

analysis of both 1-butanol and 1-pentanol (80%).

Homologation of *B*-Methoxyborinane with (Chloro(trimethylsilyl)methyl)lithium. (Chloro(trimethylsilyl)methyl)lithium (5.5 mmol) was prepared as described above for the homologation of tri-*n*-butylborane and treated with *B*-methoxyborinane (4 mL, 5 mmol) at -78°C . Following the addition, the reaction mixture was stirred for 12 h as the temperature was slowly raised from -78 to 25°C . *n*-Hexadecane (0.5 mL, 1.7068 mmol) was added into the reaction mixture to serve as the internal standard. The ^{11}B NMR of the reaction mixture revealed the formation of *B*-methoxy-2-(trimethylsilyl)borepane ($\delta +54$). The solvent was removed under water aspirator, and the residue thus obtained was extracted with *n*-pentane (5×25 mL). *n*-Pentane was removed at reduced pressure, and the crude *B*-methoxy-2-(trimethylsilyl)borepane thus obtained was dissolved in THF (6 mL). Tetrabutylammonium fluoride (5.5 mL, 5.5 mmol) was added to the above reaction mixture. Following the addition, the contents were refluxed for 5 h and oxidized with alkaline H_2O_2 to provide 1,6-hexanediol in 75% GC yield.¹⁵

Homologation of Tri-*n*-butylborane with (Methoxy(phenylthio)methyl)lithium. *sec*-Butyllithium (4.2 mL, 5.5 mmol) was added dropwise to a mixture of methoxymethyl phenyl sulfide (0.85 mL, 6 mmol) in THF (10 mL) at -55°C . Following the addition, the reaction mixture was stirred for 1 h and then cooled to -78°C . Tri-*n*-butylborane (5 mL, 5 mmol) was added to the reaction mixture and the cold bath allowed to reach room temperature in 4 h. *n*-Hexadecane (0.5 mL, 1.7068 mmol) was added to the reaction mixture. The ^{11}B NMR spectrum of the reaction mixture showed the formation of borate complex ($\delta -0.2$).

Oxidation of the borate complex with hydrogen peroxide (15 mL) at pH 8 (phosphate buffer, 2.5 mL) gave 1-pentanal, which was reduced with borane-dimethyl sulfide to afford 1-pentanol in 81% GC yield.

Homologation of *B*-Methoxyborinane with (Methoxy(phenylthio)methyl)lithium. (Methoxy(phenylthio)methyl)lithium (5.5 mmol) was prepared as described above and treated with *B*-methoxyborinane (4 mL, 5 mmol) at -55°C . The reaction mixture was allowed to reach -5°C in 2 h. The ^{11}B NMR spectrum of the reaction mixture showed the formation of borate complex ($\delta -7$). Finely powdered mercury(II) chloride (1.49 g, 5.5 mmol) was added all at once with vigorous stirring. The migration was complete as the temperature was raised from -5°C to room temperature over 12 h, as indicated by the ^{11}B NMR spectrum ($\delta +54$). The reaction mixture was oxidized as described above to afford the crude 6-hydroxyhexanal, reduced with borane-dimethyl sulfide to yield 1,6-hexanediol (76% by GC).¹⁵

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Registry No. $\text{ClCH}_2(\text{SiMe}_3)$, 2344-80-1; $\text{CH}_2(\text{OMe})\text{SPh}$, 13865-50-4; HCCl_3 , 67-66-3; LiOCEt_3 , 32777-93-8; LiClCl_3 , 2146-66-9; HCClF_2 , 75-45-6; $\text{BrCH}_2\text{CO}_2\text{Et}$, 105-36-2; BrCH_2CN , 590-17-0; HCCl_2OMe , 4885-02-3; LiCHCl_2 , 2146-67-0; $\text{LiCHCl}(\text{SiMe}_3)$, 63830-85-3; $\text{LiCH}(\text{OMe})\text{SPh}$, 57788-49-5; tri-*n*-butylborane, 122-56-5; *B*-methoxyborinane, 38050-70-3; dibutylpentylborane, 30101-38-3; 1,6-hexanediol, 629-11-8; 1-pentanol, 71-41-0.

Reductive Synthesis and Characterization of the Complexes $\text{CpM}(\text{NO})\text{L}_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$; $\text{L} = \text{Lewis Base}$)¹

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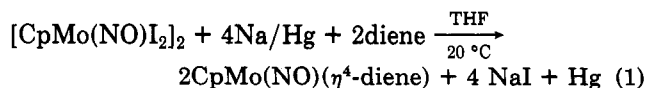
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The synthesis of the previously inaccessible complexes $\text{CpM}(\text{NO})\text{L}_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$; $\text{L} = \text{P}(\text{OMe})_3, \text{PMePh}_2, \text{P}(n\text{-Bu})_3, \text{SbPh}_3, \text{or } 1/2(\text{dppe})$) is described. The new complexes are preparable in moderate to high yields by the reduction of the iodo dimers $[\text{CpM}(\text{NO})\text{I}_n]_2$ ($\text{M} = \text{Cr}, n = 1$; $\text{M} = \text{Mo}$ or $\text{W}, n = 2$) with sodium amalgam in THF in the presence of the appropriate Lewis base, L. The $\text{CpM}(\text{NO})\text{L}_2$ compounds have been fully characterized by conventional spectroscopic methods and exhibit metal-dependent trends in ν_{NO} ($\text{Cr} \gg \text{Mo} > \text{W}$), $\delta(^{31}\text{P})$ ($\text{Cr} > \text{Mo} \gg \text{W}$), and $^2J_{31\text{P}-31\text{P}}$ ($\text{Cr} < \text{Mo} < \text{W}$). Monitoring by IR spectroscopy of the progress of the reductive syntheses of the $\text{CpM}(\text{NO})\text{L}_2$ complexes when $\text{M} = \text{Mo}$ reveals the transient formation of intermediate nitrosyl complexes, some of which (i.e., $\text{CpMo}(\text{NO})\text{I}_2\text{L}$ and $[\text{CpMo}(\text{NO})\text{IL}_2]\text{I}$) are isolable from independent stoichiometric reactions. These experimental observations have led to the formulation of a unified mechanism for these reductive syntheses which accounts for the dependence of the yields of $\text{CpM}(\text{NO})\text{L}_2$ on the nature of M, L, and the solvent employed.

Introduction

We recently reported² that reduction of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with sodium amalgam in the presence of acyclic conjugated dienes in THF results in the formation of novel η^4 -*trans*-diene complexes, i.e., eq 1. However, the



product organometallic complexes are isolable in only 10% yield, and the congeneric complexes containing chromium or tungsten are not preparable in an analogous manner. We reasoned that these disheartening results reflected either the intrinsically unstable nature of an intermediate species such as solvated "CpM(NO)" ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$) or the relative inefficiency of the unsaturated organic molecules to function as trapping agents for such an in-

(1) (a) Organometallic Nitrosyl Chemistry. 27. For part 26 see: Legzdins, P.; Sánchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525. (b) Taken in part from: Hunter, A. D. Ph.D. Dissertation, The University of British Columbia, 1985.

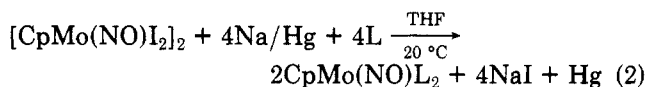
(2) Hunter, A. D.; Legzdins, P.; Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 1791.

Table I. Analytical and Mass Spectral Data for the Complexes

complex	color	mp, °C	analytical data						low-resolution mass spectral data ^a P ⁺ , <i>m/z</i> ^b
			C		H		N		
			calcd	found	calcd	found	calcd	found	
CpCr(NO)[P(OMe) ₃] ₂	orange	96–97	33.43	33.33	5.87	5.77	3.55	3.62	395
CpMo(NO)[P(OMe) ₃] ₂	yellow	79–80	30.08	30.03	5.28	5.20	3.19	3.10	441
CpW(NO)[P(OMe) ₃] ₂ ^c	yellow	63–64	25.07	25.21	4.40	4.50	2.66	2.70	527
CpCr(NO)(PMePh ₂) ₂	red	161–162	68.00	68.35	5.70	5.69	2.56	2.42	532 ^d
CpMo(NO)(PMePh ₂) ₂	orange	~65 dec	62.95	62.83	5.28	5.36	2.37	2.30	593
CpW(NO)(PMePh ₂) ₂	orange	~110 dec	54.80	54.55	4.60	4.59	2.06	2.15	679
CpMo(NO)[P(<i>n</i> -Bu) ₃] ₂ ^e	red	52–57	58.47	59.60	9.98	10.44	2.35	2.47	597
CpMo(NO)(SbPh ₃) ₂	orange	~100 dec	54.89	54.73	3.93	3.98	1.56	1.63	<i>f</i>
CpMo(NO)(Ph ₂ PCH ₂ CH ₂ PPh ₂)	orange	~160 dec	63.17	62.89	4.96	4.96	2.38	2.35	591
CpMo(NO)I ₂ (PMePh ₂)	red	~130 dec	33.52	33.78	2.81	2.86	2.17	2.20	447 ^g
CpMo(NO)I ₂ [P(OMe) ₃]	red	124–125	16.89	16.84	2.48	2.40	2.46	2.47	447 ^g
CpMo(NO)I ₂ (OPMePh ₂)	yellow	~160 dec	32.70	32.69	2.74	2.60	2.12	2.32	447 ^g
[CpMo(NO)I(PMePh ₂) ₂]	yellow	~150 dec	44.05	44.03	3.70	3.70	1.66	1.69	
[CpMo(NO)I(Ph ₂ PCH ₂ CH ₂ PPh ₂)]	brown	~185 dec	44.15	43.95	3.47	3.49	1.66	1.60	

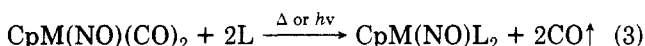
^a Probe temperatures 100–150 °C. ^b Assignments involve the most abundant naturally occurring isotopes in each species (i.e., ⁵²Cr, ⁹⁸Mo, and ¹⁸⁴W). ^c Oxygen analysis. Calcd: 21.15. Found: 21.45. ^d Attributable to [P–Me]⁺. ^e Sample slightly contaminated with P(*n*-Bu)₃ which has similar solubility properties and volatility. ^f No signal due to P⁺ detectable; highest *m/z* observable is 487. ^g Attributable to [P–L]⁺ where L = Lewis base ligand.

intermediate complex. Consequently, we decided to attempt the reductions analogous to reaction 1 in the presence of phosphines or phosphites (L) with a view to effecting the conversions



It was our hope that the use of relatively strong Lewis bases such as L = PMePh₂ or P(OMe)₃ in reaction 2 would permit the spectroscopic detection and perhaps isolation of any intermediate species, thereby providing some insight into the probable mechanisms of transformations (1) and (2).

We also deemed it worthwhile to expand our investigations of reaction 2 to include the related chromium and tungsten systems since the anticipated product complexes CpM(NO)L₂ (M = Cr, Mo, or W) are desirable electron-rich nitrosyl compounds that are not generally preparable by other synthetic routes. Indeed the only four such complexes known at the time we initiated our work were CpM(NO)(Ph₂PCH₂CH₂PPh₂) (M = Cr³ or Mo⁴) and CpM(NO)(PPh₃)₂ (M = Cr⁴ or Mo⁴). They had been obtained from the reactions



where M = Cr or Mo and 2L = Ph₂PCH₂CH₂PPh₂ or L = PPh₃.^{3,4} However, the isolated yields of products from these reactions were generally low, and the analogous tungsten complexes could not be synthesized at all in this manner.

In this paper, we wish to report the results of our studies involving several series of such CpM(NO)L₂ (M = Cr, Mo, or W) compounds.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions in a well-ventilated fume hood unless specified otherwise. General procedures routinely employed in these laboratories have been described in detail previously.⁵ The halo nitrosyl reagents [CpCr(NO)I]₂,⁶

[CpMo(NO)I]₂,⁷ [CpMo(NO)I]₂,⁷ [CpMo(NO)Br]₂,⁸ and [CpW(NO)I]₂⁹ were prepared by the published procedures. The Lewis bases containing group 15 elements¹⁰ were used as purchased from commercial suppliers except for P(OMe)₃ which was distilled from sodium and stored under N₂ prior to use.¹¹ All ³¹P chemical shifts are reported in parts per million downfield from external H₃PO₄.

Reactions of [CpM(NO)L]₂ (M = Cr, n = 1; M = Mo or W, n = 2) with Na/Hg in the Presence of Lewis Bases, L. All of these reactions involved an excess of the sodium amalgam and 2 equiv of Lewis base per transition metal. The experimental procedures, using the molybdenum complexes as representative examples throughout, were as follows.

A. L = P(OMe)₃; M = Cr, Mo, or W. An excess of solid sodium amalgam (9.00 g, 9.36 mmol of Na) was liquefied by the addition of mercury (~3 mL),¹² THF (50 mL) was added, and the mixture was stirred rapidly at room temperature. To this stirred mixture were added P(OMe)₃ (0.94 mL, 7.96 mmol) and [CpMo(NO)I]₂ (1.77 g, 1.99 mmol) to obtain a deep red supernatant solution whose IR spectrum exhibited a ν_{NO} at 1678 (s) cm⁻¹. Stirring was continued for 1 h (to ensure completion of the reaction) whereupon the solution had become yellow-brown and its nitrosyl absorption had shifted to 1592 (s) cm⁻¹. The final supernatant solution was filter cannulated away from the mercury-containing residue. The residue was washed with THF (2 × 10 mL), the washings were combined with the initial filtrate, and solvent was removed from the resulting solution in vacuo to obtain a brown oil. This oil was then extracted with Et₂O (4 × 40 mL) until the extracts were colorless, and the combined extracts were taken to dryness under reduced pressure. The resulting brownish residue was recrystallized from Et₂O–hexanes at –20 °C to obtain 1.02 g (58% yield) of CpMo(NO)[P(OMe)₃]₂ as large yellow crystals.

The analogous chromium and tungsten complexes were isolated similarly as orange needles (33% yield) and yellow crystals (46% yield), respectively.

The analytical, mass spectral, IR, and ¹H and ³¹P NMR data for these and the other new complexes synthesized during this

(7) [CpMo(NO)I]₂ was prepared by a modification of the procedure described by: James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* 1971, 1068.

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

(9) Legzdins, P.; Martin, D. T.; Nurse, C. R. *Inorg. Chem.* 1980, 19, 1560.

(10) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(11) Hunter, A. D.; Legzdins, P. *Inorg. Chem.* 1984, 23, 4198.

(12) Alternatively, the requisite sodium amalgam may also be generated directly in situ.

(3) Sellmann, D.; Kleinschmidt, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1977, 32B, 1010.

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

(5) Legzdins, P.; Martin, J. T.; Oxley, J. C. *Organometallics* 1985, 4, 1263.

(6) Legzdins, P.; Nurse, C. R. *Inorg. Chem.* 1985, 24, 327.

Table II. IR and ^{31}P and 1H NMR Data for the Complexes

	IR (THF)		$^{31}P\{^1H\}$ NMR (C_6D_6), δ		1H NMR (C_6D_6), δ	
	ν_{NO} , cm^{-1}				$(\eta^5-C_5H_5)$	L
$CpCr(NO)[P(OMe)_3]_2$	1624	229.3			4.73 (t, $^3J_{H-31P} = 2.28$ Hz)	3.52 (m, 18 H, $N^b = 11.00$ Hz, CH_3)
$CpMo(NO)[P(OMe)_3]_2$	1592	206.1			5.21 (t, $^3J_{H-31P} = 0.79$ Hz)	3.52 (m, 18 H, $N = 11.69$ Hz, CH_3)
$CpW(NO)[P(OMe)_3]_2$	1579	171.0			5.13 (t, $^3J_{H-31P} = 0.81$ Hz)	3.54 (m, 18 H, $N = 11.74$ Hz, CH_3)
$CpCr(NO)(PMePh_2)_2$	1597	75.4			4.51 (t, $^3J_{H-31P} = 2.15$ Hz)	7.6–6.9 (m, 20 H, C_6H_5), 1.39 (m, 6 H, $N = 7.04$ Hz, CH_3)
$CpMo(NO)(PMePh_2)_2$	1559	52.4			4.93 (t, $^3J_{H-31P} = 0.93$ Hz)	7.6–6.9 (m, 20 H, C_6H_5), 1.50 (m, 6 H, $N = 6.92$ Hz, CH_3)
$CpW(NO)(PMePh_2)_2$	1548	16.2			4.93 (t, $^3J_{H-31P} = 0.90$ Hz)	7.6–6.9 (m, 20 H, C_6H_5), 1.61 (m, 6 H, $N = 7.67$ Hz, CH_3)
$CpMo(NO)[P(n-Bu)_3]_2$	1551				5.05 (t, $^3J_{H-31P} = 0.63$ Hz)	2.1–1.2 (m, 36 H, $(CH_2)_3CH_3$), 1.15–0.85 (m, 18 H, $(CH_2)_3CH_3$)
$CpMo(NO)(SbPh_3)_2$	1587				5.00 (s)	7.7–7.4 (m, 12 H, C_6H_5), 7.25–6.95 (m, 18 H, C_6H_5)
$CpMo(NO)(Ph_2PCH_2CH_2PPh_2)$	1568				4.92 (t, $^3J_{H-31P} \approx 0.5$ Hz)	8.3–8.0 (m, 4 H, C_6H_5), 7.5–6.9 (m, 16 H, C_6H_5), 2.7–1.8 (m, 4 H, CH_2)
$CpMo(NO)I_2(PMePh_2)^c$	1668				5.71 (d, $^3J_{H-31P} = 2.63$ Hz)	7.7–7.4 (m, 10 H, C_6H_5), 2.68 (d, 3 H, $^2J_{H-31P} = 9.86$ Hz, CH_3)
$CpMo(NO)I_2[P(OMe)_3]^c$	1678				6.02 (d, $^3J_{H-31P} = 2.55$ Hz)	3.88 (d, 9 H, $^3J_{H-31P} = 11.00$ Hz, CH_3)
$CpMo(NO)I_2(OPMePh_2)^c$	1669				6.19 (s)	8.0–7.4 (m, 10 H, C_6H_5), 2.20 (d, 3 H, $^2J_{H-31P} = 13.22$ Hz, CH_3)
$[CpMo(NO)I(PMePh_2)_2]I^c$	1668	10.7			5.77 (t, $^3J_{H-31P} = 2.18$ Hz)	7.9–7.4 (m, 20 H, C_6H_5), 2.86 (t, 6 H, $N = 9.48$ Hz, CH_3)
$[CpMo(NO)I(Ph_2PCH_2CH_2PPh_2)I]^c$	1684	62.7, 36.3 (d, $^2J_{31P-31P} = 41$ Hz)			5.67 (d, $^3J_{H-31P} = 2.42$ Hz)	8.12–8.02 (m, 4 H, C_6H_5), 7.70–7.25 (m, 16 H, C_6H_5), 4.78 (br, 1 H, $P-CH_AH_B-CH_CH_D-P$), 3.38 (dm, 1 H, $P-CH_AH_B-CH_CH_D-P$), 3.07 (ddt, 1 H, $P-CH_AH_B-CH_CH_D-P$), 1.85 (m, 1 H, $P-CH_AH_B-CH_CH_D-P$)

^aThe integrations of the resonances due to the cyclopentadienyl protons were often lower than required because of their long relaxation times.⁵ ^b $N = |J_{AX} + J_{AX'}|$ as defined in Figure 3. ^cNMR spectra recorded in $CDCl_3$.

work are collected in Tables I and II.

B. L = PMePh₂; M = Cr, Mo, or W. As in case A, solid sodium amalgam (10.0 g, 10.4 mmol of Na) was liquefied with Hg (~3 mL), THF (80 mL) was added, and the stirred mixture was treated with PMePh₂ (1.67 mL, 9.00 mmol) and $[CpMo(NO)I_2]_2$ (2.00 g, 2.25 mmol). The IR spectrum of the initially red supernatant solution displayed a nitrosyl absorption at 1668 (s) cm^{-1} . However, in this case, as the reaction mixture was stirred, the solution became green-brown after 5 min, and its IR spectrum at this point revealed that new bands at 1614 (s) and 1559 (w) cm^{-1} had appeared at the expense of the 1668 cm^{-1} feature. After 10 min of reaction, the supernatant solution was orange, and the only ν_{NO} evident in its IR spectrum was a strong band at 1559 cm^{-1} . The final orange solution was removed from the mercury-containing residue (vide supra) and was taken to dryness in vacuo to obtain an orange-brown solid.¹³ This solid was extracted with Et_2O (150 mL) in a Soxhlet extractor for 3 days, and the volume of the extracts was then diminished to ~10 mL under reduced pressure. The orange crystals which had precipitated during these latter operations were isolated by cannula filtration,

washed with Et_2O (10 mL) and hexanes (2 × 20 mL), and dried under vacuum (5×10^{-3} mm) at ambient temperature. In this manner, 2.37 g (89% yield) of $CpMo(NO)(PMePh_2)_2$ as an analytically pure, orange crystalline solid were obtained.

The congeneric chromium and tungsten complexes were obtained analogously as red (84% yield) and orange (81% yield) crystals, respectively.

C. L = P(n-Bu)₃; M = Mo. To a stirred mixture containing liquefied sodium amalgam [10.0 g of solid Na/Hg (10.4 mmol of Na) in 3 mL of Hg] and THF (80 mL) was added P(n-Bu)₃ (2.25 mL, 9.00 mmol) and then $[CpMo(NO)I_2]_2$ (2.00 g, 2.25 mmol). The progress of the reaction was monitored by IR spectroscopy of the supernatant solution. After 1 min, the solution was red, and ν_{NO} 's were evident at 1691 (m), 1659 (m), and 1611 (w) cm^{-1} . After 3 min, the solution had become brown, the absorption at 1691 cm^{-1} had vanished, and the nitrosyl bands now appeared at 1654 (m), 1611 (s), and 1551 (w) cm^{-1} . During the next 15 min, the band at 1654 cm^{-1} gradually disappeared while that at 1551 cm^{-1} increased in intensity at the expense of the 1611 cm^{-1} feature. Finally, after 1 h, only the absorption at 1551 cm^{-1} persisted in the ν_{NO} region, and the solution was orange-red. This solution was cannula filtered away from the mercury-containing residue, and solvent was removed from the filtrate in vacuo to obtain a red oil. This oil was extracted with hexanes (50 mL), the volume of the extracts was diminished to ~10 mL under reduced pressure, and the resulting solution was transferred by syringe to the top of an alumina column (3 × 6 cm, Woelm neutral, activity 1) made up in hexanes. The column was first washed with hexanes (150

(13) Recrystallization of this solid from CH_2Cl_2 -hexanes produced orange crystals in ~80% yield of the desired product complex as a dichloromethane solvate, i.e., $CpMo(NO)(PMePh_2)_2 \cdot \frac{1}{2}CH_2Cl_2$. Anal. Calcd for $C_{31.5}H_{31}NO_2P_2ClM$: C, 59.68; H, 5.09; N, 2.21. Found: C, 60.00; H, 5.14; N, 2.39. Its 1H NMR spectrum (C_6D_6) contained the features presented in Table II for the unsolvated material and a singlet of the correct intensity at δ 4.29 attributable to CH_2Cl_2 .

mL) in an attempt to remove any unreacted $P(n\text{-Bu})_3$. Subsequent elution of the column with Et_2O (100 mL) removed a single red band which was collected. Removal of solvent from the eluate in vacuo afforded a red liquid which was sequentially exposed to a dynamic vacuum (4×10^{-3} mm) at ambient temperature for 24 h and then cooled at -20°C for 16 h to induce the formation of sticky red crystals of $\text{CpMo}(\text{NO})[\text{P}(n\text{-Bu})_3]_2$ (2.03 g, 76% yield) slightly contaminated with $\text{P}(n\text{-Bu})_3$ (Table I).

The preparation of the analogous Cr and W complexes was not attempted.

D. $L = \text{SbPh}_3$; $M = \text{Mo}$. This reaction was effected and worked up in a manner identical with that described in section A for $L = \text{P}(\text{OMe})_3$ to obtain a 15% yield of $\text{CpMo}(\text{NO})(\text{SbPh}_3)_2$ as an analytically pure, orange crystals.

No attempt was made to prepare the congeneric chromium and tungsten complexes.

E. $2L = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; $M = \text{Mo}$. This reaction was effected and worked up in a manner identical with that described in section C for $L = \text{P}(n\text{-Bu})_3$. These operations afforded a 66% yield of $\text{CpMo}(\text{NO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ as an orange, crystalline solid.

Again, no attempt was made to synthesize the analogous chromium and tungsten complexes.

F. $L = \text{P}(t\text{-Bu})_3$; $M = \text{Mo}$ or W . $L = \text{PPh}_3$ or AsPh_3 ; $M = \text{Mo}$. These reactions were performed in a manner identical with that described above in case C for $\text{P}(n\text{-Bu})_3$. However, workup of these solutions in the usual fashion (vide supra) afforded no nitrosyl-containing products.

Reaction of $[\text{CpMo}(\text{NO})\text{Br}_2]_2$ with Na/Hg and PMePh_2 in THF. This reaction was set up as described for the diiodo dimer in case B above, and it proceeded similarly. Monitoring the conversion by IR spectroscopy of the supernatant solution revealed the appearance and eventual disappearance of nitrosyl bands at 1665 and 1610 cm^{-1} until only the band at 1559 cm^{-1} characteristic of the product persisted. This $\text{CpMo}(\text{NO})(\text{PMePh}_2)_2$ product was isolated in 88% yield by the procedure outlined in part B.

Reaction of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ with Na/Hg and PMePh_2 in Et_2O . Again, this reaction was performed on the scale outlined in part B above. The purple solid reactant was slowly consumed and replaced by an orange solid during 10 min. Because of the low solubility of the nitrosyl complexes in Et_2O , IR monitoring of the supernatant solution was singularly uninformative. Crystallization of the final orange solid from Et_2O afforded $\text{CpMo}(\text{NO})(\text{PMePh}_2)_2$ in 60% yield.

Reaction of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ with $\text{NaC}_{10}\text{H}_8$ and PMePh_2 in THF. A solution of sodium naphthalene was prepared by introducing sodium metal (~ 0.06 g) into a THF (30-mL) solution of naphthalene (0.29 g, 2.25 mmol) and by stirring of the mixture for 1.5 h at ambient temperature to obtain a dark green solution. To this stirred solution were added stoichiometric amounts of PMePh_2 (0.42 mL, 2.25 mmol) and then $[\text{CpMo}(\text{NO})\text{I}_2]_2$ (0.50 g, 0.56 mmol). The solution rapidly (< 1 min) became red, and its IR spectrum at this point exhibited only the ubiquitous nitrosyl band at 1559 cm^{-1} . The final mixture was worked up in the customary manner to obtain 0.52 g (78% yield) of $\text{CpMo}(\text{NO})(\text{PMePh}_2)_2$.

Reaction of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OC}-\text{H}_3)_2]$ and PMePh_2 in THF. To a stirred, freshly prepared, red solution (ν_{NO} 1668 cm^{-1}) of PMePh_2 (0.42 mL, 2.25 mmol) and $[\text{CpMo}(\text{NO})\text{I}_2]_2$ (0.50 g, 0.56 mmol) in THF (50 mL) was added dropwise a toluene solution of $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ (0.66 mL, 2.25 mmol).⁵ The solution gradually became brown in 5 min, and its IR spectrum displayed the familiar band at 1559 cm^{-1} . $\text{CpMo}(\text{NO})(\text{PMePh}_2)_2$ was isolated in the customary manner (cf. part B) from the final mixture in 59% yield (0.38 g).

Reactions of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ with PMePh_2 , $\text{P}(\text{OMe})_3$, or OPMePh_2 . These three reactions were performed in an identical manner. The procedure involving PMePh_2 is presented in detail as a representative example.

To a rapidly stirred, purple suspension of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ (6.00 g, 6.75 mmol) in CH_2Cl_2 (50 mL) was added dropwise PMePh_2 (2.51 mL, 27.0 mmol). The purple solid was gradually consumed over 30 min, and the final reaction mixture consisted of a clear, red solution whose IR spectrum exhibited a ν_{NO} at 1668 cm^{-1} . This solution was filtered through a Florisil column (2×3 cm) sup-

ported on a medium-porosity frit. Addition of hexanes (50 mL) over 1 h induced the precipitation of a brick-red solid. This precipitate was collected by filtration, washed with hexanes, (3×25 mL), and dried in vacuo (5×10^{-3} mm) for 3 h at room temperature to obtain 8.36 g (96% yield) of $\text{CpMo}(\text{NO})\text{I}_2(\text{PMePh}_2)$ as an analytically pure, red powder.

$\text{CpMo}(\text{NO})\text{I}_2(\text{P}(\text{OMe})_3)$ and $\text{CpMo}(\text{NO})\text{I}_2(\text{OPMePh}_2)$ ¹⁴ were isolated similarly in 82% yield as brick-red microcrystals and a yellow powder, respectively.

Reaction of $\text{CpMo}(\text{NO})\text{I}_2(\text{PMePh}_2)$ with PMePh_2 . To a red solution of $\text{CpMo}(\text{NO})\text{I}_2(\text{PMePh}_2)$ (1.50 g, 2.33 mmol) in THF (50 mL) was added PMePh_2 (0.43 mL, 2.33 mmol), and the mixture was stirred at room temperature for 2 h. The solution remained red throughout, and its IR spectrum (ν_{NO} 1668 cm^{-1}) did not change. The final solution was taken to dryness under reduced pressure, and the remaining residue was purified by crystallization from CH_2Cl_2 -hexanes to obtain 1.88 g (95% yield) of $[\text{CpMo}(\text{NO})\text{I}(\text{PMePh}_2)_2]\text{I}$ as a yellow powder.

Reaction of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ with dppe . A red solution of $[\text{CpMo}(\text{NO})\text{I}_2]_2$ (2.00 g, 2.25 mmol) in THF (60 mL) was treated with 2 equiv of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe , 1.79 g, 4.50 mmol), and the mixture was stirred at ambient temperature for 10 min, the solution remaining red throughout. Removal of volatiles in vacuo and crystallization of the residue from CH_2Cl_2 -hexanes produced 2.32 g (61% yield) of $[\text{CpMo}(\text{NO})\text{I}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]\text{I}$ as a light brown powder.

Thermal Decomposition of $[\text{CpMo}(\text{NO})\text{I}_2]$. A red suspension of $[\text{CpMo}(\text{NO})\text{I}_2]$ (0.60 g, 0.94 mmol) was stirred in refluxing toluene (60 mL) for 21 h, whereupon the solid was consumed and a brown solution formed. An IR spectrum of this solution revealed that the nitrosyl band characteristic of the reactant at 1574 cm^{-1} had been replaced by weaker absorptions at 1674 and 1760 cm^{-1} . The brown solution was taken to dryness in vacuo, and the residue was purified by chromatography on Florisil (2×6 cm) with CH_2Cl_2 as eluant. This operation produced a single green band which was eluted from the column and collected. The eluate was again taken to dryness under reduced pressure, and the remaining solid was recrystallized from CH_2Cl_2 -hexanes to obtain 0.10 g (30% yield based on NO) of $\text{CpMo}(\text{NO})\text{I}$ as green crystals. The product complex was readily identifiable by its characteristic spectroscopic properties:¹⁶ IR (CH_2Cl_2) ν_{NO} 1676, 1765 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.08 (s).

Reaction of $[\text{CpMo}(\text{NO})\text{I}_2]$ with Na/Hg and PMePh_2 in THF. To a stirred, two-phase system consisting of solid sodium amalgam (4.00 g, 4.16 mmol of Na) that had been liquefied with Hg (~ 2 mL) and THF (40 mL) were added PMePh_2 (1.17 mL, 6.29 mmol) and $[\text{CpMo}(\text{NO})\text{I}_2]$ (1.00 g, 1.57 mmol). An IR spectrum of the initially red supernatant solution contained just one nitrosyl band at 1617 cm^{-1} . After the reaction mixture was stirred for 0.5 h, the solution had become a lighter red, and its IR spectrum displayed ν_{NO} 's at 1580 (w), 1559 (m), and 1530 (w) cm^{-1} . This final supernatant solution was filter cannulated away from the mercury-containing residue. The residue was washed with THF (2×30 mL), the washings were combined with the initial filtrate, and solvent was removed from the resulting solution in vacuo to obtain a red solid. This solid was treated with CH_2Cl_2 (20 mL), and the mixture was filtered through a column of Florisil (2×3 cm) supported on a medium-porosity frit to obtain an orange filtrate. The filtrate was taken to dryness under reduced pressure, and the remaining orange solid was recrystallized from Et_2O to obtain 0.63 g (34% yield) of $\text{CpMo}(\text{NO})(\text{PMePh}_2)_2$.

Reaction of $[\text{CpMo}(\text{NO})\text{I}(\text{PMePh}_2)_2]\text{I}$ with Na/Hg in THF. Solid sodium amalgam (5.60 g, 5.80 mmol of Na) was liquefied by the addition of mercury (~ 3 mL), THF (40 mL) was added, and the mixture was stirred rapidly at ambient temperature. The addition of $[\text{CpMo}(\text{NO})\text{I}(\text{PMePh}_2)_2]\text{I}$ (1.00 g, 1.18 mmol) to this stirred mixture resulted in the immediate formation

(14) The OPMePh_2 reagent required for the synthesis of this complex was prepared by the oxidation of PMePh_2 with an excess of 30% H_2O_2 in acetone.¹⁵ Subsequent recrystallization of the final reaction residue from CH_2Cl_2 - Et_2O -hexanes produced OPMePh_2 as a waxy, white solid in 77% yield: ^1H NMR (CDCl_3) δ 7.9-7.4 (m, 10 H, C_6H_5), 2.02 (d, 3H, $J_{\text{H-C}} = 13.2$ Hz, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 27.97; mp 107-108 $^\circ\text{C}$.

(15) This is a modification of the procedure published by: Steube, C.; LeSueur, W. M.; Norman, G. R. *J. Am. Chem. Soc.* 1955, 77, 3526.

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

of a yellow powder suspended in a green supernatant solution (ν_{NO} at 1644 (w) and 1614 (m) cm^{-1}). Further stirring of the reaction mixture for 0.5 h caused the yellow solid to dissolve and the supernatant solution to become concomitantly orange (ν_{NO} at 1559 (s) cm^{-1}). Treatment of this solution in the manner described in part B above afforded CpMo(NO)(PMePh₂)₂ (0.56 g, 80% yield).

Reactions of CpMo(NO)I₂L [L = PMePh₂ or P(OMe)₃] with Excess Na/Hg in THF. To a stirred mixture containing liquefied Na/Hg [4.50 g of solid sodium amalgam (4.70 mmol of Na) in 3 mL of Hg] and THF (40 mL) was added solid, brick-red CpMo(NO)I₂(PMePh₂) (1.00 g, 1.55 mmol). The initial solution was red, and its IR spectrum contained a strong nitrosyl band at 1668 cm^{-1} due to the reactant and weaker bands at 1645 and 1614 cm^{-1} attributable to intermediate species. Within a few minutes, the solution became deep green, and only the 1614 (s) cm^{-1} band persisted in its IR spectrum. Finally, after 15 min of reaction, the supernatant solution was red-brown, and its IR spectrum exhibited a single nitrosyl absorption at 1559 (m) cm^{-1} characteristic of CpMo(NO)(PMePh₂)₂. This product was isolated in the usual manner (cf. part B above) in 38% yield (0.35 g).

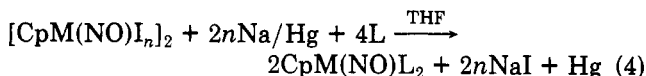
The analogous reaction involving CpMo(NO)I₂[P(OMe)₃] proceeded cleanly from a red solution (ν_{NO} 1678 cm^{-1}) to a green one (ν_{NO} 1626 cm^{-1}). However, beyond this stage, the supernatant solution rapidly became brown, and the nitrosyl bands in its IR spectrum dramatically decreased in total intensity. After 15 min, a weak absorption at 1592 cm^{-1} due to CpMo(NO)[P(OMe)₃]₂ persisted, and this product was isolable in the customary manner (cf. part A above) in only 5% yield.

Reactions of CpMo(NO)I₂L [L = PMePh₂ or P(OMe)₃] with One Equivalent of Na/Hg in THF. Solid sodium amalgam (1.18 g, 1.23 mmol of Na) was liquefied with Hg (5 mL), and then THF (40 mL) was added. To this stirred mixture was added CpMo(NO)I₂(PMePh₂) (1.00 g, 1.55 mmol) whereupon the familiar red supernatant solution (ν_{NO} 1668 cm^{-1}) was produced. After 5 min of reaction, the solution became green, and its IR spectrum verified the consumption of the nitrosyl reactant, exhibiting only a single ν_{NO} at 1614 cm^{-1} . An ESR spectrum of an aliquot of this solution at room temperature displayed a strong, broad signal. The reaction mixture was stirred for an additional 20 min, and the green solution was then cannula filtered away from the mercury-containing residue (vide supra). Slow concentration of the green filtrate under reduced pressure caused it to become red and ultimately produced a red-brown oil. All attempts to isolate the green product [ν_{NO} 1614 (THF) and 1610 cm^{-1} (CH₂Cl₂)] were thwarted by its proclivity to decompose thermally.

The analogous reaction involving CpMo(NO)I₂[P(OMe)₃] (0.088 g, 0.16 mmol) also produced a green solution (ν_{NO} 1626 cm^{-1}) having a similarly strong, broad ESR signal. This paramagnetic product also could not be isolated because of its thermal instability.

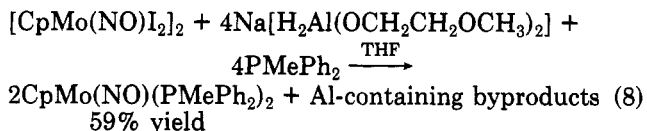
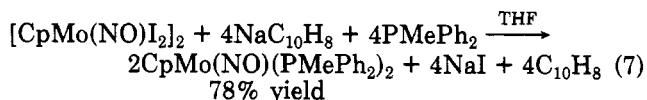
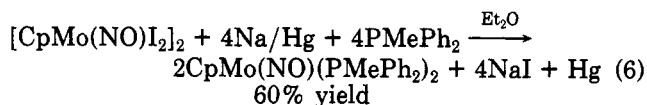
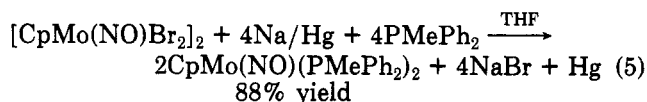
Results and Discussion

Syntheses and Physical Properties of the CpM(NO)L₂ (M = Cr, Mo, or W; L = Lewis Base) Complexes. As we had anticipated, reduction of the iodo nitrosyl dimers [CpM(NO)I_n]₂ (M = Cr, $n = 1$; M = Mo or W, $n = 2$) by sodium amalgam in THF in the presence of a variety of Lewis bases, L, does indeed produce CpM(NO)L₂ complexes in moderate to high isolated yields, i.e., eq 4. The transformations summarized by eq 4 are clean,



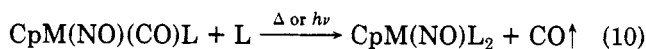
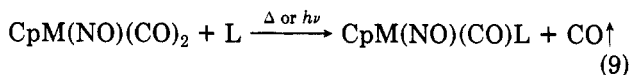
rapid, and straightforward, and an excess of sodium amalgam may be used with no deleterious effects. This synthetic methodology encompasses all three transition metals of the group 6 triad and is particularly successful for strong Lewis bases.¹⁷ The new complexes that have

been prepared in this fashion are presented in Tables I and II. The primary limitation of reaction 4 appears to be the steric bulk of the Lewis bases employed. If bulky phosphines such as P(*t*-Bu)₃ (M = Mo or W) or PPh₃ (M = Mo) are employed, no nitrosyl-containing products are formed, and even the somewhat less sterically demanding SbPh₃ (M = Mo) only affords low yields of the desired product. Nevertheless, for Lewis bases that are incorporated efficiently into the metals' coordination spheres by reaction 4, a number of variants of the synthetic methodology also produce the CpM(NO)L₂ complexes. This feature is clearly illustrated by the various methods by which CpMo(NO)(PMePh₂)₂ may be generated, as summarized in eq 5–8. From a practical point of view, however, it



should be noted that the changes of solvent or reducing agent introduced in reactions 6, 7, and 8 do lead to a slightly more cumbersome experimental procedure for isolation of the nitrosyl product.

In general, reaction 4 is the synthetic method of choice for the preparation of CpM(NO)L₂ complexes since the previously employed synthetic routes that lead to this class of compounds, i.e., eq 9 and 10, are, as noted in the In-



roduction, of limited utility. For instance, the thermal substitution reaction presented in eq 9 is a relatively facile S_N2 process¹⁸ of apparently general applicability^{4,18–20} which proceeds most rapidly for M = Mo¹⁸ and more basic phosphines.¹⁷ However, the requisite second step (eq 10) fails thermally for most Lewis bases,⁴ the notable exception being Ph₂PCH₂CH₂PPh₂ (M = Cr or Mo) which benefits thermodynamically from the "chelate effect".^{3,21} The substitution reaction 9 can also be effected photochemically, being particularly efficient when M = Cr.²² Again, however, difficulties arise in carrying out the second substitution under these experimental conditions since the

(18) Casey, C. P.; Jones, W. D.; Harsy, S. G. *J. Organomet. Chem.* **1981**, *206*, 3.

(19) Brunner, H.; Schindler, H. D.; Schmidt, E.; Vogel, M. *J. Organomet. Chem.* **1970**, *24*, 515.

(20) (a) Brunner, H.; Doppelberger, J. *Bull. Soc. Chim. Belg.* **1975**, *84*, 923. (b) Reisner, M. G.; Bernal, I.; Brunner, H.; Doppelberger, J. *J. Chem. Soc., Dalton Trans.* **1978**, 1664. (c) King, R. B.; Gimeno, J. *Inorg. Chem.* **1978**, *17*, 2396.

(21) Behrens, H.; Schindler, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1968**, *23B*, 1110.

(22) Herberhold, M.; Smith, P. D.; Alt, H. G. *J. Organomet. Chem.* **1980**, *191*, 79 and references therein.

(17) For a discussion of the Lewis basicities and steric requirements of phosphines and phosphites see: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 31.

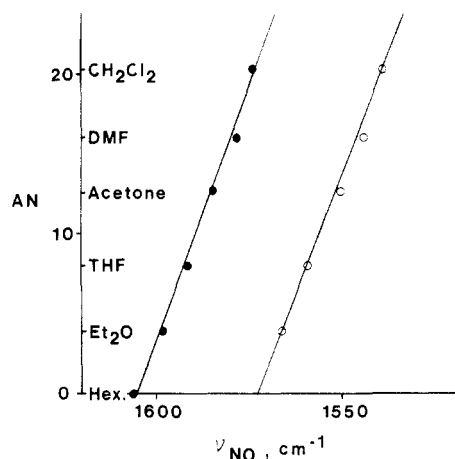


Figure 1. Variation of ν_{NO} with the acceptor number (AN) of the solvent (\bullet = $\text{CpMo}(\text{NO})[\text{P}(\text{OMe})_3]_2$; \circ = $\text{CpMo}(\text{NO})(\text{PMePh}_2)_2$).

desired conversion (eq 10) is accompanied by competing side reactions.²³ Nevertheless, photochemical methods have been used to synthesize $\text{CpM}(\text{NO})(\text{PPh}_3)_2$ ($\text{M} = \text{Cr}, \text{Mo}$)⁴ in low yields (among a variety of other products) and $\text{CpM}(\text{NO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ ($\text{M} = \text{Cr}^3$ or Mo^4) in good yields by reactions 9 and 10. No such tungsten complexes have been previously prepared by either thermal or photochemical means.

The various $\text{CpM}(\text{NO})\text{L}_2$ compounds isolated during our work (Table I) are yellow-to-red, diamagnetic solids. The $\text{P}(\text{OMe})_3$ - and $\text{P}(n\text{-Bu})_3$ -containing complexes are very soluble in common organic solvents such as THF, CH_2Cl_2 , benzene, and Et_2O and are somewhat less soluble in hexanes. The other complexes exhibit less solubility in benzene and Et_2O and are insoluble in hexanes. The phosphite derivatives are thermally unstable in the solid state, decomposing in a matter of weeks at ambient temperatures, but they remain unchanged indefinitely at -20°C . In contrast, the solid phosphine complexes appear to be thermally stable when maintained at room temperatures for extended periods of time (i.e., up to 1 year). All the $\text{CpM}(\text{NO})\text{L}_2$ species are very air-sensitive both in the solid state and in solutions, the $\text{P}(n\text{-Bu})_3$ complex of molybdenum being particularly notable in this regard, and they also decompose in halogenated solvents, rapidly in CHCl_3 and more slowly in CH_2Cl_2 . Their formulations as monomeric, 18-electron complexes are supported by their elemental analysis and low-resolution mass spectral data (Table I).

The spectroscopic properties of the $\text{CpM}(\text{NO})\text{L}_2$ compounds (Table II) are consistent with their possessing the familiar "three-legged piano-stool" molecular structures, i.e.



Thus, IR spectra of THF solutions of the complexes exhibit single strong absorptions in the region $1625\text{--}1550\text{ cm}^{-1}$ attributable to terminal nitrosyl ligands.^{4,21} The ν_{NO} values exhibit the expected dependences on M^{24} and L^{17} (i.e., $\text{Cr} \gg \text{Mo} > \text{W}$ and $\text{P}(\text{OMe})_3 > \text{PMePh}_2 > \text{P}(n\text{-Bu})_3$). However, the frequency of the nitrosyl-stretching absorptions observed is strongly dependent on the solvent medium

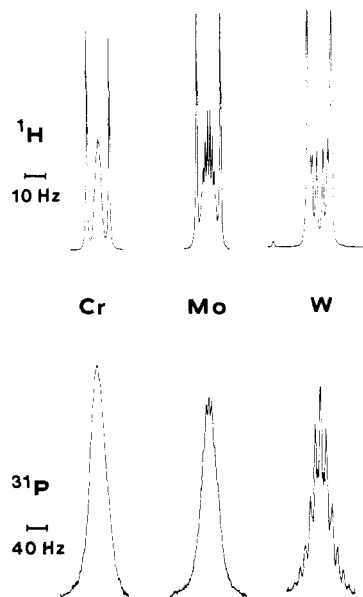


Figure 2. ^1H and ^{31}P NMR spectra of $\text{CpM}(\text{NO})[\text{P}(\text{OMe})_3]_2$ in the $\text{P}(\text{OMe})_3$ region.

employed. Indeed, the ν_{NO} 's vary linearly with the "acceptor number" of the solvent,²⁵ as illustrated in Figure 1 for $\text{CpMo}(\text{NO})(\text{PMePh}_2)_2$ and $\text{CpMo}(\text{NO})[\text{P}(\text{OMe})_3]_2$. This variation simply reflects the ability of the indicated solvents to function as Lewis acids toward the $\text{CpMo}(\text{NO})\text{L}_2$ complexes via the lone pair of electrons on the oxygen atoms of the NO groups.²⁶ Previous studies in these laboratories have demonstrated that the related $\text{CpM}(\text{NO})(\text{CO})_2$ ($\text{M} = \text{Cr}, \text{Mo}$, or W) complexes form analogous isonitrosyl linkages with strong Lewis acids such as Cp_3Ln ($\text{Ln} =$ a lanthanide metal).²⁷ Hence, it is not surprising that the relatively electron-rich NO ligands in the $\text{CpM}(\text{NO})\text{L}_2$ complexes can function as Lewis bases toward weaker Lewis acids such as the organic solvents indicated in Figure 1. The acid-base interactions in the latter cases are not sufficiently strong, however, to permit the isolation of these adducts.

The ^{31}P NMR spectra of the $\text{CpM}(\text{NO})\text{L}_2$ complexes exhibit a number of interesting features, the $^{31}\text{P}\{^1\text{H}\}$ data being presented in Table II. First, for a given L, the shielding of the ^{31}P resonances increases in the order $\text{Cr} < \text{Mo} < \text{W}$. This trend is as expected²⁸ on the basis of the relative electron densities available at the metal centers and is in accord with the trend in ν_{NO} values discussed in the preceding paragraph. However, the magnitude of the chemical shift differences between analogous Mo and W complexes (~ 35 ppm) is somewhat larger than might be anticipated.²⁸ For instance, for the compounds $\text{M}(\text{CO})_5\text{L}$ and *cis*- and *trans*- $\text{M}(\text{CO})_4\text{L}_2$ ($\text{L} =$ phosphine), a consecutive shift of the ^{31}P NMR signal to higher field by only ~ 20 ppm occurs as M varies from Cr to Mo to W.²⁸ Secondly, the $^{31}\text{P}\text{--}^{183}\text{W}$ coupling constants of the $\text{CpW}(\text{NO})\text{L}_2$ compounds are much larger than those observed for related carbonyl complexes. Thus, $J_{^{31}\text{P}\text{--}^{183}\text{W}}$ for CpW -

(25) (a) Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* 1975, 106, 1235. (b) Gutmann, V. *Ibid* 1977, 108, 429.

(26) Interaction of the solvents with other base sites on the $\text{CpMo}(\text{NO})\text{L}_2$ complexes such as the metal center or the cyclopentadienyl ring would cause ν_{NO} to increase in energy as the Lewis acidity of the solvent increased,²⁷ a trend exactly opposite to that observed experimentally (Figure 1).

(27) Crease, A. E.; Legzdins, P. *J. Chem. Soc., Dalton Trans.* 1973, 1501 and references therein.

(28) Pregosin, P. S.; Kunz, R. W. In "NMR, Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds; Springer-Verlag: New York, 1979; Vol. 16.

(23) McPhail, A. T.; Knox, G. R.; Robertson, C. G.; Sim, G. A. *J. Chem. Soc. A* 1971, 205.

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

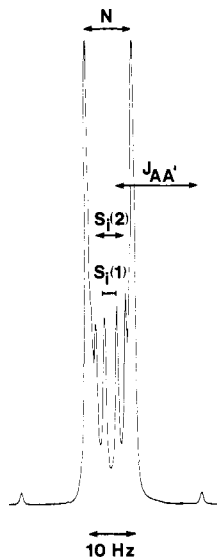


Figure 3. ¹H NMR spectrum of CpW(NO)[P(OMe)₃]₂ in the P(OMe)₃ region.

(NO)[P(OMe)₃]₂ and CpW(NO)(PMePh₂)₂ is 689 and 481 Hz, respectively, whereas for CpW(CO)₂LX (X = SnMe₃, PbMe₃, or Me) it is ~490 Hz when L = P(OMe)₃ and ~305 Hz when L = PMePh₂.²⁸ PMePh₂.²⁸ Indeed, the ³¹P-¹⁸³W coupling constant of CpW(NO)[P(OMe)₃]₂ appears to be the largest of its kind yet reported and resembles most nearly those found for analogous nitrosyl complexes, e.g., 595 Hz for [CpW(NO)H{P(OPh)₃}]₂.⁵ Finally, as shown in Figure 2, the proton-coupled ³¹P NMR spectra of the CpM(NO)[P(OMe)₃]₂ species are highly second order (i.e., X₉AA'X₉' spin systems). Nevertheless, the signals are clearly resolved for the tungsten complex but progressively less so for the molybdenum and chromium congeners.

The ¹H NMR spectra of the CpM(NO)L₂ complexes (Table II) also display several informative features. The resonance for the cyclopentadienyl protons of each compound is a triplet due to coupling of the signal to two equivalent phosphorus nuclei. The values of ³J_{H-³¹P} of ~0.6–0.9 Hz for the molybdenum and tungsten compounds and ~2.2 Hz for the chromium analogues are apparently normal.⁴ More interesting are the multiplets due to the protons of the methyl groups in the P(OMe)₃ and PMePh₂ complexes. As shown in Figure 2, these multiplets of the CpM(NO)[P(OMe)₃]₂ compounds are examples of second-order spectra reflecting the presence of chemically equivalent but magnetically inequivalent methyl protons. While these entities constitute an X₉AA'X₉' spin system, the methyl proton signals exhibited by the tungsten complex approach the limit of an AX₉ spin system and those of the chromium compound approach the limit of an A₂X₁₈ spin system, while those of the molybdenum complex are somewhere in between these limiting cases.²⁹ These spectral patterns can be analyzed by the method developed by Harris for such X_nAA'X_n' spin systems,³⁰ a method that has been previously employed to analyze the ¹H NMR spectra of complexes such as M(CO)₄LL' (M = Cr, Mo, or W; L, L' = phosphine or phosphite),^{31a,b} [M(Me)-

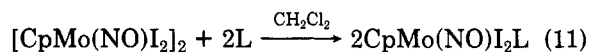
Table III. ¹H NMR Parameters for Methyl Resonances of CpM(NO)[P(OMe)₃]₂ (M = Mo, W)

parameter ^a	Mo	W
δ	3.52	3.54
N ^b	11.69	11.74
S _i (1)	1.21	3.06
S _i (2)	3.49	7.52
L ^c	11.91	12.16
² J _{PP'}	-58.0	-22.6 ^d
³ J _{HP}	11.8	11.9
⁵ J _{HP}	-0.1	-0.2

^a All parameters except δ are recorded in Hz with C₆D₆ as solvent. ^b N = |³J_{HP} + ⁵J_{HP}|. ^c L = |³J_{HP} - ⁵J_{HP}|. ^d For this complex, the value can be measured directly from the spectrum (Figure 3) and this gives a value of |J_{PP'}| = 21.1 Hz (a good agreement).³³

(CO)₂L₂L'⁺ (M = Fe or Ru; L = PMe₃; L' = phosphine),^{31c} and W(NO)₂Cl₂L₂ (L = P(OMe)₃, PMePh₂, etc.).³² Such an analysis affords values of N, S_i(1) and S_i(2) (see Figure 3) from which the absolute values of the coupling constants J_{AA'},³³ J_{AX}, and J_{AX'} (and the relative signs of J_{AX} and J_{AX'}) may be computed (absolute signs were assigned by comparison to literature values^{28,31} for related compounds). These latter values correspond to ²J_{31P-31P}, ³J_{31P-1H}, and ⁵J_{31P-1H}, respectively, for the P(OMe)₃ complexes and are tabulated for the molybdenum- and tungsten-containing species in Table III. Regrettably, the requisite signals for the chromium complex are not sufficiently resolved (see Figure 2) to permit the computation of its ²J_{31P-31P} coupling constant. Nevertheless, it is clear that this parameter is much more negative (i.e., |²J_{31P-31P}| is larger) than that for the molybdenum congener. A similar trend of |²J_{31P-31P}| decreasing as the metal is varied from Cr to Mo to W is also evident in the ¹H NMR spectra of the CpM(NO)-(PMePh₂)₂ compounds.²⁹ Such a trend has been observed previously in other systems^{28,31} and has been rationalized for octahedral complexes²⁸ in terms of a decrease in energy of the E_g bonding molecular orbital (with respect to the T_{1u} and A_{1g} orbitals) as a periodic group of transition metals is descended. It is tempting to speculate that similar changes in the relative orbital energetics of the CpM(NO)L₂ complexes may be at least partly responsible for the observed trends in their physical properties such as ν_{NO} (Cr >> Mo > W), δ(³¹P) (Cr > Mo >> W), and ²J_{31P-31P} (Cr < Mo < W). However, such an inference must obviously await a detailed theoretical analysis and a photoelectron spectroscopic study of these compounds.

Syntheses and Physical Properties of the Complexes CpMo(NO)I₂L and [CpMo(NO)IL₂]I (L = Lewis Base). Monitoring of the progress of reduction reaction 4 when M = Mo by IR spectroscopy reveals that several intermediate species are formed on the way to the final CpMo(NO)L₂ products (vide infra). Some of these intermediate complexes may be synthesized and isolated independently. For instance, reaction 11 (where L =



PMePh₂, P(OMe)₃, or OPMePh₂) proceeds smoothly to afford the indicated products in high isolated yields. The physical properties of the product complexes (summarized in Tables I and II) are similar to those reported previously³⁴ for the analogous compounds having L = PPh₃,

(29) The ¹H NMR spectra of the CpM(NO)(PMePh₂)₂ complexes exhibit similar trends. However, the much lower J_{H-³¹P} coupling constants existent in these systems result in the internal lines appearing as envelopes rather than as well-resolved signals.

(30) Harris, R. K. *Can. J. Chem.* 1964, 42, 2275.

(31) See, for example: (a) Bertrand, R. D.; Ogilvie, F. B.; Verkade, J. G. *J. Am. Chem. Soc.* 1970, 92, 1908, 1916. (b) Schenk, W. A.; Buchner, W. *Inorg. Chim. Acta* 1983, 70, 189. (c) Pankowski, M.; Chodkiewicz, W.; Simonin, M.-P. *Inorg. Chem.* 1985, 24, 533.

(32) The methyl proton signals displayed by these complexes approach the limit of an A₂X_{6n} (where n = 1 for L = PMePh₂ and n = 3 for L = P(OMe)₃) spin system¹¹ and thus give rise to a virtual triplet.³⁰

(33) If the outer pair of lines is observable (Figure 3), J_{AA'} is measurable directly.

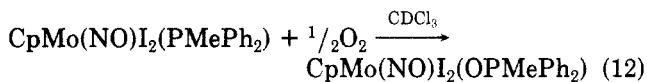
(34) (a) King, R. B. *Inorg. Chem.* 1967, 6, 30. (b) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* 1971, 1596.

Table IV. Nitrosyl-Stretching Frequencies of Complexes Detectable by IR Spectroscopy during Reductions of $[\text{CpMo}(\text{NO})\text{X}_2]_2$ by Na/Hg in THF in the Presence of 4L^a

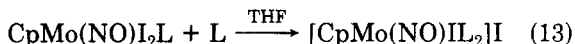
complex	$\nu_{\text{NO}}(\text{THF}), \text{cm}^{-1}$			
	X = I			X = Br, L = PMePh ₂
	L = PMePh ₂	L = P(OMe) ₃	L = P(<i>n</i> -Bu) ₃	
CpMo(NO)X ₂ · (THF)	1691	1691	1691	1691
CpMo(NO)X ₂ L	1668	1678	1659	1665 ^b
$[\text{CpMo}(\text{NO})\text{XL}_2]\text{X}$	1668	<i>c</i>	1654	1665 ^b
CpMo(NO)XL·	1614	1626	1611	1610
CpMo(NO)L ₂	1559	1592	1551	1559

^aFor reference, the ν_{NO} of $[\text{CpMo}(\text{NO})\text{I}]_2$ in THF is 1617 cm^{-1} .
^bAssigned by analogy to the analogous iodo complexes. ^cThis complex is presently unknown.

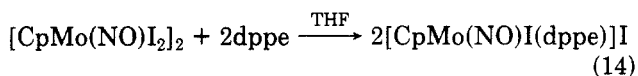
PMe₂Ph, or P(OPh)₃ and are consistent with the CpMo(NO)I₂L complexes possessing monomeric "four-legged piano-stool" molecular structures in which the two iodo ligands are mutually *cis*. It should also be noted at this point that the PMePh₂ complex is cleanly oxidized to its OPMePh₂ analogue by elemental oxygen, i.e., eq 12 (verifiable by ¹H NMR spectroscopy), whereas uncomplexed PMePh₂ is unaffected by O₂ under identical experimental conditions.



The second substitution reaction, i.e., eq 13 (where L = PMePh₂), also proceeds straightforwardly. The isolable

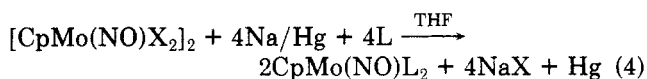


$[\text{CpMo}(\text{NO})\text{I}(\text{PMePh}_2)_2]\text{I}$ salt resembles its PMe₂Ph analogue,^{34b} and its physical properties (Tables I and II) indicate that the cation possesses a *trans*, "four-legged piano-stool" molecular structure. The dppe analogue of $[\text{CpMo}(\text{NO})\text{I}(\text{PMePh}_2)_2]\text{I}$ is preparable in an identical manner, i.e., eq 14, but the spectroscopic properties of the

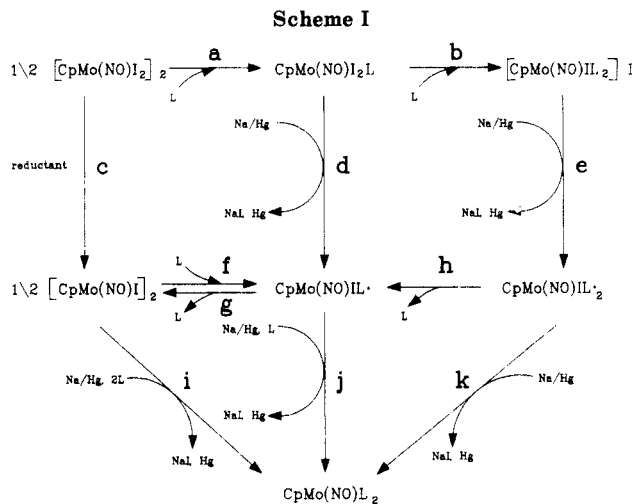


product complex indicate that in this case the organometallic cation possesses the *cis* geometry as a consequence of the chelating nature of the diphosphine ligand.

Mechanism of the Reductive Synthesis of the CpM(NO)L₂ Complexes. Monitoring of the progress of reaction 4 (where X = Br or I) by IR spectroscopy indicates

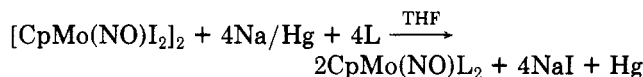


the transient formation of a number of intermediate nitrosyl complexes prior to the ultimate formation of the desired CpMo(NO)L₂ products. Complete details of such monitoring of individual reactions are presented in the Experimental Section. These conversions are particularly convenient to follow since they proceed at relatively slow rates and the intermediate species generally attain detectable concentrations. The various molybdenum-containing intermediates that have been detected during reaction 4 are summarized in Table IV. The transient existence of these species is consistent with the overall reaction 4 proceeding via the sequential transformations summarized in Scheme I for X = I. The proposed mechanism presented in this scheme best accounts for our experimental observations (including various stoichiometric reactions described in the Experimental Section)^{1b} and is



most in accord with literature precedents.

Our experimental observations indicate that the overall reduction reaction



proceeds via steps a, d, and j of Scheme I when L = P(OMe)₃ or weaker Lewis bases. However, when L = PMePh₂, it proceeds via a more complex pathway after step a is traversed. In this case, steps b + e and d compete, with reduction step e becoming dominant after ~1 min into reaction 4 at which point step b should be essentially complete. Once the $[\text{CpMo}(\text{NO})\text{I}(\text{PMePh}_2)_2]$ radical is formed, it is then rapidly converted to the $[\text{CpMo}(\text{NO})\text{I}(\text{PMePh}_2)_2]$ product via either step k or steps h and j. Analyses of the IR spectral changes accompanying reaction 4 when L = P(*n*-Bu)₃ and the analogous conversion involving $[\text{CpMo}(\text{NO})\text{Br}_2]_2$ and L = PMePh₂ (Table IV) suggest that these two reductions also follow the more complex pathway.

It is interesting to note that during the similar reductions of $[\text{CpW}(\text{NO})\text{I}_2]_2$ and $[\text{CpCr}(\text{NO})\text{I}]_2$, no partly reduced, intermediate nitrosyl complexes are detectable by IR spectroscopy. In the tungsten case, the nitrosyl bands of the unreduced reactant (either $\text{CpW}(\text{NO})\text{I}_2\text{L}$ or $[\text{CpW}(\text{NO})\text{IL}_2]\text{I}$) are cleanly replaced by the analogous absorptions of the $\text{CpW}(\text{NO})\text{L}_2$ products. This observation indicates that in this case the steps analogous to j and k in Scheme I must be faster than those analogous to d and e if a similar mechanism is operative. [Exactly the opposite is true for the molybdenum complexes.] In the chromium case, the initially observed nitrosyl bands are those of the well-known⁶ $\text{CpCr}(\text{NO})\text{IL}$ radicals (e.g., ν_{NO} in THF at 1668 cm^{-1} for L = PMePh₂). The reduction pathway in this case thus involves steps analogous to f and j and not i as occurs for the congeneric molybdenum complexes (for which step f does not occur).

Conclusions

This work has established that reduction of the iodo nitrosyl dimers $[\text{CpM}(\text{NO})\text{I}_n]_2$ (M = Cr, *n* = 1; M = Mo or W, *n* = 2), with sodium amalgam in THF in the presence of group 15 Lewis bases, L, conveniently affords the otherwise inaccessible CpM(NO)L₂ complexes in moderate to high isolated yields. The spectroscopic properties of the CpM(NO)L₂ products exhibit a number of interesting, metal-dependent trends. The observed changes in ν_{NO} (Cr \gg Mo > W), $\delta(^{31}\text{P})$ (Cr > Mo \gg W), and $^2J_{^{31}\text{P},^{31}\text{P}}$ (Cr < Mo < W) may well be a manifestation of the differing orbital energetics of the compounds (i.e., a diminishing

separation in energy between the highest occupied molecular orbitals and the next highest filled molecular orbitals) as the metal varies from Cr to Mo to W.

Our experimental observations of various bulk and stoichiometric reduction reactions have led us to propose a unified mechanism for the overall reduction reactions of the $[\text{CpM}(\text{NO})\text{I}_n]_2$ dimers which is presented in Scheme I for the case when $M = \text{Mo}$ and $n = 2$. Nevertheless, confirmation of the exact natures of the various electron-transfer steps presented in this scheme as well as positive identification of the radical intermediates thus formed must await a detailed electrochemical study of these processes.

Despite the considerable insight into the overall reduction reaction (4) that has been gained during this work, some questions remain unanswered. The most intriguing of these is why the use of bulky phosphines such as $\text{P}(t\text{-Bu})_3$ or PPh_3 during these reactions fails to produce any nitrosyl-containing products, even when such products

(e.g., $\text{CpM}(\text{NO})(\text{PPh}_3)_2$ ($M = \text{Cr}, \text{Mo}$)) are preparable by other synthetic routes.

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Registry No. $\text{CpCr}(\text{NO})[\text{P}(\text{OMe})_3]_2$, 100898-71-3; $\text{CpMo}(\text{NO})[\text{P}(\text{OMe})_3]_2$, 100898-72-4; $\text{CpW}(\text{NO})[\text{P}(\text{OMe})_3]_2$, 100898-73-5; $\text{CpCr}(\text{NO})(\text{PMePh}_2)_2$, 100898-74-6; $\text{CpMo}(\text{NO})(\text{PMePh}_2)_2$, 100898-75-7; $\text{CpW}(\text{NO})(\text{PMePh}_2)_2$, 100898-76-8; $\text{CpMo}(\text{NO})[\text{P}(n\text{-Bu})_3]_2$, 100898-77-9; $\text{CpMo}(\text{NO})(\text{SbPh}_3)_2$, 100898-78-0; $\text{CpMo}(\text{NO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$, 32842-38-9; $\text{CpMo}(\text{NO})\text{I}_2(\text{PMePh}_2)$, 100898-79-1; $\text{CpMo}(\text{NO})\text{I}_2[\text{P}(\text{OMe})_3]$, 100898-80-4; $\text{CpMo}(\text{NO})\text{I}_2(\text{OPMePh}_2)$, 100898-81-5; $[\text{CpMo}(\text{NO})\text{I}(\text{PMePh}_2)_2]_2$, 100898-82-6; $[\text{CpMo}(\text{NO})\text{I}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]_2$, 100908-90-5; $[\text{CpCr}(\text{NO})\text{I}]_2$, 94090-65-0; $[\text{CpMo}(\text{NO})\text{I}]_2$, 55836-28-7; $[\text{CpW}(\text{NO})\text{I}]_2$, 71341-43-0; $[\text{CpMo}(\text{NO})\text{Br}]_2$, 40671-96-3; $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$, 22722-98-1; OPMePh_2 , 2129-89-7; $\text{CpMo}(\text{NO})_2\text{I}$, 56403-79-3.

Catalytic Asymmetric Hydrogenation of Prochiral Enamides by Rhodium(I) Complexes Containing the Enantiomers of $(R^*, R^*)-(\pm)$ -1,2-Phenylenebis(methylphenylphosphine) and Its Arsenic Isosteres

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Soluble (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) complexes containing the enantiomers of $(R^*, R^*)-(\pm)$ -1,2-phenylenebis(methylphenylphosphine) or their arsenic isosteres have been shown to be highly efficient catalysts for the asymmetric hydrogenation of a variety of prochiral *Z*-substituted enamide acids and esters, producing α -amino acid derivatives with optical yields as high as 94%. The enantioselectivity of the reaction, however, is remarkably dependent upon the nature of the β -substituent on the enamide-olefin bond. The catalyst containing the bis(tertiary arsine) outperformed the corresponding phosphorus compound in several instances. Both ligands form rigid dissymmetric five-membered chelate rings in which the chirality is due solely to a pair of equivalent asymmetric tertiary phosphorus or arsenic donor groups. Hydrogenation of the catalyst precursor bis(tertiary phosphine) complexes in dichloromethane produces crystalline catalytic dimers of the type $[\text{Rh}_2(\text{diphos})_2](\text{PF}_6)_2$ that have been assigned structures involving arene bridging on the basis of ^{31}P NMR spectroscopy. A ^1H NMR investigation of an isolated enamide complex of the bis(tertiary phosphine) has shown that hydrogenation of the minor diastereomer leads to the major amino acid product, thus supporting the view that it is the relative stabilities of intermediate product diastereomers that determines stereoselectivity in these systems. An unusual dynamic NMR behavior was observed for one of the diastereomers at temperatures below -50°C , which has been rationalized in terms of a restricted rotation of one of the phosphorus-phenyl rings by the carbomethoxy group of the coordinated enamide.

The spectacular success of soluble rhodium(I) complexes containing chiral bis(diphenylphosphino)alkanes in catalyzing the asymmetric hydrogenation of prochiral enamides¹ has been attributed to the steric influence of a dissymmetric edge-face array of the four phenyl groups on the phosphorus donor atoms in the chelate ring.² In five-^{2,3} and six-membered⁴ alicyclic systems the preferred

equatorial disposition of bulky substituents in the flexible chiral linkage between the donor atoms is responsible for a remarkable degree of control over the enantiomeric ring conformation adopted, which in turn determines the chirality of the dissymmetric array of phenyl groups. It was therefore of interest to examine the properties of catalysts containing rigid chelate ring systems, where the dissymmetry can be associated directly with a pair of equivalent asymmetric phosphorus or arsenic donor groups.

In this paper we report the preparation of a pair of isostructural cationic rhodium(I) complexes containing an enantiomer of $(R^*, R^*)-(\pm)$ -1,2-phenylenebis(methyl-

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