (1.2 mmol) of a 3.4 M solution of $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ in toluene. The reaction mixture became brown, and a brown solid precipitated. The final mixture was treated with distilled water (0.04 mL) and filtered through a column (2 × 3 cm) of anhydrous $MgSO_4$ supported on a medium-porosity frit. The filtrate was taken to dryness in vacuo, and the resulting brown solid was transferred as a benzene slurry (10 mL) to the top of a Florisil column (2 × 4 cm) made up in benzene. Elution of the column with benzene resulted in the development of a single orange-yellow band which was collected. Removal of solvent from the eluate under reduced pressure and subsequent crystallization of the residue from CH_2Cl_2–hexanes afforded 0.20 g (23% yield) of $CpW(NO)IH[P(OPh)_3]$ as orange microcrystals.

Preparation of $CpW(NO)IH(PMe_3)$. Addition of neat PMe_3 (0.40 mL, 0.30 g, 4.0 mmol) to a solution of $[CpW(NO)IH]_2$ (generated as described above) caused an immediate color change to orange and the precipitation of a brown solid. The supernatant solution was filter cannulated away from the precipitate, and its

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[15] $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ was purchased as a 3.4 M solution in toluene from the Aldrich Chemical Co. under the trade name Red-Al.

Table II. NMR Data for the Complexes

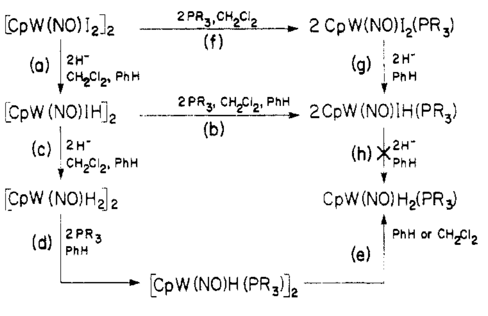
complex	solv	isomer	^{1}H data δ (*J*, Hz)			^{31}P data δ
			Cp	L[a]	W–H	
$CpW(NO)I_2[P(OPh)_3]$	$CDCl_3$		5.90 (d, 5, $^3J_{HP}$ = 3)	7.2 (br, 15)		
	C_6D_6		5.43 (d, 5, $^3J_{HP}$ = 3)	7.1 (br, 15)		
$CpW(NO)I_2[P(OMe)_3]$	$CDCl_3$		5.98 (d, 5, $^3J_{HP}$ = 2)	3.83 (d, 9, $^3J_{HP}$ = 11)		
	C_6D_6		5.43 (d, 5, $^3J_{HP}$ = 3)	3.45 (d, 9, $^3J_{HP}$ = 11)		
$CpW(NO)I_2(PPh_3)$	$CDCl_3$		5.91 (d, 5, $^3J_{HP}$ = 1.2)	7.5 (br, 15)		
	C_6D_6		5.26 (d, 5, $^3J_{HP}$ = 2)	7.1 (br, 15)		
$CpW(NO)I_2(PMe_3)$[b]	$CDCl_3$	A	5.94 (d, 5, $^3J_{HP}$ = 2.8)	1.90 (d, 9, $^3J_{HP}$ = 10.2)		
	C_6D_6	A	5.06 (d, 5, $^3J_{HP}$ = 2.8)	1.08 (d, 9, $^3J_{HP}$ = 10.2)		
		B	5.20 (s, 5)	1.54 (d, 9, $^3J_{HP}$ = 10)		
$CpW(NO)IH[P(OPh)_3]$	$CDCl_3$		5.25 (s, 5)	7.2 (br, 15)	−2.04 (d, 1, $^2J_{HP}$ = 112, $^1J_{HW}$ = 54)	
	C_6D_6		4.85 (s, 5)	7.1 (br, 15)	−2.06 (d, 1, $^2J_{HP}$ = 112, $^1J_{HW}$ = 54)	115
$CpW(NO)IH[P(OMe)_3]$	$CDCl_3$		5.81 (s, 5)	3.73 (d, 9, $^3J_{HP}$ = 12)	−1.44 (d, 1, $^2J_{HP}$ = 101, $^1J_{HW}$ = 57)	
	C_6D_6		5.12 (s, 5)	3.36 (d, 9, $^3J_{HP}$ = 12)	−1.41 (d, 1, $^2J_{HP}$ = 101, $^1J_{HW}$ = 57)	131
$CpW(NO)IH(PPh_3)$	$CDCl_3$		5.63 (s, 5)	7.4 (br, 15)	0.31 (d, 1, $^2J_{HP}$ = 85, $^1J_{HW}$ = 58)	
	C_6D_6		5.10 (s, 5)	7.4 (br, 15)	0.10 (d, 1, $^2J_{HP}$ = 85, $^1J_{HW}$ = 58)	14.1
$CpW(NO)IH(PMe_3)$	$CDCl_3$	A	5.60 (d, 5, $^3J_{HP}$ < 1)	1.87 (d, 9, $^3J_{HP}$ = 9.5)	−0.65 (d, 1, $^2H_{HP}$ = 84, $^1J_{HW}$ = 66)	
		B	5.73 (dd, 5, $^3J_{HP}$, $^3J_{HH}$ = 1.5, < 1)	1.80 (d, 9, $^3J_{HP}$ = 9.7)		
	C_6D_6	A	5.11 (s, 5)	1.39 (d, 9, $^3J_{HP}$ = 9)	−1.13 (d, 1, $^2J_{HP}$ = 84, $^1J_{HW}$ = 66)	
		B	4.80 (d, 5, *J* = 1.8)	1.20 (d, 9, $^3J_{HP}$ = 9.5)		
$CpW(NO)H_2[P(OPh)_3]$	$CDCl_3$		5.10 (s, 5)	7.3 (br, 15)	−1.82 (d, 1, $^2J_{HP}$ = 86, $^1J_{HW}$ = 88)	
	C_6D_6		4.69 (s, 5)	7.2 (br, 15)	−1.58 (d, 2, $^2J_{HP}$ = 87, $^1J_{HW}$ = 87)	137
$CpW(NO)H_2[P(OMe)_3]$	C_6D_6		5.17 (s, 5)	3.47 (d, 9, $^3J_{HP}$ = 12)	−1.74 (d, 2, $^2J_{HP}$ = 81, $^1J_{HW}$ = 87)	
$[CpW(NO)I_2]_2$	$CDCl_3$		6.30 (s)			
	C_6D_6		5.00 (s)			
$[CpW(NO)IH]_2$[c]	$CDCl_3$		6.21 (s, 10)		−1.21 (s, 2, $^1J_{HW}$ = 88.3, $^1J_{H'W}$ = 70.8, $^2J_{H'H}$ = 3.7)	
	C_6D_6		5.31 (s, 10)		−1.21 (s, 2)[d]	
$[CpW(NO)H_2]_2$[c]	$CDCl_3$	A	5.95 (s, 10)		H_A: 6.99 (m, 2, $^1J_{HW}$ = 95) H_X: −2.05 (m, 2, $^1/_2(^1J_{H_XW} + {}^1J_{H_X'W})$ = 93)	
		B	5.93 (s, 10)		H_A: 6.55 (dd, 2, $^1H_{H_AW}$ = 99, $^2J_{H_AH_M}$ = 3.0, $^2J_{H_AH_X}$ = 8.5) H_M: 1.39 (~q, 1, $^1J_{H_MW}$ = 92, $^2H_{H_MH_X}$ = 2.5) H_X: −5.94 (td, 1, $^1J_{H_XW}$ = 96)	
	C_6D_6[e]	A	5.23 (s, 10)		H_A: 7.01 (m, 2) H_X: −1.90 (m, 2)	
		B	5.26 (s, 10)		H_A: 6.64 (dd, 2) H_M: 1.66 (~q, 1) H_X: −5.99 (td, 1)	
$[CpW(NO)H\{P(OPh)_3\}]_2$	$CDCl_3$[f]		4.97 (s, 10)	7.4 (br, 30)	1.10 (m, 2)	
	C_6D_6		5.17 (d, 10, $^3J_{HP}$ = 1)	7.0 (br, 30)	1.32 (t, 2, $^2J_{HP}$ = 24, $^1H_{HW}$ = 55)	151 ($^1J_{PW}$ = 595)
$[CpW(NO)H\{P(OMe)_3\}]_2$	C_6D_6	A	5.23 (s, 10)	3.67 (d, 18, $^3J_{PH}$ = 12)	0.82 (t, 2, $^2J_{HP}$ = 24, $^1J_{HW}$ = 53)	
		B	5.60 (d, 10, $^3J_{HP}$ = 1)	3.55 (d, 18, $^3J_{HP}$ = 12)	0.84 (t, 2, $^2J_{HP}$ = 26, $^1J_{HW}$ = 54)	

[a] L = phosphine or phosphite on W. [b] In $CDCl_3$, $CpW(NO)I_2(PMe_3)$ exists exclusively as isomer A. [c] See text for a complete discussion of the ^{1}H NMR spectrum of this complex. [d] $[CpW(NO)IH]_2$ is not sufficiently soluble in C_6D_6 to permit resolution of the ^{183}W satellites. [e] Couplings not as well resolved as in $CDCl_3$. [f] Couplings not resolved in $CDCl_3$.

volume was diminished to 50 mL under reduced pressure. Hexanes (60 mL) were added, and the resulting solution was further concentrated to 40 mL and let stand overnight. This resulted in the formation of a light brown, microcrystalline precipitate which was collected by filtration and washed with hexanes (5 × 10 mL) to obtain 0.98 g (36% yield based on original $[CpW(NO)I_2]_2$) of a solid which analyzed as $CpW(NO)IH(PMe_3)$.

Preparation of $[CpW(NO)H_2]_2$. The stirred, dark green filtrate containing $[CpW(NO)IH]_2$ (vide supra) was treated dropwise with a 3.4 M toluene solution of $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ until the green color just disappeared (~0.7 mL). The final reaction mixture consisted of a large amount of a fine, brown precipitate and a dark red-brown supernatant solution. The mixture was then rapidly filtered through a 3 × 4 cm column of Celite supported on a medium-porosity glass frit, and the column was washed with benzene (2 × 15 mL). The resulting red-brown filtrate was concentrated under reduced pressure to ~10 mL and let stand for several hours, whereupon a powdery, orange precipitate formed. The powder was collected by filtration, washed with benzene (3 × 5 mL), and dried in vacuo (5 × 10^{-3} mm) to obtain 0.16 g (10% yield based on original $[CpW(NO)I_2]_2$) of analytically pure $[CpW(NO)H_2]_2$. This powder could be converted

Scheme I



where R = Me, Ph, OMe, or OPh

to small, well-formed crystals by recrystallization from toluene at −25 °C.

Preparation of [CpW(NO)H{P(OPh)$_3$}]$_2$ and CpW(NO)H$_2$[P(OPh)$_3$]. A mixture of [CpW(NO)H$_2$]$_2$ (0.10 g, 0.18 mmol) and benzene (30 mL) was stirred and warmed with a warm water bath (~50 °C) until a clear, orange solution resulted (~10 min). To this solution was added neat P(OPh)$_3$ (93 μL, 0.35 mmol); the resulting solution was stirred at room temperature for 6 h, during which time it developed a very intense, purple coloration. Solvent was removed from the final mixture in vacuo, and the purple, oily residue was crystallized from benzene–hexanes to obtain 0.086 g (41% yield) of [CpW(NO)H{P(OPh)$_3$}]$_2$ as purple microcrystals which were isolated by filtration in the usual manner (vide supra).

A portion of the purple crystals was dissolved in CH$_2$Cl$_2$ (10 mL), and the resulting solution was stirred for 3 h whereupon it became orange. Addition of hexanes (15 mL) to this solution induced the precipitation of a small amount of analytically pure CpW(NO)H$_2$[P(OPh)$_3$] as an orange powder which was collected in the customary fashion.

Results and Discussion

The interrelationships between the compounds investigated during the present study are summarized in Scheme I. The preparation and characterization of each of the hydrido nitrosyl complexes contained in this scheme shall now be considered in some detail.

Preparation of [CpW(NO)IH]$_2$. As we reported earlier,[10] [CpW(NO)IH]$_2$ may be synthesized by the treatment of [CpW(NO)I$_2$]$_2$ with an equimolar amount of Na[H$_2$Al(OCH$_2$CH$_2$OCH$_3$)$_2$] in CH$_2$Cl$_2$–benzene (step a of Scheme I), i.e., eq 1. We have now discovered that the

$$[\mathrm{CpW(NO)I_2}]_2 \xrightarrow[\mathrm{CH_2Cl_2\text{-}PhH}]{\mathrm{Na[H_2Al(OCH_2CH_2OCH_3)_2]}} [\mathrm{CpW(NO)IH}]_2 \tag{1}$$

hydrido nitrosyl product of this conversion may be isolated as analytically pure, dark green microcrystals in 35% yield by filtration of the final reaction mixture through Celite and subsequent concentration of the filtrate in vacuo. Several features of reaction 1 merit special mention. First, the reaction and separation of products must be effected as quickly as possible in order to obtain optimum yields of [CpW(NO)IH]$_2$ since the desired transformation is also accompanied by the formation of brown byproducts which appear to catalyze the decomposition of the hydrido nitrosyl product. Second, the stoichiometry of the reagents is important since Na[H$_2$Al(OCH$_2$CH$_2$OCH$_3$)$_2$] reacts further with [CpW(NO)IH]$_2$ (vide infra). Third, the mixed solvent system specified is necessary, the presence of the CH$_2$Cl$_2$ facilitating the solubilization of both the nitrosyl reactant and product. Furthermore, if reaction 1 is attempted in benzene alone, the yield of the desired product is diminished; and if pure CH$_2$Cl$_2$ is used as the solvent, the isolated organometallic product is contaminated with NaI. Finally, if [CpW(NO)IH]$_2$ is obtained in an impure state, it is prone to undergo rapid decomposition both in solution and in the solid state to a brown, intractable solid.[10]

Pure [CpW(NO)IH]$_2$ is an intensely colored, dark green solid which is thermally stable at room temperature in the solid state. As a solid, it may also be handled in air for short periods of time without the occurrence of noticeable decomposition. The complex is only slightly soluble in nondonor solvents to produce air-sensitive solutions, its solubility increasing in the order hexanes, Et$_2$O (insoluble) < toluene < benzene < CH$_2$Cl$_2$. The resulting solutions are intensely green in color and appear red to transmitted light. Donor solvents, however, appear to cleave the dimer after initial solubilization (cf. step b of Scheme I) with $t_{1/2} \simeq$ 20 min in THF, i.e., eq 2. In solvents in which it retains

$$\begin{array}{ll} [\mathrm{CpW(NO)IH}]_2 + 2\mathrm{THF} \rightarrow & 2\mathrm{CpW(NO)IH(THF)} \qquad (2) \\ \text{green; initial } \nu_{\mathrm{NO}} & \text{orange; final } \nu_{\mathrm{NO}} \\ = 1650\ \mathrm{cm^{-1}} & = 1632\ \mathrm{cm^{-1}} \end{array}$$

its dimeric nature, [CpW(NO)IH]$_2$ is also much less thermally stable than as a solid thereby precluding its recrystallization. For instance, over the course of 3 days at room temperature, an initially green C$_6$D$_6$ solution of the compound slowly deposits the ubiquitous, brown intractable solid. Analysis of the final, colorless supernatant liquid by ^{1}H NMR (a sharp singlet at δ 1.50) and GC–MS[16] confirms the complete consumption of the hydrido nitrosyl complex and reveals the presence of undeuterated cyclopentane, C$_5$H$_{10}$, in ~60–70% yield (based on the available hydride H atoms) as the principal organic product. Evidently, this decomposition product results from the autohydrogenation by [CpW(NO)IH]$_2$ of its cyclopentadienyl ligands. This mode of decomposition contrasts with that exhibited by its unisolable molybdenum congener which apparently evolves H$_2$ in solution and converts to the well-known [CpMo(NO)I]$_2$.[10] [The tungsten analogue of this latter complex has yet to be prepared.]

Spectroscopic Properties of [CpW(NO)IH]$_2$. The dimeric nature of the complex is confirmed by its low-resolution mass spectrum (probe temperature 130 °C) which displays peaks attributable to the parent ion (*m/z* 814, ^{184}W) and ions arising from the sequential loss of ligands. Unfortunately, overlapping of some medium to strong intensity peaks in the lower mass range makes unambiguous assignments difficult, especially in light of the polyisotopic nature of tungsten.

IR spectra of [CpW(NO)IH]$_2$, either as a concentrated Nujol mull or as a CH$_2$Cl$_2$ solution, display strong absorptions attributable to terminal NO groups (e.g., 1646 cm^{-1} in CH$_2$Cl$_2$) but are devoid of absorptions characteristic of terminal W–H linkages.[8] [Bands due to bridging ν_{WH} are expected to be very weak.][17] The ^{1}H NMR spectrum of the complex in CDCl$_3$ (Table II), particularly the hydride region (Figure 1), exhibits several interesting features. The hydride region consists of a singlet surrounded by two AA′X quartets, due to coupling to ^{183}W ($I = {}^1/_2$, natural abundance 14.4%), whose combined area integrates to ~25% of the total hydride resonance. [The coupling constants presented in Table II were calculated by using the conventional algebraic equation.][18] Furthermore, if the ^{1}H NMR spectrum is recorded under customary Fourier transform conditions of ~2.5 s between pulses, the relative intensities of the C$_5$H$_5$:W–H resonances are 3.5:1 rather than the expected 5:1. At first glance, this feature is somewhat surprising since it is well-known that

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(16) This GC–MS experiment utilized a 30-m Carbowax capillary column at 1 °C.

(17) Reference 4, p 64.

(18) Becker, E. D. "High Resolution NMR", 2nd ed.; Academic Press: New York, 1980; Chapter 7.

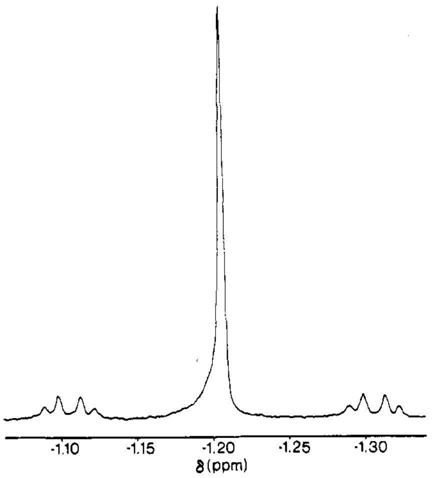


Figure 1. The hydride region of the 400-MHz ^1H NMR spectrum of $[CpW(NO)IH]_2$ in $CDCl_3$.

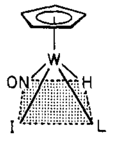
M–H signals have lengthy relaxation times.[19] Consequently, we performed a T_1 experiment[20] and so discovered that the T_1 for the C_5H_5 resonance is 15.3 s whereas that for the W–H resonance is 2.74 s. Reports of such a relatively long relaxation time for cyclopentadienyl protons are uncommon, only one previous mention of this phenomenon having appeared in the chemical literature.[21] Nevertheless, we have found analogously low integrations for most of the C_5H_5 resonances in the ^1H NMR spectra of the complexes investigated during this study when a suitable delay between pulses was not employed (Table II). T_1 values were not measured for any of the other compounds.

Obviously, both the IR and ^1H NMR spectra of $[CpW(NO)IH]_2$ convey important information about the molecular structure of this dimeric complex. However, we defer a detailed discussion of this matter until after the physical properties of some other, related complexes have been delineated.

Complexes CpW(NO)IHL (L = Phosphine or Phosphite). Treatment of green solutions of $[CpW(NO)IH]_2$ with 2 equiv of a phosphine or a phosphite results in a rapid color change to orange as the virtually quantitative transformation (eq 3) occurs (i.e., step b of Scheme I). When L = $P(OPh)_3$, $P(OMe)_3$, or PPh_3, the product complexes can be isolated by chromatography of the final reaction mixtures on Florisil and subsequent crystallization from CH_2Cl_2–hexanes (in yields of ~40% based on the original $[CpW(NO)I_2]_2$ employed to generate $[CpW(NO)IH]_2$ according to reaction 1). The CpW(NO)IHL compounds are also obtainable by treatment of the appropriate diiodo precursor with an equimolar amount of $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ in benzene (i.e., step g of Scheme I), but the overall yields of the desired products are significantly lower. For instance, when L = $P(OPh)_3$, the isolated yield of $CpW(NO)IH[P(OPh)_3]$ via steps a and b of Scheme I is 43%, whereas via steps f and g it is only 19%. Curiously, further treatment of the CpW(NO)IHL species with $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ results in no reaction (i.e., step h of Scheme I). Consequently, the $CpW(NO)H_2(PR_3)$ complexes are presently only accessible via step e, a process which is considered later in detail.

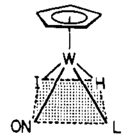
$$[CpW(NO)IH]_2 + 2L \xrightarrow{CH_2Cl_2\text{–}PhH} 2CpW(NO)IHL \qquad (3)$$

The organometallic products of reaction 3 are orange, diamagnetic solids which are stable in air for short periods of time. They are quite soluble in polar organic solvents, but only sparingly soluble in nonpolar ones, to give moderately air-sensitive solutions. Their spectral properties are consistent with their possessing monomeric "four-legged piano stool" molecular structures with terminal W–NO and W–H bonds. Thus, their low-resolution mass spectra (probe temperatures ~100 °C) display peaks corresponding to the parent ions P^+, $(P - I)^+$, and $(P - L)^+$. Their IR spectra exhibit ν_{NO}'s in the region 1643–1615 cm^{-1} (Table I) with the frequency decreasing, as expected, as the documented[22] electron-donating ability of L increases, i.e., L = $P(OPh)_3 < P(OMe)_3 < PPh_3 < PMe_3$. Furthermore, weak absorptions assignable[4] to terminal ν_{WH} are also observable at ~1900 cm^{-1} in these spectra. Interestingly, these latter stretching frequencies increase as the electron-donating ability of L increases (Table I), thereby reflecting a concomitant increase in the strength of the W–H linkages. The ^1H NMR spectra of these complexes in $CDCl_3$ or C_6D_6 (Table II) reveal the presence of only one isomer in solution, the singlet C_5H_5 resonance and the relatively large $^2J_{^1H-^{31}P}$ values observed being indicative[23] of a cis orientation of the L and H ligands in the metal's coordination sphere, i.e.,[24] I and II. In addition to coupling to ^{31}P, the hydride resonances also exhibit coupling to ^{183}W, these latter satellites integrating to the expected 15% of the total intensity of the hydride signal. There is no correlation between the chemical shifts of the C_5H_5 or the W–H resonances in these ^1H NMR spectra and the electron-donating abilities of L (including PMe_3, vide infra). This feature is in accord with Darensbourg's observations on the spectroscopic properties of the $[HW(CO)_4(PR_3)]^-$ anions.[25] However, as summarized in Table II, the values of $^1J_{^1H-^{183}W}$ do increase and those of $^2J_{^1H-^{31}P}$ do decrease as the electron-donating ability of L increases. These trends contrast with those found for $[HW(CO)_4(PR_3)]^-$ for which $^2J_{^1H-^{31}P}$ values were found to correlate with the steric, rather than the electronic, properties of the phosphine, and no trend in $^1J_{^1H-^{183}W}$ values was observed.[25] On the basis of all these data, it is not possible to determine whether the NO ligand in the CpW(NO)IHL complexes is situated trans to L (structure I)[24] or trans to H (structure II).[24] Such a distinction must await a single-crystal X-ray diffraction analysis of one of these compounds.



I

or



II

When L in reaction 3 is PMe_3, the situation is slightly more complicated than with the other L's just considered. The $CpW(NO)IH(PMe_3)$ product is formed as a mixture

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[19] Jesson, J. P. In "The Hydrogen Series. Vol. 1. Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; Chapter 4, p 79.

[20] T_1 measurements were made on a modified Nicolet-Oxford H-270 spectrometer using a 180°–τ–90° pulse sequence. The absolute signal intensities were processed by standard Nicolet software to obtain the T_1 values.

[21] Adam, M. J.; Hall, L. D. *J. Organomet. Chem.* **1980**, *186*, 289.

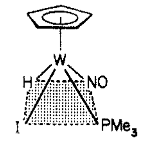
[22] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313 and references therein.

[23] Kalck, P.; Poilblanc, R. *J. Organomet. Chem.* **1970**, *24*, 445 and references therein.

[24] Since the W atom in the CpW(NO)IHL compounds is a chiral center, the molecular structures drawn represent only one of two possible enantiomers.

[25] Slater, S. G.; Luck, R.; Schumann, B. F.; Darensbourg, M. *Organometallics* **1982**, *1*, 1662.

of isomers (designated by A and B in Tables I and II). One of the isomers (A) is isolable in 11% yield by employing the procedure described above for the other CpW(NO)IHL complexes. Fractional crystallization of the final reaction mixture, on the other hand, affords an analytically pure, light brown mixture of the two isomers in 36% yield. The spectroscopic properties of pure isomer A indicate that it is isostructural with the other CpW(NO)IHL compounds. Comparison of the IR spectrum of the isomeric mixture in CH_2Cl_2 with that of pure A alone (Table I) reveals (a) a broadening of the nitrosyl stretching absorption and its slight shift to lower frequency and (b) the appearance of a new ν_{WH} at 1898 cm^{-1}. The ^1H NMR spectrum of the isomeric mixture in C_6D_6 displays separate resonances for the two isomers, the initial ratio of A:B being ~5:1. In particular, the C_5H_5 resonance for isomer B in this spectrum consists of a doublet of doublets resulting from coupling of the signal to both the hydride hydrogen and the phosphorus atom of the PMe_3 ligand. These observations suggest[23] that in isomer B the H and PMe_3 ligands are mutually trans, i.e.[24]



Curiously, however, no distinct resonance attributable to the hydride atom of isomer B is evident in the ^1H NMR spectrum of the mixture of isomers.

In closing this section, it is informative to compare the properties of all the CpW(NO)IHL complexes with those exhibited by the analogous $CpW(CO)_2HL$[23] and $CpW(NO)I_2L$[14] series. The first, and most striking, difference between the CpW(NO)IHL and $CpW(CO)_2HL$ compounds is their ease of isomerization. The carbonyl complexes undergo such rapid cis–trans isomerization is solution that the individual isomers cannot be isolated independently.[23] The CpW(NO)IHL complexes are, as we have seen, generally preparable as only the cis isomers, and no isomerization occurs in solution under ambient conditions. In the one case when mixtures of isomers can be prepared (i.e., when L = PMe_3), the trans isomer undergoes spontaneous isomerization to the cis form over the course of a week in $CDCl_3$ at 20 °C. Similarly, preparation of the $CpW(NO)I_2L$ complexes according to step f of Scheme I, i.e., eq 4, results in only one isomer when L = $P(OPh)_3$,

$$[CpW(NO)I_2]_2 + 2L \xrightarrow{CH_2Cl_2} 2\ CpW(NO)I_2L \quad (4)$$

$P(OMe)_3$, or PPh_3. Again, when L = PMe_3, two isomers (A and B in Table II) are formed in the ratio of ~5:1. In this case, however, isomer B is even less thermodynamically stable than in the case of $CpW(NO)IH(PMe_3)$, converting into A upon dissolution in $CDCl_3$ and somewhat more slowly in C_6D_6.

The second difference between these carbonyl and nitrosyl complexes is that the hydride resonances in the ^1H NMR spectra of the CpW(NO)IHL compounds appear at much lower field (i.e., by 6–8 ppm) than the corresponding signals due to their $CpW(CO)_2HL$ analogues. Indeed, the hydride resonances of all the hydrido nitrosyl complexes investigated during this study are much less shielded than is customary for middle and late transition-metal hydrides.[26,27] This may well be a manifestation of the strong electron-accepting ability of NO ligands.[28]

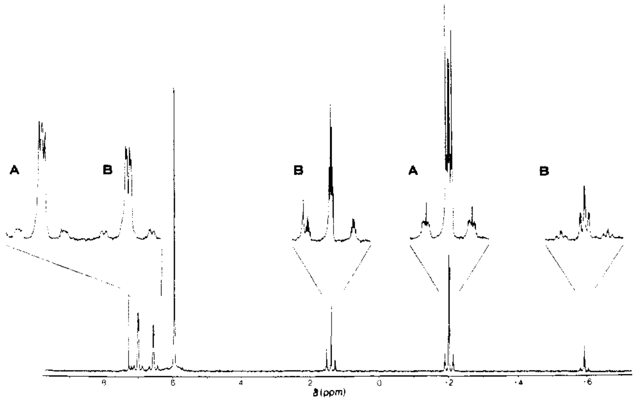


Figure 2. The 400-MHz ^1H NMR spectrum of $[CpW(NO)H_2]_2$ in $CDCl_3$.

A comparison of the IR data summarized in Table I reveals another trend of interest. When one of the I atoms in $CpW(NO)I_2L$ is replaced by an H atom, ν_{NO} diminishes by 20–25 cm^{-1}. This fact probably reflects the lower electronegativity of the H atom and the correspondingly greater electron density available on the metal center of the hydrido nitrosyl complexes for back-bonding to the NO ligands. However, no trend in the chemical shifts of the ^1H NMR signals due to the cyclopentadienyl protons is apparent when this ligand replacement is effected (Table II).

Synthesis and Properties of $[CpW(NO)H_2]_2$. As step c of Scheme I indicates, further treatment of green $[CpW(NO)IH]_2$ with an equimolar amount of $Na[H_2Al(OCH_2CH_2OCH_3)_2]$ in CH_2Cl_2–benzene results in the formation of orange $[CpW(NO)H_2]_2$, i.e., eq 5. For practical pur-

$$[CpW(NO)IH]_2 \xrightarrow[CH_2Cl_2\text{–}PhH]{Na[H_2Al(OCH_2CH_2OCH_3)_2]} [CpW(NO)H_2]_2 \quad (5)$$

poses, reaction 5 is best effected as outlined in the Experimental Section by utilizing the $[CpW(NO)IH]_2$ generated in situ by reaction 1. For reasons analogous to those described for reaction 1 (vide supra), similar care concerning manipulative details, stoichiometry of reagents, and choice of solvents must be exercised in order to obtain optimum (albeit rather low) yields of $[CpW(NO)H_2]_2$ from this transformation. The dihydrido nitrosyl dimer isolated from the final reaction mixture is an orange powder which may be rendered microcrystalline by recrystallization from toluene at −25 °C. Pure $[CpW(NO)H_2]_2$ is a diamagnetic solid which is stable in air for short periods of time and is remarkably thermally stable, remaining unchanged even when maintained at 100 °C under N_2 for 15 h. Its solubility properties are very similar to those exhibited by $[CpW(NO)IH]_2$. Furthermore, like $[CpW(NO)IH]_2$, the dihydride dimer undergoes decomposition during 1 week in $CDCl_3$ at room temperature with concomitant formation of cyclopentane. Interestingly, however, C_6D_6 solutions of $[CpW(NO)H_2]_2$ show no evidence of decomposition even after several weeks under identical conditions.

The IR spectrum of $[CpW(NO)H_2]_2$ in CH_2Cl_2 exhibits a strong ν_{NO} at 1599 cm^{-1} and a much weaker terminal ν_{WH} at 1906 cm^{-1}, the latter feature contrasting with the

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(26) (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231. (b) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889 and references therein.

(27) Low-field ^1H NMR resonances are generally characteristic of hydrido complexes of the early transition metals; see, for example: (a) Belmonte, P. A.; Schrock, R. R.; Day, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 3082. (b) Gell, K. J.; Posin, B.; Schwartz, J; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846 and references therein.

(28) Chen, H. W.; Jolly, W. L.; Xiang, S.-F.; Legzdins, P. *Inorg. Chem.* **1981**, *20*, 1779 and references therein.

analogous spectrum of $[CpW(NO)IH]_2$ which does not display such an absorption. The low-resolution mass spectrum (probe temperature 120 °C) of $[CpW(NO)H_2]_2$ is consistent with its dimeric formulation, exhibiting peaks corresponding to the parent ion (m/z 562, ^{184}W) and ions arising from the sequential loss of ligands. However, the ^1H NMR spectra of the complex (Table II and Figure 2), particularly in $CDCl_3$,[29] provide the most information about its molecular structure. The $CDCl_3$ spectrum reveals the existence of two isomers (A and B) in solution, the isomer ratio A:B being ~1.3:1 at 35 °C. The assignments of the observed resonances to the individual isomers (as shown in Figure 2 and tabulated in Table II) have been confirmed by a series of homonuclear decoupling experiments. Exclusive of the ^{183}W satellites, isomers A and B exhibit AA′XX′ and A_2MX patterns, respectively, which are attributable to their hydride ligands. Analysis of these splitting patterns on this basis[18] permits calculation of all the coupling constants for isomer B. However, analogous data cannot be extracted for isomer A since some of the signals required to solve the AA′XX′ system are not resolved. Indeed, the only significant coupling constants that can be determined for isomer A are $^1J_{H_AW}$ (H_A = terminal hydride) and $^1/_2(^1J_{H_XW}) + {}^1J_{H_{X'}W})$.

One final point about the ^1H NMR spectra of $[CpW(NO)H_2]_2$ may be made in passing. Both isomers A and B of this compound exhibit one set of hydride resonances at relatively low field (e.g., δ 6.99 for A and δ 6.55 for B in $CDCl_3$). Indeed, this is considerably lower than the fields at which the hydride signals due to the various CpW(NO)IHL complexes occur (cf. Table II). To the best of our knowledge, only the recently reported[30] $W(CHCMe_3)(H)Cl_3(PMe_3)_2$ displays a larger positive chemical shift (δ 9.88 in $CDCl_3$) for a tungsten hydride resonance.

Molecular Structures of $[CpW(NO)H_2]_2$ and $[CpW(NO)IH]_2$. Numerous possible molecular structures of $[CpW(NO)H_2]_2$ having different configurations of bridging and terminal hydride ligands can be envisaged. The ^1H NMR spectrum of this complex in $CDCl_3$ (Figure 2), however, clearly indicates that each of the isomers A and B possesses two bridging and two terminal H atoms. Specifically, the chemical shifts of the hydride resonances assigned to each isomer and their respective ^{183}W satellites confirm this fact. It has been previously noted[26] that in molecules of this kind the resonances for bridging hydrides occur at higher field than those for terminal hydrides.[31] Consequently, the low-field hydride signals for each isomer (which have a relative intensity of 2) may be attributed to terminal W–H linkages, and the remaining hydride signals may be attributed to three-center, two-electron $\overbrace{W\text{–}H\text{–}W}$ linkages. This assignment has been confirmed by careful integration of the ^{183}W satellites associated with each hydride signal which reveals that these satellites represent ~28% of the total areas for each of the bridging H peaks centered at δ 1.39, −2.05, and −5.94 whereas they only represent ~16% of the total areas for each of the terminal H peaks centered at δ 6.99 and 6.55. In a binuclear system, the relative proportions of isotopomers containing zero, one, and two ^{183}W nuclei (14.4% natural abundance) is 73.3:24.7:2.1.[32] Hence, the three higher field hydride resonances are due to H atoms that show almost equal (and large) coupling to a ^{183}W nucleus when it is at *either* metal center. On the other hand, the two lower field hydride resonances only show coupling to a ^{183}W nucleus (with large, one-bond coupling constants of 90–100 Hz) when it is at *only one* of the two metal centers. Kaesz and co-workers have found that for $Cp_2H_2W\text{–}W(CO)_5$, $^2J_{HW}$ = 19.2 Hz;[33] with this in mind, shoulders on the two low-field resonances may be attributed to two-bond, tungsten–hydrogen coupling across the $H\text{—}W\text{=}^{183}W$ system, with $^2J_{HW}$ ≃ 13 and ≃15 Hz for isomers A and B, respectively. This attribution is also consistent with the absence of such shoulders on the three upfield resonances due to the bridging hydrides, for which such a two-bond coupling is not possible.

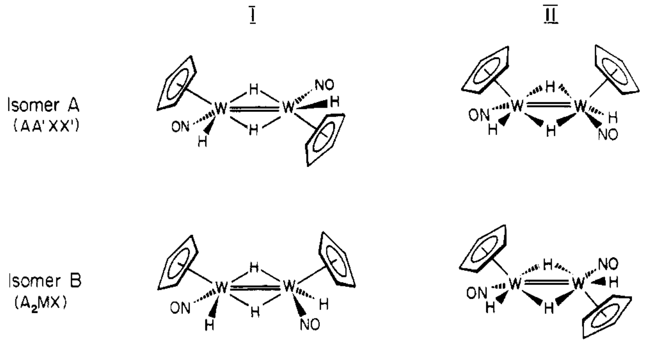

Figure 3. Possible molecular structures of $[CpW(NO)H]_2(\mu\text{-}H)_2$.

On the basis of this evidence, we therefore formulate $[CpW(NO)H_2]_2$ as $[CpW(NO)H]_2(\mu\text{-}H)_2$ and suggest the possible molecular structures shown in Figure 3. As indicated, all structures contain the two bridging and two terminal hydride ligands as well as a formal tungsten–tungsten double bond so that each metal center may attain the favored 18-valence-electron configuration. Obviously, diastereomers and enantiomers of the molecular arrangements depicted in Figure 3 would also be in accord with the spectroscopic properties considered above. Inspection of the indicated structures reveals that they are all closely related. For instance, structure AI may be formally converted into BI (or AII into BII) by a 180° rotation of one end of the molecule about the W=W axis, and AI may be converted into BII (or BI into AII) by a 90° rotation of the two bridging H atoms out of the Cp—W=W—Cp plane. In solution at 35 °C, however, no such interconversions occur on the NMR time scale, and both isomers A and B are stereochemically rigid. This fact apparently reflects the strength of the $\underbrace{H\text{—}\overbrace{W\text{=}W}\text{—}H}$ linkage. Exactly which of the isomeric structures shown in Figure 3 exist in the solid state of this complex remains unknown at present since we have not yet succeeded in growing sufficiently large crystals of $[CpW(NO)H]_2(\mu\text{-}H)_2$ for X-ray crystallographic analysis.

The $\underbrace{H\text{—}\overbrace{W\text{=}W}\text{—}H}$ linkage invoked for the dihydridonitrosyl dimer is not without precedents in the chemical literature, having been demonstrated crystallographically by Churchill[34] for $[(\mu\text{-}H)_2W_2(CO)_8]^{2-}$ and having been proposed by Alt[35] for $[CpW(CO)_2]_2(\mu\text{-}H)_2$. In the latter

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(29) Similar, but less well-resolved, features are also evident in the ^1H NMR spectrum of $[CpW(NO)H_2]_2$ in C_6D_6, a solvent in which the dimeric complex is less soluble than in $CDCl_3$.

(30) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739.

(31) For instance, the bridging hydride resonance of $[(\mu\text{-}H)W_2(CO)_8\{P(OMe)_3\}_2]^-$ in CD_3CN occurs at δ −11.8 whereas the terminal hydride resonance of $[HW(CO)_4P(OMe)_3]^-$ in CD_3CN occurs at δ −4.5.[25]

(32) Since the isotopomer with two ^{183}W nuclei is so scarce (and was never observed in these complexes due to their low solubility), the expected relative proportions of isotopomers having zero and one ^{183}W nucleus would be 74.8:25.2.

(33) Deubzer, B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1968**, *90*, 3276.

(34) Churchill, M. R.; Chang, S. W. Y. *Inorg. Chem.* **1974**, *10*, 2413.

(35) Alt, H. G.; Mahmoud, K. A.; Rest, A. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 544.

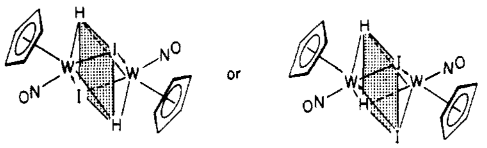
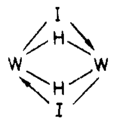


Figure 4. Possible molecular structures of $[CpW(NO)]_2(\mu\text{-}I)_2(\mu\text{-}H)_2$.

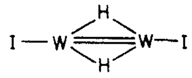
case, the structural proposal was also based on ^1H NMR evidence as the ^{183}W satellites of the hydride resonance were found to be 24% of the total signal intensity. Our observations on the valence isoelectronic $[CpW(NO)H]_2(\mu\text{-}H)_2$ support this proposal.

Mindful of the spectral properties of $[CpW(NO)H]_2(\mu\text{-}H)_2$, we turn now to a consideration of the molecular structure of $[CpW(NO)IH]_2$. As shown in Figure 1, the ^1H NMR spectrum of this complex in $CDCl_3$ exhibits a hydride resonance having ^{183}W satellites of ~25% intensity. In addition, these satellites are two AA′X quartets, a feature indicative of the complex retaining its dimeric nature in solution. Since multibond hydrogen–tungsten coupling is known to be small[36] (with $^2J_{HW}$ = 19.2 Hz being the largest such coupling constant yet reported),[33] our observation of strong H–W coupling in the ^1H NMR spectrum of $[CpW(NO)IH]_2$ (i.e., $^1J_{HW}$ = 88.3 Hz, $^1J_{HW'}$ = 70.8 Hz) along with the intensity of the ^{183}W satellites leads us to reformulate this complex as $[CpW(NO)]_2(\mu\text{-}I)_2(\mu\text{-}H)_2$ and to suggest the possible molecular structures shown in Figure 4.[37] This type of bimetallic structure with both bridging hydride and halide anions is relatively rare, having been confirmed crystallographically only for $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2$.[38] Such a formulation for the hydrido iodo dimer also accounts for the absence of an absorption attributable to terminal W–H linkages in its IR spectrum.

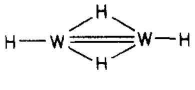
We formulate the complex as having a



bridging system rather than



linkages on the basis of its reactivity with Lewis bases. Its reactions with phosphines and phosphites are rapid at ambient temperatures and lead to symmetrical cleavages of the dimer (cf. reaction 3). In other words, they closely resemble the analogous transformations of $[CpW(NO)I]_2(\mu\text{-}I)_2$ (reaction 4). In contrast, the reaction of phosphite with the



linkage in $[CpW(NO)H]_2(\mu\text{-}H)_2$ is much slower and follows a markedly different pathway (vide infra). The thermal instability of $[CpW(NO)]_2(\mu\text{-}I)_2(\mu\text{-}H)_2$ in solution has so far precluded its isolation as crystals suitable for X-ray analysis.

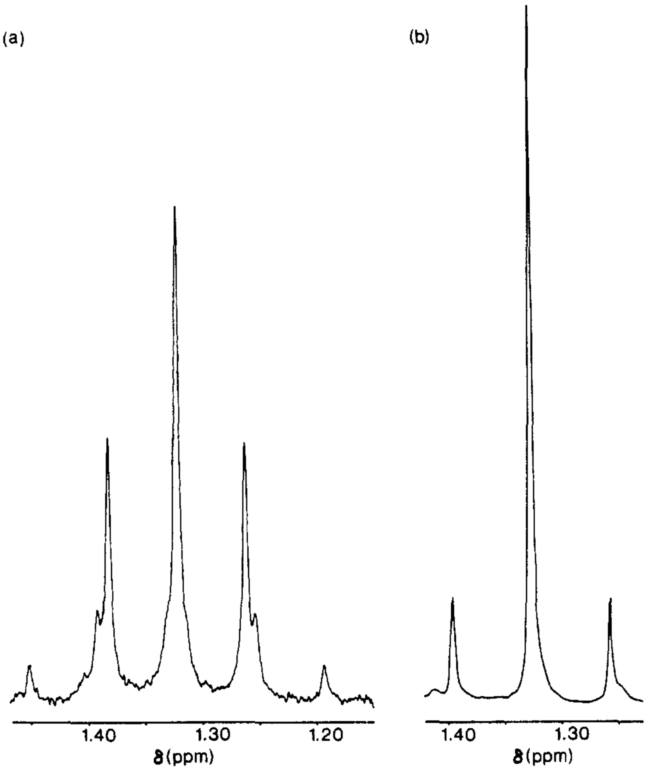


Figure 5. The hydride regions of the 400-MHz (a) ^1H and (b) $^1H\{^{31}P\}$ FT NMR spectra of $[CpW(NO)H\{P(OPh)_3\}]_2$ in C_6D_6.

Reactions of $[CpW(NO)H]_2(\mu\text{-}H)_2$ with PR_3 (R = OPh or OMe). Upon the addition of 2 equiv of $P(OPh)_3$ to a benzene solution of $[CpW(NO)H]_2(\mu\text{-}H)_2$ at room temperature, the reaction mixture gradually changes in color from orange to intense purple as the transformation (eq 6) occurs (i.e., step d of Scheme I). The organometallic

$$[CpW(NO)H_2]_2 + 2P(OPh)_3 \xrightarrow{PhH} [CpW(NO)H\{P(OPh)_3\}]_2 + H_2 \quad (6)$$

product of reaction 6 can eventually be isolated as a purple, microcrystalline solid in 41% yield. This solid may be handled in air for short periods of time without any detrimental effects, and it is moderately soluble in most common organic solvents to produce purple, air-sensitive solutions.

The IR spectrum of $[CpW(NO)H\{P(OPh)_3\}]_2$ in CH_2Cl_2 exhibits a strong ν_{NO} at 1591 cm^{-1} (which is very similar to that of the dihydride dimer, i.e., 1599 cm^{-1}) but no absorption that may be attributed to a terminal ν_{WH}. The ^1H NMR spectrum of the complex in C_6D_6 contains the customary signals due to the protons of the phosphite and cyclopentadienyl ligands (Table II) and, more importantly, just one complex multiplet attributable to the hydride hydrogens (Figure 5a). Careful integration of this spectrum, recorded with a sufficient delay between pulses to permit the cyclopentadienyl resonances to relax properly, verifies that the C_5H_5:W–H ratio is indeed 5:1. The appearance of the hydride resonance in the analogous $^1H\{^{31}P\}$ NMR spectrum (Figure 5b) establishes the magnitude of $^1J_{^1H-^{183}W}$ as 55 Hz. This fact permits the assignment of the complex multiplet shown in Figure 5a as a doublet (due to ^1H–^{183}W coupling) of triplets superimposed on a 1:2:1 triplet (due to ^1H–^{31}P coupling, $^2J_{^1H-^{31}P}$ = 24 Hz). Intergration of either of the hydride signals shown in Figure 5 reveals the ^{183}W satellites to constitute ~25% of the total signal intensity. Finally, the ^{31}P NMR spectrum of $[CpW(NO)H\{P(OPh)_3\}]_2$ in C_6D_6, recorded with only the phosphite protons decoupled, consists of a 1:2:1 triplet ($^2J_{^{31}P-^1H}$ = 24 Hz) which suggests coupling to two equivalent hydride hydrogens situated trans to the phosphite phosphorus atoms.[23]

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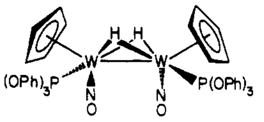
[36] Kidd, R. G.; Goodfellow, R. J. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; Chapter 8.

[37] Our original formulation of this compound as having only bridging iodides[10] was based on incomplete spectral evidence.

[38] Sattelberger, A. P.; Wilson, R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7111.

Taken together, the spectroscopic properties of $[CpW(NO)H\{P(OPh)_3\}]_2$ confirm its dimeric nature and indicate $[CpW(NO)\{P(OPh)_3\}]_2(\mu\text{-}H)_2$ it is best formulated as $[CpW(NO)\{P(OPh)_3\}]_2(\mu\text{-}H)_2$. A plausible molecular structure for this complex is as depicted in III, an arrangement which may be considered to involve two approximately octahedrally coordinated metal centers sharing a common face of their coordination polyhedra. The single W–W bond is invoked to provide each metal with an 18-valence-electron configuration. The two phosphite ligands are shown as being trans to each other since molecular models of this compound suggest that a cis configuration of the $P(OPh)_3$ groups would be very unfavorable on steric grounds. In solution, however, the two hydride ligands must be interchanging rapidly on the NMR time scale so as to maintain, on average, a trans orientation with respect to both phosphorus atoms.



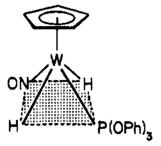
III

As summarized in step e of Scheme I, when a purple solution of $[CpW(NO)H_2[P(OPh)_3]_2(\mu\text{-}H)_2$ is stirred at room temperature (for a few days in benzene or a few hours in CH_2Cl_2), it gradually becomes orange. The addition of hexanes to the final solution induces the precipitation of a small amount of $CpW(NO)H_2[P(OPh)_3]$ as an analytically pure, orange powder. This complex evidently results from a disproportionation reaction of the dimeric reactant, i.e., eq 7, but the exact natures of the other organometallic products formed during this process remain to be ascertained. In any event, the occurrence of the individual reactions 6 and 7 clearly confirms that the reaction of $[CpW(NO)H]_2(\mu\text{-}H)_2$ with Lewis bases such as $P(OPh)_3$ does not proceed simply in a manner analogous to that of steps f and b in Scheme I, i.e., eq 8.

$$[CpW(NO)\{P(OPh)_3\}]_2(\mu\text{-}H)_2 \xrightarrow[-\text{“}CpW(NO)\{P(OPh)_3\}\text{”}]{CH_2Cl_2\text{ or PhH}} CpW(NO)H_2[P(OPh)_3] \quad (7)$$

$$[CpW(NO)H]_2(\mu\text{-}H)_2 + 2P(OPh)_3 \not\xrightarrow[\text{PhH}]{CH_2Cl_2\text{ or}} 2CpW(NO)H_2[P(OPh)_3] \quad (8)$$

The complex $CpW(NO)H_2[P(OPh)_3]$ is an orange, diamagnetic, relatively air-stable solid which is soluble in most common organic solvents. An IR spectrum of a CH_2Cl_2 solution of this compound (Table I) exhibits absorptions characteristic of terminal nitrosyl and hydride ligands. Its ^1H NMR spectrum (C_6D_6, Table II) verifies that C_5H_5:W–H = 5:2 and displays a hydride resonance pattern which is qualitatively similar to that exhibited by $CpW(NO)IH[P(OPh)_3]$ (vide supra). These observations are completely consistent with the dihydrido complex possessing a monomeric, "four-legged piano-stool" molecular structure in which the two equivalent hydride ligands are mutually trans, i.e., IV.



IV

^1H NMR monitoring verifies that the reaction between $[CpW(NO)H]_2(\mu\text{-}H)_2$ and $P(OMe)_3$ in C_6D_6 proceeds rapidly in a stepwise manner completely analogous to that just considered for $P(OPh)_3$ (i.e., reactions 6 and 7). The only difference is that in the presence of the less sterically demanding phosphite, the intermediate $[CpW(NO)\{P(OMe)_3\}]_2(\mu\text{-}H)_2$ complex is formed as a mixture of isomers (designated A and B in Table II). The isomers exhibit resonances consistent with their having molecular structures analogous to III, the $P(OMe)_3$ ligands being cis to each other in isomer A and trans in isomer B. Both isomers disproportionate in solution at room temperature (the sterically crowded A more rapidly than B) to form $CpW(NO)H_2[P(OMe)_3]$ exclusively as the trans isomer (cf. structure IV). No other hydrido nitrosyl complexes of tungsten are detectable in the final solution.

Acknowledgment. We are grateful to the Natural Science and Engineering Research Council of Canada for support of this work in the form of grants to P.L. We also thank Professor M. D. Fryzuk for providing the $^1H\{^{31}P\}$ NMR spectrum, Mr. J. A. Balatoni for performing the T_1 measurements, and the staff of the departmental NMR laboratory for their assistance in obtaining the numerous, high-quality spectra presented in this paper.

Registry No. $CpW(NO)I_2[P(OPh)_3]$, 73199-12-9; $CpW(NO)I_2[P(OMe)_3]$, 96429-75-3; $CpW(NO)I_2(PPh_3)$, 73199-13-0; *cis*-$CpW(NO)I_2(PMe_3)$, 96429-76-4; *trans*-$CpW(NO)I_2(PMe_3)$, 96480-05-6; $CpW(NO)IH[P(OPh)_3]$, 73199-23-2; $CpW(NO)IH[P(OMe)_3]$, 96429-77-5; $CpW(NO)IH(PPh_3)$, 96429-78-6; $CpW(NO)IH(PMe_3)$ (isomer A), 96429-79-7; $CpW(NO)IH(PMe_3)$ (isomer B), 96553-51-4; $[CpW(NO)I_2]_2$, 71341-43-0; $[CpW(NO)IH]_2$, 96444-56-3; $[CpW(NO)H_2]_2$, 96429-80-0; $[CpW(NO)H\{P(OPh)_3\}]_2$, 96444-57-4; $CpW(NO)H_2[P(OPh)_3]$, 96429-81-1; $CpW(NO)H_2[P(OMe)_3]$, 96429-82-2; $[CpW(NO)\{P(OMe)_3\}]_2(\mu\text{-}H)_2$ (isomer A), 96429-83-3; $[CpW(NO)\{P(OMe)_3\}]_2(\mu\text{-}H)_2$ (isomer B), 96480-53-4; $CpW(NO)IH(THF)$, 96429-84-4; $P(OMe)_3$, 121-45-9; PMe_3, 594-09-2; $P(OPh)_3$, 101-02-0; PPh_3, 603-35-0.