because of the low number of observed reflections. The tetraethylammonium cation was found a little disordered, as indicated by the high thermal parameters of the carbon atoms and by some residual peaks close to the carbon atoms. The hydride was clearly localized in the final difference Fourier. All hydride atoms of the anion were placed at their geometrically calculated positions and introduced in the final structure factor calculation, together with the hydridic one, with fixed isotropic thermal parameters. The final cycles of refinement were carried out on the basis of 265 variables; after the last cycle, no parameters shifted by more than 0.7 esd. The biggest remaining peaks in the final difference map, close to the Ru atoms and the ethyl carbon atoms, were equivalent to about 0.6 e/Å^3. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the K and g values were 0.593 and 0.0059, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 14.

The final atomic coordinates for the non-hydrogen atoms are given in Table IV. The atomic coordinates for the hydrogen atoms of the anion and the hydridic one are given in Table SI; thermal parameters for the non hydrogen atoms are given in Table SII.

In independent cycles of refinement the coordinates $-x$, $-y$, $-z$ were used for the non-hydrogen atoms because of the acentric space group. No improvement in the R value was obtained |R(x, y, z) = R(-x, -y, -z) = 0.0574|. The former model was maintained and the reported data refer to this model.

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Novel Physical and Chemical Properties of Acyclic, Conjugated Dienes Coordinated to Cp'Mo(NO) Groups [Cp' = η^5-C$_5$H$_5$ (Cp) or η^5-C$_5$Me$_5$ (Cp*)][1,2]

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Reduction of [Cp'Mo(NO)I$_2$]$_2$ (Cp' = η^5-C$_5$H$_5$ (Cp) or η^5-C$_5$Me$_5$ (Cp*)) by sodium amalgam in THF at −20 °C in the presence of acyclic, conjugated dienes affords novel Cp'Mo(NO)(η^4-*s-trans*-diene) complexes in isolated yields of ∼10–60%. When the diene is 2,3-dimethylbutadiene, Cp'Mo(NO)(η^4-*cis*-2,3-dimethylbutadiene) product complexes are also isolable in addition to the *trans*-diene-containing isomers. However, these *cis*-diene compounds are kinetic products and convert in solutions irreversibly to the isomeric *trans*-diene complexes. Treatment of [CpMo(NO)I$_2$]$_2$ with 2 equiv of C$_4$H$_6$Mg(THF)$_2$ in Et$_2$O results in the precipitation of the adduct CpMo(NO)I$_2$·C$_4$H$_6$Mg·$^1/_2$(Et$_2$O) whose physical properties indicate that it contains an Mo–NO→Mg isonitrosyl linkage. Thermolysis of the adduct in THF at room temperature for 5 days produces CpMo(NO)(η^4-*trans*-C$_4$H$_6$) in 38% yield. A detailed analysis of the ^{1}H and ^{13}C NMR spectroscopic properties of the 14 new η^4-diene-containing complexes isolated during this work has been carried out. This analysis has established unequivocally the different conformations of the diene ligands in these "piano stool" organometallic molecules. Furthermore, it has provided evidence that the *cis*- and *trans*-diene ligands are bonded to the Cp'Mo(NO) groups in a similar manner, the bonding rationale in MO terms involving substantial diene π$_2$→Mo and Mo→diene π$_3$* electron donation in both cases. The Mo-η^4-*trans*-diene linkage in CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene) is relatively kinetically inert to substitution, converting only slowly to CpMo(NO)(L)(η^2-diene) species when exposed to Lewis bases, L, such as PMePh$_2$, PMe$_3$, or CO, the latter at 60 psig in hexanes at 20 °C for 5 days.

Introduction

Many monomeric transition-metal complexes containing acyclic, conjugated dienes have been prepared since the first report of (η^4-C$_4$H$_6$)Fe(CO)$_3$ appeared in 1930.[4] Several of these complexes, particularly those containing iron, have found interesting applications in organic synthesis.[5] In the vast majority of these complexes, the diene ligand is attached to a central metal in the well-known, planar η^4-*s-cis* manner.[6] The only examples to date of η^4-*s-trans*

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Table I. Analytical, IR, and Mass Spectral Data for the η^4-Diene Complexes 1-14

	compd no.	isolated yield, %	C		H		N		low resolutn mass spectra[a] P+, m/z[b]	ν_{NO}, cm^{-1} (CH$_2$Cl$_2$, THF)	
			calcd	found	calcd	found	calcd	found			
CpMo(NO)(η^4-*trans*-butadiene)	1	37	44.10	43.81	4.52	4.46	5.71	5.63	247	1599	1612
CpMo(NO)(η^4-*trans*-2-methylbutadiene)	2	21	46.34	46.41	5.06	5.24	5.41	5.16	261	1593	1610
CpMo(NO)(η^4-*trans*-2,3-dimethylbutadiene)	3	37	48.36	48.94	5.53	5.84	5.13	4.54	275	1590	1608
CpMo(NO)(η^4-*trans*-(E)-1,3-pentadiene)	4	21	46.34	46.32	5.02	5.32	5.40	5.21	261	1589	1605
CpMo(NO)(η^4-*trans*-2,4-dimethyl-1,3-pentadiene)	5	19	50.18	49.98	5.92	5.85	4.87	4.80	289	1584	1599
CpMo(NO)(η^4-*trans*-(E,E)-2,4-hexadiene)	6	33	48.36	48.48	5.53	5.57	5.13	5.16	275	1582	1602
CpMo(NO)(η^4-*trans*-(E,Z)-2,4-hexadiene)	7	53	48.36	48.70	5.53	5.40	5.13	5.30	275	1587	1604
CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene)	8	59	51.83	51.95	6.36	6.44	4.65	4.66	303	1584	1599
CpMo(NO)(η^4-*trans*-(E,E)-1,4-diphenylbutadiene)	9	9	63.49	63.53	4.79	4.82	3.53	3.43	399	1595	1612
Cp*Mo(NO)(η^4-*trans*-2,3-dimethylbutadiene)	10	41	56.00	56.55	7.28	7.63	4.08	4.00	345	1574	1593
Cp*Mo(NO)(η^4-*trans*-(E)-1,3-pentadiene)	11	31	54.74	54.68	7.00	7.20	4.26	4.29	331	1568	1586
Cp*Mo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene)	12	47	58.22	57.76	7.87	7.70	3.77	3.70	373	1566	1585
CpMo(NO)(η^4-*cis*-2,3-dimethylbutadiene)	13	13	48.36	48.49	5.53	5.30	5.13	5.40	275	1552	1567
Cp*Mo(NO)(η^4-*cis*-2,3-dimethylbutadiene)	14	11	56.00	55.89	7.28	7.11	4.08	4.01	345	1539	1548

[a] Probe temperatures 70-150 °C. [b] Assignments for ^{98}Mo.

diene coordination to a single metal center occur in Cp'$_2$M(η^4-diene) complexes (Cp' = η^5-C$_5$H$_5$ (Cp) or η^5-C$_5$Me$_5$ (Cp*); M = Zr or Hf).[7] During our continuing investigations of the effects exerted by Cp'M(NO) groups on their ancillary hydrocarbon ligands,[8] we have discovered that the 14-electron Cp'Mo(NO) fragments readily bind acyclic, conjugated dienes. The most interesting feature of these Cp'Mo(NO)(η^4-diene) product complexes is that their thermodynamically most stable forms contain unprecedented types of metal-*trans*-diene linkages. In this paper we report complete details of the synthesis, characterization, and some chemical properties of these novel Cp'Mo(NO)(η^4-diene) compounds. Portions of this work have been previously communicated.[9]

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions. General procedures routinely employed in these laboratories have been described in detail previously.[10] The halo nitrosyl reagents [CpMo(NO)I$_2$]$_2$,[11] [CpMo(NO)I]$_2$,[11] [Cp*Mo(NO)I$_2$]$_2$,[12] and [CpMo(NO)Br$_2$]$_2$[13] were prepared by the published procedures. Isomerically pure dienes were purchased from the Aldrich Chemical Co. and were used without further purification.

The specialized NMR experiments outlined below were performed on a Varian XL-300 spectrometer using the techniques described. To avoid unnecessary heating of the samples during decoupling experiments, the low-power Waltz-16[14] broad-band proton-decoupling technique (^{13}C{^{1}H}) was used. The use of gated decoupling [{^{1}H} off during data acquisition ($\sim$0.8 s) and on

between acquisitions ($\sim$1.6 s)] permitted the collection of proton-coupled ^{13}C NMR spectra with excellent signal to noise ratios and resolution in reasonable times (1-8 h). Proton nuclear Overhauser effect (NOE) difference experiments were collected by using a 90° pulse (48 μs) with gated, low-power homonuclear decoupling [i.e. decoupling off during data acquisition ($\sim$2 s) and on between acquisition ($\sim$4 s)] of the Cp resonance, usually one or more diene methyl resonances, and the "undecoupled spectrum" (where irradiation occurred at one field width ($\sim$1500 Hz) downfield of the edge of the spectrum (i.e. at $\sim$9.5 ppm)). Between 256 and 4864 transients (i.e. $\sim$1-24 h) of the interleaved spectra were collected and phased, and then the appropriate pairs of FIDs were subtracted and Fourier transformed to give the final difference spectra. The two-dimensional heterocorrelation (2D HETCOR) experiments used Varian's 2D HETCOR pulse program. The 90° ^{13}C pulse was 11 μs, the 90° ^{1}H pulse from the decoupler was 80 μs, the acquisition time was $\sim$0.1 s, and presaturation was used. The proton and carbon-13 spectral widths were 5 and 132 ppm centered at 2.8 and 70 ppm, respectively. The number of incremental spectra was 128, each containing between 32 and 160 2K transients (i.e. between 2.4- and 12-h acquisition time). Zero filling and a 2D-Fourier transformation resulted in a spectrum with a resolution of 6 and 100 Hz in the proton and carbon dimensions, respectively.

Preparation of CpMo(NO)(η^4-*trans*-diene) Complexes 1-9. These reactions typically involved a 10% excess of solid sodium amalgam[15] (liquefied with 2-5 mL of mercury) and a 5-20-fold excess of the acyclic, conjugated diene. The transformations were effected similarly for all the dienes used, the only exception being 2,3-dimethylbutadiene. The experimental procedure, using the case where diene = 2,5-dimethyl-2,4-hexadiene as a representative example, was as follows.

A flask was charged with solid sodium amalgam (10.0 g, 10.4 mmol of Na), liquid Hg (3 mL), THF (100 mL), and 2,5-dimethyl-2,4-hexadiene (2.0 mL), and it was cooled to $\sim$-20 °C by using a saturated CaCl$_2$(aq)/dry ice bath. After 5 min, [CpMo(NO)I$_2$]$_2$ (2.00 g, 2.25 mmol) was added to the cooled mixture in the flask. The dark violet nitrosyl dimer gradually dissolved to produce a red solution whose IR spectrum exhibited a single nitrosyl-stretching absorption at 1691 cm^{-1}. After 2 min, the reaction mixture had become dark brown, and an IR spectrum of the supernatant solution exhibited two ν_{NO}'s at 1691 and 1686 cm^{-1}. After 10 min, the IR spectrum of the now green-brown solution contained two additional nitrosyl bands at 1653 and 1547 cm^{-1}. Over the next 10 min, the two higher energy ν_{NO}'s decreased in intensity while the two lower energy ν_{NO}'s concomitantly increased in intensity. After the disappearance of the 1691 and 1686 cm^{-1} bands from the IR spectrum of the supernatant solution,

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Table II. Numbering Scheme for the Diene Complexes 1–14

1–12   13, 14
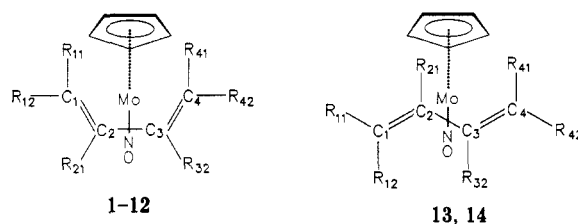
compd no.	diene substituents					
	R_{11}	R_{12}	R_{21}	R_{32}	R_{41}	R_{42}
1	H	H	H	H	H	H
2A	H	H	Me	H	H	H
2B	H	H	H	Me	H	H
3	H	H	Me	Me	H	H
4A	H	H	H	H	H	Me
4B	Me	H	H	H	H	H
5A	Me	Me	H	Me	H	H
5B	H	H	Me	H	Me	Me
6	Me	H	H	H	H	Me
7A	Me	H	H	H	Me	H
7B	H	Me	H	H	H	Me
8	Me	Me	H	H	Me	Me
9	Ph	H	H	H	H	Ph
10	H	H	Me	Me	H	H
11A	H	H	H	H	H	Me
11B	Me	H	H	H	H	H
12	Me	Me	H	H	Me	Me
13	H	H	Me	Me	H	H
14	H	H	Me	Me	H	H

first the band at 1653 cm^{-1} and then the one at 1547 cm^{-1} decreased in intensity as a new absorption at 1599 cm^{-1} appeared and grew. Finally, after 30 min of reaction, the brown supernatant solution exhibited only the single ν_{NO} at 1599 cm^{-1} in its IR spectrum. This solution was then quickly filter cannulated away from the mercury-containing residue and was taken to dryness in vacuo. The resulting dark brown oily residue was extracted with Et$_2$O (6 × 25 mL) until the extracts were colorless, and solvent was removed from the yellow-brown extracts under reduced pressure. The brown solid so obtained was then extracted with hexanes (5 × 20 mL) until the extracts were again colorless. The volume of the dark yellow hexanes extracts was reduced in vacuo to ∼20 mL, and the remaining solution was filtered through a Florisil column (3 × 5 cm) supported on a medium porosity frit. The column was washed with hexanes (3 × 50 mL) until the washings were colorless. The combined washings and filtrate were

taken to dryness under reduced pressure to obtain 0.40 g (59% yield) of analytically pure CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene) (8) as a bright yellow, microcrystalline solid.

The use of other acyclic, conjugated dienes (except 2,3-dimethylbutadiene, vide infra) in place of 2,5-dimethyl-2,4-hexadiene in the above procedure afforded the analogous CpMo(NO)(η^4-*trans*-diene) complexes 1–9 in variable yields (Table I). The analytical, mass spectral, IR, and ^{1}H and ^{13}C NMR data for these and the other new η^4-diene complexes synthesized during this work are collected in Tables I–VI.

The analogous reduction of [CpMo(NO)Br$_2$]$_2$ in the presence of 2,5-dimethyl-2,4-hexadiene produced complex 8 in less than 0.5% isolated yield. Furthermore, reduction of [CpMo(NO)I$_2$]$_2$ by Na/Hg in the presence of cycloheptatriene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, cyclooctatetraene, 1,3-cyclohexadiene, 1,4-pentadiene, 2,3-butanedione, 3-buten-2-one, diphenylacetylene, ethylene, or norbornadiene simply resulted in the decomposition of the organometallic reagent and the loss of all nitrosyl-containing species from solution. Similar reductions of [CpMo(NO)I]$_2$ and [CpW(NO)I$_2$]$_2$ in the presence of various, acyclic conjugated dienes resulted in the occurrence of similar decomposition processes.

Reduction of [CpMo(NO)I$_2$]$_2$ by Na/Hg in the Presence of 2,3-Dimethylbutadiene. Method A: 2Na/Mo. Solid sodium amalgam (9.61 g, 10.0 mmol of Na) was liquefied with Hg (3 mL). THF (100 mL), 2,3-dimethylbutadiene (2 mL), and [CpMo-(NO)I$_2$]$_2$ (2.00 g, 2.25 mmol) were then added at room temperature to produce a red supernatant solution. After the reaction mixture had been stirred for 5 min, it had become brown in color, and the supernatant solution displayed a strong nitrosyl absorption at 1567 cm^{-1} in its IR spectrum. The reaction mixture was stirred for an additional 15 min and was then filter cannulated away from the mercury-containing residue. The dark brown filtrate was taken to dryness in vacuo to obtain a brown tar. This tar was extracted with cold (∼0 °C) Et$_2$O (4 × 25 mL) to obtain orange extracts whose IR spectrum exhibited two ν_{NO}'s at 1618 (m) and 1580 (s) cm^{-1}. The cold Et$_2$O solution was again taken to dryness under reduced pressure, and the resulting orange solid was extracted with cold (∼0 °C) hexanes until the extracts were colorless (i.e. 5 × 20 mL). An IR spectrum of the orange hexanes solution exhibited ν_{NO}'s at 1630 (m) and 1590 (s) cm^{-1}. The volume of this solution was reduced to ∼30 mL in vacuo at 0 °C, and Et$_2$O (3 mL) was then added. Chromatography of this cold solution on a Florisil column (4 × 15 cm) with a cold 10% Et$_2$O/hexanes mixture as eluant resulted in the development of two bands which were eluted from the column and collected. The first band was yellow (ν_{NO} at 1630 cm^{-1}) and afforded 0.42 g (47% yield) of analytically pure CpMo(NO)(η^4-*trans*-2,3-dimethylbutadiene) (3) as a yellow powder upon solvent removal in vacuo. The second band was orange-red (ν_{NO} at 1581 cm^{-1}) and afforded 0.12 g (13%

Table III. ^{1}H NMR Chemical Shifts of the Diene Complexes 1–14

compd no.	chemical shifts (δ in ppm; C$_6$D$_6$ unless specified otherwise)						
	Cp	R_{11}	R_{12}	R_{21}	R_{32}	R_{41}	R_{42}
1[a]	5.58 (s)	3.30 (m)	2.67 (m)	2.67 (m)	3.40 (ddd)	2.12 (ddd)	3.57 (ddd)
2A[b]	5.49 (s)	3.54 (d)	2.76 (d)	1.25 (s)	3.17 (dd)	2.73 (dd)	3.74 (dd)
2B[b]	5.53 (s)	3.35 (dd)	2.88 (dd)	2.37 (dd)	1.53 (s)	1.94 (dd)	3.45 (dd)
3	5.04 (s)	3.31 (dd)	3.01 (d)	0.90 (s)	1.70 (s)	2.37 (d)	3.48 (dd)
4A[c]	4.94 (s)	1.47 (d)	3.56 (dq)	2.10 (dd)	3.22 (ddd)	3.37 (dd)	2.71 (dd)
4B[c]	4.95 (s)	2.84 (dd)	2.71 (dd)	1.99 (ddd)	3.33 (dd)	2.48 (dq)	1.92 (d)
5A[d]	4.85 (s)	3.11 (d)	2.64 (d)	1.31 (s)	1.46 (s)	1.48 (s)	2.15 (s)
5B[d]	5.20 (s)	2.05 (s)	2.00 (s)	1.45 (s)	1.57 (s)	2.65 (d)	3.25 (d)
6	4.94 (s)	1.49 (d)	3.55 (m)	2.02 (dd)	3.17 (dd)	2.46 (m)	1.93 (d)
7A[e]	4.90 (s)	1.52 (d)	3.50 (m)	2.75 (dd)	2.92 (dd)	0.89 (d)	4.37 (m)
7B[e]	4.91 (s)	3.90 (m)	1.79 (d)	1.68 (dd)	3.79 (dd)	2.45 (m)	1.94 (d)
8	4.93 (s)	1.68 (s)	1.89 (s)	2.44 (d)	3.41 (d)	1.05 (s)	2.14 (s)
9	4.64 (s)	6.88–7.32 (m)	3.39 (d)	4.37 (dd)	2.98 (dd)	4.68 (d)	6.88–7.32 (m)
10	1.69 (s)[f]	3.27 (d)	1.76 (d)	1.00 (s)	1.74 (s)	2.66 (d)	3.37 (d)
11A[g]	1.87 (s)[f]	2.43 (dd)	2.85 (dd)	1.51 (m)	3.44 (t)	2.06 (m)	1.90 (s)
11B[g]	1.87 (s)[f]	1.89 (s)	1.98 (d)	3.44 (t)	1.52 (m)	2.85 (dd)	2.44 (dd)
12	1.70 (s)	1.68 (s)	1.84 (s)	2.34 (d)	3.59 (d)	1.13 (s)	2.03 (s)
13	5.13 (s)	−0.36 (d)	3.84 (d)	2.22 (s)	2.22 (s)	−0.36 (d)	3.84 (d)
14	1.68 (s)[f]	−0.49 (d)	3.45 (d)	2.20 (s)	2.20 (s)	−0.49 (d)	3.45 (d)

[a] Recorded in CD$_2$Cl$_2$. [b] Isomers 2A and 2B exist in a 1:3 ratio. Recorded in CDCl$_3$. [c] Isomers 4A and ,4B exist in a 1:2 ratio. [d] Isomers 5A and 5B exist in a 1:4 ratio. [e] Isomers 7A and 7B exist in a 7:5 ratio. [f] This is a η^5-C$_5$Me$_5$ = Cp*. [g] Isomers 11A and 11B exist in a 1:1 ratio and may be separated by chromatography on a Florisil column.

Table IV. ¹H NMR Coupling Constants of the Diene Complexes 1-14

compd no.	coupling constants (C$_6$D$_6$, in Hz)								
	J_{11-12}	J_{41-42}	J_{11-21}	J_{32-42}	J_{12-21}	J_{32-41}	J_{21-32}	J_{11-42}	J_{21-41}
1[a]	2.3	3.1	6.9	6.2	14.0	13.1	9.8	0.6	1.0
2A[b]	1.9	3.6		6.6		14.0			0.8
2B[b]	2.8	3.1	7.0		14.4				0.8
3	2.7	3.6						1.0	
4A	6.4	2.7		6.2	12.8	13.8	10.0		
4B	2.4	6.0	6.8		13.8	12.0	11.7		
5A	2.3								
5B		2.4							
6	6.4	6.0			12.6	11.9	10.5		
7A	6.3	6.9		7.6	12.5		11.4		
7B	6.8	6.1	5.7			11.6	11.4		
8							11.8		
9		12.0				13.5	10.5		
10	2.9	2.8							
11A	2.5		6.8		14.1	11.4	11.4		
11B		2.6		6.7	11.3	14.1			
12							11.5		
13	5.0	5.0							
14	4.9	4.9							

[a]Recorded in CD$_2$Cl$_2$. [b]Recorded in CDCl$_3$.

Table V. ¹³C NMR Chemical Shifts of the Diene Complexes

compd no.	chemical shifts (C$_6$D$_6$, δ in ppm)[a]										
	Cp	C$_1$	C$_2$	C$_3$	C$_4$	R$_{11}$	R$_{12}$	R$_{21}$	R$_{32}$	R$_{41}$	R$_{42}$
1	94.88 (d)	51.76 (t)	82.98 (d)	98.04 (d)	55.08 (dd)		21.28 (q)				
2A	96.69 (d)	53.95 (t)	105.22 (s)	92.81 (d)	54.15 (t)						
2B	95.08 (d)	50.46 (t)	79.70 (d)	115.80 (s)	55.28 (t)				18.10 (q)		
3	96.42 (d)	54.59 (t)	103.05 (s)[b]	109.90 (s)[b]	54.45 (t)			23.87 (q)	21.31 (q)		
4A	95.75 (d)	50.24 (t)	78.95 (d)	99.81 (d)	72.99 (d)						20.68 (q)
4B	94.90 (d)	70.43 (d)	86.60 (d)	92.80 (d)	54.05 (dd)	20.23 (q)					
5A	97.75 (d)	55.10 (t)	113.00 (s)	90.28 (d)	82.20 (s)			26.15 (q)		32.40 (q)	33.15 (q)
5B	96.42 (d)	88.45 (s)	81.23 (d)	113.05 (s)	55.23 (t)	32.40 (q)	25.15 (q)	18.15 (q)			
6	95.73 (d)	68.78 (d)	82.68 (d)	94.96 (d)	71.88 (d)	20.35 (q)					20.86 (q)
7A	96.82 (d)	70.34 (d)	86.92 (d)	90.12 (d)	70.54 (d)	20.60 (q)				16.15 (q)	
7B	95.08 (d)	69.14 (d)	77.88 (d)	99.12 (d)	72.35 (d)		20.95 (q)				16.20 (q)
8	97.43 (d)	86.18 (s)[b]	83.24 (d)	92.28 (d)	86.77 (s)[b]	31.01 (q)	23.32 (q)			23.44 (q)	31.04 (q)
9	97.85 (d)	71.93 (d)	75.99 (d)	91.60 (d)	75.57 (d)	124-131 (m) 142-144 (m)					124-131 (m) 142-144 (m)
10	105.84 (s)[c]	60.57 (t)	102.80 (s)	109.26 (d)	59.20 (t)			22.35 (q)	21.20 (q)		
11A	106.35 (s)[c]	58.50 (t)	88.42 (d)	99.05 (d)	79.51 (d)						19.41 (q)
11B	104.52 (s)[c]	79.45 (d)	99.45 (d)	88.50 (d)	58.51 (t)	19.41 (q)					
12	105.49 (s)[c]	83.44 (s)[b]	88.87 (d)	91.27 (d)	88.52 (s)[b]	28.89 (q)	24.03 (q)			20.48 (q)	29.58 (q)
13	95.01 (d)	52.15 (dd)	117.33 (s)	117.33 (s)	52.15 (dd)			22.57 (q)	22.57 (q)		
14	104.79 (s)[c]	58.24 (dd)	117.01 (s)	117.01 (s)	58.24 (dd)			23.91 (q)	23.91 (q)		

[a]The letters in parentheses denote $^1J_{HC}$ multiplicities. [b]Note: These C$_2$ vs C$_3$ or C$_1$ vs C$_4$ assignments are tentative. [c]This is η⁵-C$_5$Me$_5$; the methyl carbons produce the following quartet resonances at δ: 10, 10.72; 11A, 10.70; 11B, 10.39; 12, 10.08; 14, 10.49 ppm.

yield) of CpMo(NO)(η⁴-cis-2,3-dimethylbutadiene) (13) as an analytically pure orange-red powder when solvent was removed under reduced pressure. Complex 13 could be obtained in crystalline form by recrystallization from Et$_2$O/hexanes at -20 °C.

Method B: $^2/_3$Na/Mo. A flask containing 3.0 g (3.1 mmol of Na) of solid sodium amalgam in 5 mL of mercury, THF (50 mL), and 2,3-dimethylbutadiene (2 mL) was cooled to ~-25 °C. The mixture was stirred rapidly as [CpMo(NO)I$_2$]$_2$ (2.00 g, 2.25 mmol) was added. After 15 min, the supernatant solution was green in color, and its IR spectrum displayed two ν$_{NO}$'s at 1653 and 1548 cm⁻¹. During the next hour, the band at 1653 cm⁻¹ was replaced by one at 1644 cm⁻¹. Workup of the final reaction mixture in a manner identical with that described in method A resulted in the isolated of trace amounts of 3 and 0.35 g (24% yield) of the new complex CpMo(NO)I(η³-C$_6$H$_{11}$) (15) as an orange, microcrystalline solid.

Anal. Calcd for C$_{11}$H$_{16}$NOIMo: C, 32.95; H, 3.99; N, 3.49. Found: C, 33.26; H, 4.00; N, 3.40. IR (THF): ν$_{NO}$ 1644 (s) cm⁻¹. Low-resolution mass spectrum (probe temperature 160 °C): m/z 403 (P⁺). ¹H NMR (C$_6$D$_6$): isomer A, δ 5.15 (s, 5 H, C$_5$H$_5$), 3.08 (d, 1 H, J = 4.0 Hz, CH$_A$H$_B$), 2.40 (d, 1 H, J = 4.0 Hz, CH$_A$H$_B$), 2.30 (s, 3 H, CH$_3$), 1.65 (s, 3 H, CH$_3$), 0.85 (s, 3 H, CH$_3$); isomer B, δ 5.08 (s, 5 H, C$_5$H$_5$), 2.90 (d, 1 H, J = 3.8 Hz, CH$_A$H$_B$), 2.81 (d, 1 H, J = 3.8 Hz, CH$_A$H$_B$), 2.24 (s, 3 H, CH$_3$), 1.54 (s, 3 H, CH$_3$), 0.93 (s, 3 H, CH$_3$); isomer ratio A:B = 5:1.

Preparation of Cp*Mo(NO)(η⁴-trans-diene) Complexes 10-12 and Cp*Mo(NO)(η⁴-cis-2,3-dimethylbutadiene) (14). Reductions of [Cp*Mo(NO)I$_2$]$_2$ in the presence of 2,3-dimethylbutadiene, (E)-1,3-pentadiene, or 2,5-dimethyl-2,4-hexadiene to form η⁴-trans- and/or η⁴-cis-diene complexes were performed in manners analogous to those described above for their respective Cp analogues but at -20 °C. Customary workup procedures afforded these Cp* complexes in somewhat higher yields than their Cp analogues. Indeed, the isolation of 14 did not even require the use of cold solvents as for 13 (vide supra). The analytical and spectroscopic data for these Cp* complexes are presented in Tables I–VI.

Reaction of [CpMo(NO)I$_2$]$_2$ with C$_4$H$_6$Mg(THF)$_2$. Method A: In Et$_2$O. To a rapidly stirred, pale yellow suspension of (butene-1,4-diyl)magnesium[16] (C$_4$H$_6$Mg(THF)$_2$, 1.00 g, 4.50 mmol) in Et$_2$O (100 mL) at ambient temperature was added [CpMo-(NO)I$_2$]$_2$ (2.00 g, 2.25 mmol). The initial mixture of suspended

(16) (a) (Butene-1,4-diyl)magnesium (prepared according to the procedure of: Wreford, S. S.; Whitney, J. F. *Inorg. Chem.* **1981**, *20*, 3918) was kindly provided by Professor M. D. Fryzuk. (b) Yasuda, H.; Kajihara, Y.; Mashima, K.; Lee, K.; Nakamura, A. *Chem. Lett.* **1981**, 519. (c) Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549.

Table VI. ^{13}C NMR $^1J_{^1H-^{13}C}$ Coupling Constants of the Diene Complexes

compd no.	coupling constants (C_6D_6, in Hz)[a]										
	Cp	C_1	C_2	C_3	C_4	R_{11}	R_{12}	R_{21}	R_{32}	R_{41}	R_{42}
1	176.2	157.5	155.7	164.1	150.4						
2A	174.7	150.1		148.0	150.9			128.2			
2B	175.7	157.5	154.9		154.2				128.0		
3	175.1	155.0			155.0			127.9[b]	127.9[c]		
4A	176.0	157.2	156.0	161.4	147.0					127.3	
4B	178.0	155.0	143.0	162.1	162.0	123.8					
5A	175.0	153.0		149.0				123.5		124.4	124.4
5B	175.0		149.9		154.0	124.4	127.3		127.0		
6	175.1	154.8	153.2	156.0	148.0	126.2					125.8
7A	175.1	153.0	155.5	163.5	153.0	126.3			126.8		
7B	175.1	153.0	162.5	154.8	152.6		127.0				125.7
8	174.6		153.1	160.3		126.0	126.5			126.5	126.0
9	175.0	155.0		165.0	150.0						
10	d	152.5			155.6			127.5	127.5		
11A	d	158.0	153.2	160.8	148.8						128.0
11B	d	152.0	158.0	158.0	126.7		126.7				
12	d		152.0	159.8		125.3	126.8			126.1	125.5
13	176.2	162.3[e]			162.3[e]			127.3[f]	127.3[f]		
		162.5			162.5						
14	d	161.3			161.3			127.3	127.3		
		161.3			161.3						

[a] Recorded by using broad-band gated decoupling, see text. [b] ^3J_A = 3.3 Hz, ^3J_B = 7.7 Hz. [c] ^3J_A = 4.4 Hz, ^3J_B = 8.3 Hz. [d] This is η^5-C_5Me_5. The methyl carbons have the following ^1J: 10, 125.0; 11A, 127.3; 11B, 126.0; 12, 126.8; 14, 126.7 Hz. [e] ^3J = 4.4 Hz. [f] ^3J_A = 4.6 Hz, ^3J_B = 6.8 Hz.

pale yellow and dark red-violet solids was replaced after 16 h by a dark green solid suspended in a very pale pink solution. The green solid was collected by filtration, washed with Et_2O (4 × 25 mL), and dried in vacuo (<0.005 Torr, 1 h, 20 °C) to obtain 2.58 g (99% yield) of $CpMo(NO)I_2\cdot C_4H_6Mg\cdot^1/_2(Et_2O)$ (16) as a green powdery solid.

Anal. Calcd for $C_{11}H_{16}NO_{1.5}I_2MgMo$: C, 23.58; H, 2.88; N, 2.50. Found: C, 23.61; H, 3.05;, N, 2.52. IR (Nujol mull): ν_{NO} 1491 (s, br), cm⁻¹. IR (CH_2Cl_2): ν_{NO} 1450 (s, br) cm⁻¹.

Exposure of this material to vacuum (<0.005 Torr) at 20 °C for 18 h resulted in partial loss of the Et_2O of solvation.

Method B: In THF with Workup Procedure I. To a stirred red solution of $[CpMo(NO)I_2]_2$ (2.00 g, 2.25 mmol) in THF (100 mL) at −78 °C (ν_{NO} 1691 (s) cm⁻¹) was added (butene-1,4-diyl)-magnesium (1.00 g, 4.50 mmol). After 5 min, the reaction mixture consisted of a dark green solid suspended in a green solution. This mixture was stirred for 1 h at −78 °C and was then allowed to warm slowly to 20 °C whereupon the green solid dissolved, the solution became brown, and a gray solid precipitated. Solvent was removed from the final reaction mixture in vacuo, and CH_2Cl_2 (20 mL) was added to produce a brown solution (ν_{NO} 1450 (s, br) cm⁻¹) over a white solid. This mixture was then filtered through a column (3 × 3 cm) of alumina (Woelm neutral, activity 2), and the column was washed with CH_2Cl_2 (3 × 20 mL) to obtain a red filtrate (ν_{NO} 1599 (w) and 1650 (s) cm⁻¹). The filtrate was taken to dryness in vacuo, and the resulting brown oil was treated with hexanes (200 mL) to obtain a pale orange solution above a brown, solid residue. The solution was filtered through alumina (3 × 4 cm, Woelm neutral, activity 1, 4 × 40 mL Et_2O wash), the filtrate was taken to dryness under reduced pressure, and the residue was recrystallized from Et_2O/hexanes to obtain yellow crystals of $CpMo(NO)(\eta^4$-$trans$-butadiene) (1) (~0.10 g, 9% yield).

Crystallization of the brown, hexanes-insoluble residue from CH_2Cl_2/hexanes afforded orange crystals (1.10 g, 65% yield) of $CpMo(NO)I(\eta^3$-$C_4H_7)$ (17).

Anal. Calcd for $C_9H_{12}NOIMo$: C, 28.98; H, 3.24; N, 3.75. Found: C, 28.70; H, 3.25; N, 3.65. IR (CH_2Cl_2): ν_{NO} 1650 (s) cm⁻¹. Low-resolution mass spectrum (probe temperature 75 °C): m/z 375 (P⁺).

Method C: In THF with Workup Procedure II. This reaction was effected in a manner identical with that just described in method B above. However, after being allowed to warm to 20 °C, the final reaction mixture in THF was stirred at ambient temperature for 5 days. After this period, the brown supernatant solution's IR spectrum exhibited ν_{NO}'s at 1656, 1612, and 1592 cm⁻¹. The final mixture was filtered through alumina (3 × 12 cm, Woelm neutral, activity 1) with a THF wash (2 × 50 mL).

The combined filtrates were taken to dryness in vacuo, and the remaining residue was crystallized from hexanes to obtain $CpMo(NO)(\eta^4$-$trans$-butadiene) (1) in 38% yield (0.42 g).

Reactions of $CpMo(NO)(\eta^4$-$trans$-2,5-dimethyl-2,4-hexadiene) (8) with $PMePh_2$ and PMe_3. Both of these conversions involved a 20–30% excess of the phosphine reagent, and both reactions proceeded similarly. Consequently, the one involving $PMePh_2$ is described as a representative example.

A bright yellow solution of $CpMo(NO)(\eta^4$-$trans$-2,5-dimethyl-2,4-hexadiene) (8) (0.10 g, 0.33 mmol) in hexanes (50 mL) was cooled to −78 °C and was then treated with neat $PMePh_2$ (0.75 mL, 0.40 mmol). The reaction mixture was allowed to warm slowly to room temperature and was stirred at this temperature for 12 h whereupon its color darkened. IR monitoring of the progress of the reaction during this time revealed that the nitrosyl absorption characteristic of the initial diene complex at 1622 cm⁻¹ was gradually replaced by a lower energy absorbance at 1589 cm⁻¹. Removal of volatiles from the final reaction mixture under reduced pressure produced a brown residue. This residue was washed with hexanes (2 × 10 mL) and crystallized from Et_2O to obtain 0.13 g (80% yield) of $CpMo(NO)(PMePh_2)(\eta^2$-2,5-dimethyl-2,4-hexadiene) (18) as pale yellow, feather-like crystals.

Anal. Calcd for $C_{26}H_{32}PNOMo$: C, 62.25; H, 6.38; N, 2.79. Found: C, 61.88; H, 6.18; N, 3.08. IR (Nujol mull): ν_{NO} 1557 cm⁻¹. IR (Et_2O) ν_{NO} 1581 cm⁻¹. ¹H NMR (C_6D_6): δ 6.9–7.0 (m, 10 H, C_6H_5), 4.93 (s, 5 H, C_5H_5), 4.82 (d, 1 H, $^3J_{HH}$ = 11.5 Hz, C=CH uncoord), 3.19 (dd, 1 H, $^3J_{HH}$ = 11.5 Hz, J_{HP} = 9.4 Hz, C=CH coord), 1.98 (d, 3 H, $^2J_{HP}$ = 7.8 Hz, PCH_3), 2.32 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3). Low-resolution mass spectrum (probe temperature 120 °C): m/z 503 (P⁺).

The reaction of 8 with PMe_3 was conducted in a similar manner, the total reaction time also being 12 h. The final η^2-diene complex $CpMo(NO)(PMe_3)(\eta^2$-2,5-dimethyl-2,4-hexadiene) (19) was isolated as a yellow, microcrystalline solid in 64% yield.

Anal. Calcd for $C_{16}H_{28}PNOMo$: C, 50.96; H, 7.44; N, 3.72. Found: C, 50.73; H, 7.27; N, 3.89. IR (Nujol mull): ν_{NO} 1537 cm⁻¹. IR (Et_2O): ν_{NO} 1584 cm⁻¹. ¹H NMR (C_6D_6): δ 4.96 (s, 5 H, C_5H_5), 4.70 (d, 1 H, $^3J_{HH}$ = 11.5 Hz, C=CH uncoord), 2.88 (dd, 1 H, $^3J_{HH}$ = 11.5, Hz, J_{HP} = 10.0 Hz, C=CH coord), 2.21 (s, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.06 (d, 9 H, $^2J_{HP}$ = 8.5 Hz, P(C$H_3)_3$).
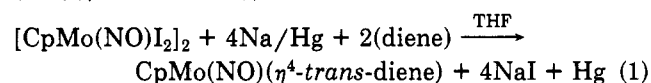
Reaction of $CpMo(NO)(\eta^4$-$trans$-2,5-dimethyl-2,4-hexadiene) (8) with CO. A yellow hexanes (50-mL) solution of 8 (0.10 g, 0.33 mmol) which exhibited a ν_{NO} at 1622 cm⁻¹ in its IR spectrum was transferred by cannula into a Fisher-Porter vessel. The vessel was filled with 60 psig of CO, and the yellow solution was stirred

at room temperature for 5 days during which time a small amount of a brown precipitate appeared. The final supernatant solution's IR spectrum displayed a ν_{CO} at 1960 cm^{-1} and a ν_{NO} at 1649 cm^{-1} after the pressure had been released. The final reaction mixture was filtered through a short (3 × 2 cm) column of Celite supported on a medium porosity frit, and the column was washed with hexanes (3 × 10 mL). The combined filtrates were taken to dryness in vacuo, and the resulting yellow powder was recrystallized from hexanes to obtain 0.09 g (81% yield) of CpMo-(NO)(CO)(η^2-2,5-dimethyl-2,4-hexadiene) (20) as bright yellow crystals.

Anal. Calcd for $C_{14}H_{19}NO_2Mo$: C, 51.07; H, 5.77; N, 4.26. Found: C, 51.30; H, 5.81; N, 4.40. IR (Nujol mull): ν_{CO} 1948 (s) cm^{-1}, ν_{NO} 1643 (s) cm^{-1}. IR (Et$_2$O): ν_{CO} 1958 (s) cm^{-1}, ν_{NO} 1640 (s) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 5.80 (d, 1 H, $^2J_{HH}$ = 10.5 Hz, C=CH uncoord), 4.95 (s, 5 H, C$_5$H$_5$), 3.81 (d, 1 H, $^2J_{HH}$ = 10.5 Hz, C=CH coord), 2.04 (s, 3 H, CH$_3$), 1.79 (s, 3 H, CH$_3$), 1.76 (s, 3 H, CH$_3$), 1.35 (s, 3 H, CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 151.2, 127.4, 95.5, 75.2, 58.3, 32.6, 26.1, 23.6, 18.5. Low-resolution mass spectrum (probe temperature 120 °C): m/z 331 (P$^+$).

Results and Discussion

Syntheses and Some Physical Properties of the CpMo(NO)(η^4-*trans*-diene) Complexes 1–9. The reduction of [CpMo(NO)I$_2$]$_2$ by sodium amalgam in the presence of various acyclic, conjugated dienes results in the formation of novel η^4-*trans*-diene complexes, CpMo-(NO)(η^4-*trans*-diene), i.e.

$$[\text{CpMo(NO)I}_2]_2 + 4\text{Na/Hg} + 2(\text{diene}) \xrightarrow{\text{THF}}$$
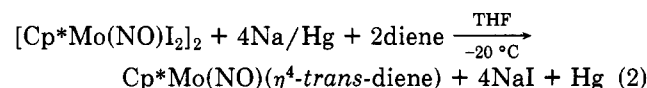$$\text{CpMo(NO)}(\eta^4\text{-}trans\text{-diene}) + 4\text{NaI} + \text{Hg} \quad (1)$$

These transformations are rapid and straightforward, and an excess (but not deficiency, vide infra) of sodium amalgam may be used with no deleterious effects. The reactions are, however, accompanied by extensive decomposition of the organometallic species present when they are effected at ambient temperature. This feature is probably a manifestation of the highly exothermic nature of the conversions which results in warming of the reaction mixtures. This difficulty can be largely overcome by performing the reductions 1 at ~−20 °C, a temperature just above the melting point of the sodium amalgam. At this lower temperature, the new *trans*-diene product complexes (Table I) are isolable in yields of ~10–60%, i.e. somewhat higher than we initially communicated. Optimum yields are achieved only if the final supernatant solutions are rapidly removed from the mercury-containing residues and taken to dryness in vacuo once monitoring of the progress of the conversions by IR spectroscopy indicates that the bands due to the desired product complex begin to diminish in intensity. This is so because the rate of decomposition of the *trans*-diene product complexes in solution (vide infra) is apparently accelerated by the presence of trace impurities in the final reaction mixtures.

The analytical, mass spectral, IR, and ^{1}H and ^{13}C NMR data for the nine CpMo(NO)(η^4-*trans*-diene) complexes (i.e. 1–9) isolated and characterized during this work are presented in Tables I–VI. Compounds 1–9 are yellow, diamagnetic solids which are quite soluble in common organic solvents. When pure, they are thermally stable as solids at 20 °C but slowly decompose in solutions (e.g. $t_{1/2} \approx 3$ days at 20 °C in C$_6$D$_6$). This decomposition results in the precipitation of a brown solid which is only soluble in solvents such as DMSO[17] and contains no nitrosyl ligands (as evidenced by its IR spectrum as a Nujol mull). Solutions of 1–9 are also somewhat air-sensitive, but as solids the complexes may be handled in air for short periods of time. The analytical and spectroscopic data for

1–9 are consistent with their formulations as monomeric, 18-electron complexes possessing "three-legged piano-stool" molecular structures. A single-crystal X-ray crystallographic analysis of 8^{9a} has established the intramolecular dimensions of one of these compounds in the solid state and has confirmed that its diene ligand is attached to the metal center in a twisted, transoidal fashion.

The IR spectra of the η^4-*trans*-diene complexes 1–9 in CH$_2$Cl$_2$ solutions exhibit single, strong absorptions in the region 1582–1599 cm^{-1} attributable to linear, terminal nitrosyl ligands. These absorptions occur at progressively lower energies with increasing methyl substitution on the diene ligand. Interestingly, the nitrosyl-stretching frequencies observed for 1–9 are intermediate between those found for CpMo(NO)(CO)$_2$[18] and CpMo(NO)(PMePh$_2$)$_2$[15] (ν_{NO} 1663 and 1539 cm^{-1}, respectively, in CH$_2$Cl$_2$) and are similar to that exhibited by CpMo(NO){P(OMe)$_3$}$_2$[15] (ν_{NO} 1574 cm^{-1} in CH$_2$Cl$_2$). Hence, the *trans*-diene complexes possess more electron-rich metal centers than their dicarbonyl analogues. Furthermore, the *trans*-diene ligands in compounds 1–9 appear to transfer nearly as much net electron density to their Mo–NO interactions as do two P(OMe)$_3$ ligands, the latter being more familiar Lewis bases.[19] Finally, it may be noted that the ν_{NO}'s of 1–9 in solutions are strongly dependent on solvent medium, varying linearly with the acceptor number of the solvent.[20] We have previously observed a similar, albeit less pronounced, trend for the analogous CpMo(NO)L$_2$ (L = phosphine or phosphite) complexes.[15] This trend simply reflects the ability of the CpMo(NO)(η^4-*trans*-diene) complexes to function as Lewis bases via the lone pair of electrons on the oxygen atoms of their relatively electron-rich NO groups toward the acid sites provided by the solvents. The Mo–NO→solvent interactions are not sufficiently strong, however, to permit the isolation of these adducts.

Syntheses and Some Physical Properties of the Cp*Mo(NO)(η^4-*trans*-diene) Complexes 10–12. By and large, the replacement of a cyclopentadienyl (Cp) ligand by its permethyl analogue (Cp*) on a transition-metal center often leads to the isolation in good yields of complexes which are otherwise unstable or available only in low yields.[12] Consequently, we also effected the reduction of [Cp*Mo(NO)I$_2$]$_2$ by sodium amalgam in the presence of several acyclic, conjugated dienes, i.e.

$$[\text{Cp*Mo(NO)I}_2]_2 + 4\text{Na/Hg} + 2\text{diene} \xrightarrow[\text{-20 °C}]{\text{THF}}$$
$$\text{Cp*Mo(NO)}(\eta^4\text{-}trans\text{-diene}) + 4\text{NaI} + \text{Hg} \quad (2)$$

Conversions 2 proceed in a manner similar to that observed for their Cp analogues in reactions 1, but the yields of the organometallic products are generally slightly higher from 2. The three Cp*Mo(NO)(η^4-*trans*-diene) complexes isolated during this work, i.e. 10–12, are yellow, crystalline solids that exhibit physical and spectroscopic properties (Tables I–VI) which are similar to those displayed by their Cp analogues 3, 4, and 8, respectively. Nevertheless, the presence of the five methyl substituents on the Cp* ligand confers greater solubility in organic solvents, greater thermal stability, and more electron richness at the molybdenum center on complexes 10–12 as compared to 3, 4, and 8. The increased electron richness is manifested by a lowering of the ν_{NO}'s exhibited by the Cp* complexes

(17) Drago, R. S. *Pure Appl. Chem.* **1980**, *52*, 2261.

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

(19) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

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

by ~20 cm^{-1}. All the spectroscopic properties of 10–12 are in accord with their possessing solution and solid-state molecular structures similar to those found for their Cp analogues (vide supra).

Syntheses and Some Physical Properties of the Cp'Mo(NO)(η^4-cis-2,3-dimethylbutadiene) Complexes [Cp' = Cp (13) or Cp* (14)]. When the diene employed in reactions 1 or 2 is 2,3-dimethylbutadiene, IR monitoring of the two conversions indicates the formation of an intermediate nitrosyl-containing product in each reaction in addition to complexes 3 and 10, respectively. These other products are the η^4-cis-2,3-dimethylbutadiene complexes 13 and 14, respectively, which may be separated from their isomers 3 and 10 and isolated as outlined in the Experimental Section. No spectroscopic evidence for the formation of other η^4-cis-diene intermediate complexes analogous to 13 and 14 has been observed during the syntheses of the other η^4-trans-diene complexes isolated during this study (Table I).

The novel Cp'Mo(NO)(η^4-cis-2,3-dimethylbutadiene) complexes 13 and 14 are red, diamagnetic solids which are soluble in common organic solvents to afford red, air-sensitive solutions. Their physical properties (summarized in Tables I–VI) support their formulations as monomeric, 18-electron species in which the 2,3-dimethylbutadiene ligands are attached to the metal centers in a planar, cisoidal fashion. A single-crystal X-ray crystallographic analysis of 13[9b] has confirmed this formulation and has established the intramolecular geometrical parameters of its "three-legged piano-stool" molecular structure. Like their trans-diene-containing isomers 3 and 10 (vide supra), 13 and 14 also exhibit solvent-dependent ν_{NO}'s in their solution IR spectra. However, the ν_{NO}'s of 13 and 14 are ~40 cm^{-1} lower in energy than those of 3 and 10 (Table I), thereby indicating that the Mo $d\pi \rightarrow$ NO π^* back-donation of electron density is significantly greater in the cis-diene complexes. This conclusion is in accord with the Fenske–Hall MO rationale of the bonding in these compounds (vide infra).[9b]

That 13 and 14 are kinetic products of reactions 1 and 2 is established by the fact that they isomerize irreversibly to 3 and 10, respectively, in solutions. These isomerizations are more rapid for 13 than 14 and proceed to completion faster in donor solvents such as THF rather than nondonor solvents such as benzene. Once formed, the bound trans-dienes in 3 and 10 (or in any of the CpMo-(NO)(η^4-trans-diene) complexes listed in Table I) do not revert to their bound cis forms even upon heating to the decomposition points of the complexes in various solvents. This behavior contrasts with that exhibited by the Cp$_2$M-(η^4-2,3-dimethylbutadiene) compounds (M = Zr or Hf) for which the isomers having η^4-s-cis-diene ligands are thermodynamically favored.[7]
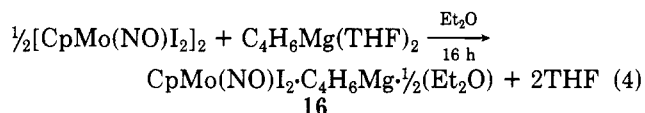
One final point concerning the reduction of [CpMo-(NO)I$_2$]$_2$ by Na/Hg in the presence of 2,3-dimethylbutadiene must be made. That point is that at least 2 equiv of sodium must be used in order to obtain η^4-diene complexes as the organometallic products. When a deficiency of the reducing agent is employed (e.g. ^{2}/$_3$Na/Mo rather than 2Na/Mo), the new complex CpMo(NO)I(η^3-C$_6$H$_{11}$) (15) is obtained instead as an orange, microcrystalline solid in 24% isolated yield. The spectroscopic properties of 15 (summarized in the Experimental Section) are consistent with it having a monomeric molecular structure similar to that established for the chiral CpW-(NO)I(η^3-C$_3$H$_5$).[21] While the exact origin of complex 15

remains unknown, it is probably formed via hydrogen-atom abstraction from either the solvent or some radical species present in the reaction mixture. We have observed spectroscopically (but not isolated) other η^3-allyl complexes analogous to 15 which invariably result whenever reactions 1 and 2 are effected with a dearth of sodium amalgam.

Reaction of [CpMo(NO)I$_2$]$_2$ with C$_4$H$_6$Mg(THF)$_2$. Like compounds 1–14, most diene-containing complexes have generally been first synthesized by trapping various coordinatively unsaturated transition-metal species with appropriate 1,3-dienes.[7] However, several other preparative routes leading to such compounds are known. Of these, a particularly useful one involves the metathesis reaction of (butene-1,4-diyl)magnesium, C$_4$H$_6$Mg(THF)$_2$,[16] with metal halides, e.g.

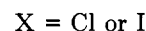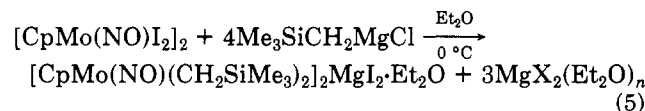$$Cp_2MCl_2 + C_4H_6Mg(THF)_2 \rightarrow Cp_2M(\eta^4\text{-}C_4H_6) + MgCl_2 \tag{3}$$
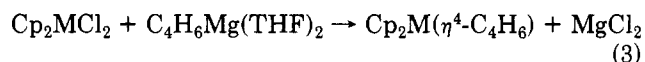
where M = Zr or Hf.[7,22] It was thus obviously of interest to determine whether CpMo(NO)(η^4-trans-C$_4$H$_6$) (1) can also be prepared by employing the (butene-1,4-diyl)magnesium reagent. When the reaction between [CpMo-(NO)I$_2$]$_2$ and the organomagnesium species is effected in Et$_2$O (in which both reagents are only sparingly soluble), compound 1 is not the product formed. Instead, the following conversion occurs:

$$\frac{1}{2}[CpMo(NO)I_2]_2 + C_4H_6Mg(THF)_2 \xrightarrow[16\ h]{Et_2O}$$
$$CpMo(NO)I_2 \cdot C_4H_6Mg \cdot \frac{1}{2}(Et_2O) + 2THF \tag{4}$$
$$\mathbf{16}$$

The green product complex 16 is insoluble in Et$_2$O and hence may be collected in virtually quantitative yield by filtration of the final reaction mixture. Its physical and chemical properties indicate that it possesses the composition shown in eq 4, but the Et$_2$O of crystallization is removable by prolonged exposure of the complex to vacuum. Present evidence suggests that 16 is best formulated as a syn- or anti-allyl complex, CpMo(NO)I(η^3-C$_3$H$_4$R), in which the substituent on the allyl group (R = CH$_2$MgI) functions as a Lewis acid toward the nitrosyl oxygen atom, e.g.
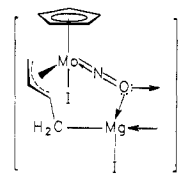
This evidence is as follows: (1) The IR spectrum of 16 exhibits only one absorption that may be attributed to a nitrosyl ligand, and this band (at 1491 (s, br) or 1450 (s) cm^{-1} in a Nujol mull or a CH$_2$Cl$_2$ solution, respectively) occurs in the region normally associated with the vibrations of isonitrosyl linkages.[23] (2) There is an excellent precedent for such an isonitrosyl linkage provided by the organometallic product of a closely related reaction effected some time ago in our laboratories, namely[8]
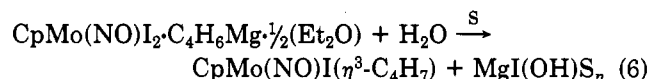
$$[CpMo(NO)I_2]_2 + 4Me_3SiCH_2MgCl \xrightarrow[0\ °C]{Et_2O}$$
$$[CpMo(NO)(CH_2SiMe_3)_2]_2MgI_2 \cdot Et_2O + 3MgX_2(Et_2O)_n \tag{5}$$

$$X = Cl\ or\ I$$

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(21) Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268.

(22) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388.

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

A partial X-ray crystallographic analysis of single crystals of $[CpMo(NO)(CH_2SiMe_3)_2]_2MgI_2\cdot Et_2O$ has confirmed the existence of two Mo–NO→Mg linkages in the solid-state molecular structure of this complex. Furthermore, the ν_{NO} of this compound as a Nujol mull is 1520 cm^{-1}, comparable to that exhibited by 16.

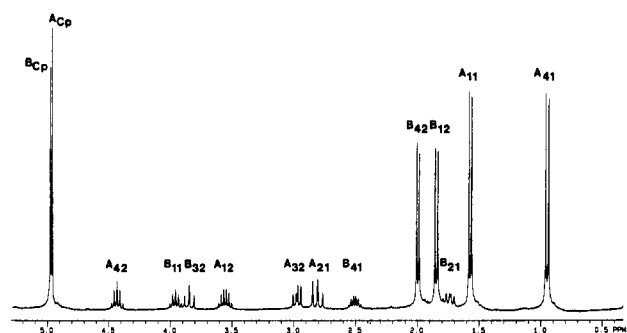(3) Finally, complex 16 is rapidly converted into $CpMo(NO)I(\eta^3\text{-}C_4H_7)$ (17) by water, i.e.

$$CpMo(NO)I_2\cdot C_4H_6Mg\cdot\frac{1}{2}(Et_2O) + H_2O \xrightarrow{S}$$
$$CpMo(NO)I(\eta^3\text{-}C_4H_7) + MgI(OH)S_n \quad (6)$$

where S = solvent. For example, addition of water to a THF solution of 16 causes an instantaneous color change from green to brown, and an IR spectrum of the brown solution displays a strong band at 1656 cm^{-1}, the characteristic ν_{NO} of 17. Even water adsorbed on alumina effects reaction 6, making this a good route to the methallyl complex 17 which has been previously synthesized by treating $[CpMo(NO)(CO)(\eta^3\text{-}C_4H_7)]^+$ with I$^-$.[24]

The originally desired η^4-*trans*-butadiene complex 1 *can* be produced from 16, not by hydrolysis but by thermolysis. Hence, maintenance of 16 in THF at room temperature for 5 days results in its conversion to 1. The final product is isolable in only 38% yield, however, because of its concomitant thermal decomposition (vide supra).

These experimental observations indicate that mechanistically the reaction of (butene-1,4-diyl)magnesium with $[CpMo(NO)I_2]_2$ is more complex than with the Cp_2MCl_2 reagents of reactions 3. The latter conversions are believed to proceed via 1,2-addition of the organomagnesium species to form an η^2-diene-containing intermediate complex.[7,25] In the case involving the nitrosyl reactant, the Lewis basicity of the nitrosyl oxygen atom and the propensity of this molybdenum center to form η^3-allyl linkages result instead in 16 being formed as the initial intermediate. Complex 16 then rearranges thermally to produce the η^4-*trans*-diene complex 1 as one of the products.

The ^{1}H and ^{13}C NMR Spectroscopic Properties of the η^4-Diene-Containing Complexes 1–14. Since our preliminary investigations of the ^{1}H NMR spectra of a few of the η^4-diene-containing complexes had revealed that they exhibited a number of interesting and informative features,[9] we have carried out a detailed analysis of the ^{1}H and ^{13}C NMR spectroscopic properties of compounds 1–14. To obtain the maximum amount of information from the NMR spectra of these compounds, it was first necessary to assign both the location on the diene ligand (i.e. C_1 vs C_4, R_{11} vs R_{12}, see Table II) and orientation with respect to the cyclopentadienyl ring of each nucleus responsible for the observed ^{1}H and ^{13}C NMR resonances. This task was accomplished by a series of 1- and 2-D NMR experiments.[26] The ^{1}H NMR spectra (summarized in Tables III and IV) were used to determine proton coupling networks, and the orientations of the diene ligand with respect to the cyclopentadienyl ring were obtained from NOE difference spectra.[27] ^{13}C (gated and broad-band decoupled) NMR experiments[28] were used to determine car-

(24) Faller, J. W.; Shvo, Y. *J. Am. Chem. Soc.* 1980, *102*, 5396.
(25) Dorf, U.; Engel, K.; Erker, G. *Organometallics* 1983, *2*, 462.
(26) For two previous examples of the use of these techniques to assign the NMR spectra of organometallic compounds, see: (a) Dunach, E.; Halterman, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* 1985, *107*, 1664. (b) Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* 1985, 332.
(27) (a) Levy, G. C.; Craik, D. J. *Science (Washington, D.C.)* 1981, *214*, 291. (b) Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* 1983, *22*, 350. (c) Hall, L. D.; Sanders, J. K. M. *J. Am. Chem. Soc.* 1980, *102*, 5703.
(28) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; John Wiley and Sons: New York, 1980.
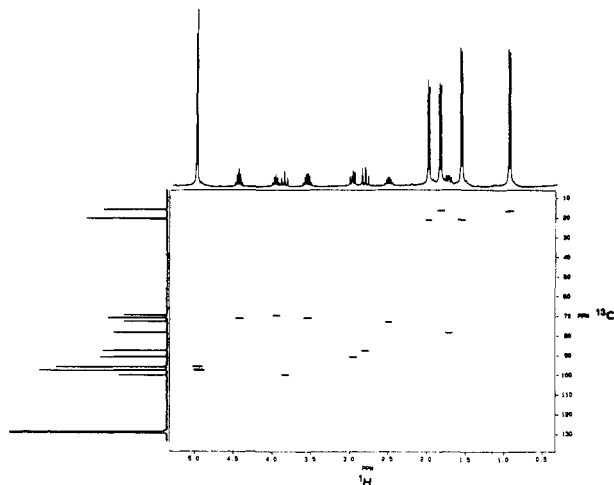

Figure 1. The 300-MHz ^{1}H NMR spectrum of 7 in C$_6$D$_6$ at 20 °C. The letters A and B designate the particular isomer, and the numerical subscripts indicate the diene substituent (i.e. xy of R_{xy} in Table II).
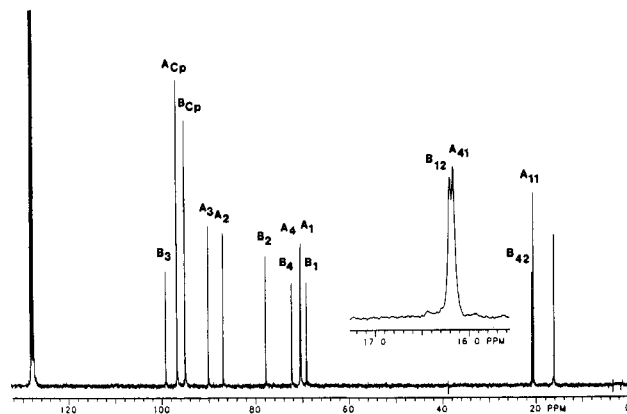
Figure 2. The 75-MHz ^{13}C{^{1}H} NMR spectrum of 7 in C$_6$D$_6$ at 20 °C. The letters A and B designate the particular isomer, the double digit subscripts specify the diene substituents (i.e. xy of R_{xy} in Table II), and the single digit subscripts indicate the diene carbon (i.e. z of C$_z$ in Table II).

bon–proton connectivities and coupling constants (Tables V and VI). Finally, 2-D HETCOR experiments were utilized to produce ^{1}H–^{13}C chemical shift correlation plots for each complex which permitted completion of the spectral assignments. The analysis of the spectra of $CpMo(NO)(\eta^4\text{-}trans\text{-}(E,Z)\text{-}2,4\text{-hexadiene})$ (7) is next presented as an illustrative example of the procedures outlined above.

The ^{1}H NMR spectrum of 7 is shown in Figure 1. Since the diene ligand does not possess an inversion center, complex 7 exists in solutions as a mixture of diastereomers.[29] These isomers, designated by the letters A and B, are present in C$_6$D$_6$ at 20 °C in a 7:5 mole ratio. Consequently, integration of the spectrum shown in Figure 1 permits the assignment of a pair of methyl doublets (e.g. A_{11} and A_{41}) and four sets of vinylic hydrogen resonances (e.g. A_{12}, A_{21}, A_{32}, and A_{42}) to each isomer. The various J_{HH} values for each isomer can be determined by homonuclear decoupling experiments, the net result being the assignment of each signal to a specific proton on the diene backbone. How the diene ligand is attached to the metal center in each diastereomer can be established by an NOE difference experiment in which the resonances due to the cyclopentadienyl protons of both diastereomers are simultaneously irradiated. If this is done, the only enhanced signal observable in the difference spectrum is that labelled A_{11}, i.e. the one due to the trans methyl group of 7A. Hence, the molecular structures of both 7A and 7B are assignable with certainty.

(29) Each $CpMo(NO)(\eta^4\text{-}trans\text{-diene})$ complex must exist as a pair of enantiomers.

Figure 3. $^1H-^{13}C$ Chemical shift correlation plot for **7** in C_6D_6 at 20 °C.

The interpretation of the ^{13}C NMR spectrum of **7** (Figure 2) is somewhat more difficult. The observed chemical shifts, multiplicities, peak intensities, and $^1J_{^{13}C^{-1}H}$ values of the ^{13}C NMR signals (collected in Tables V and VI) permit a tentative assignment of these signals to the two isomeric complexes **7A** and **7B**. However, definitive assignments can only be made with the aid of a 2-D heterocorrelation (HETCOR) experiment since the ^1H NMR spectrum has been completely assigned. Such a contour plot for **7** in C_6D_6 at 20 °C is presented in Figure 3. It provides the requisite cross-correlation of the $^1H-^{13}C$ chemical shifts that allows the ^{13}C NMR data for **7** to be interpreted unambiguously. The ^1H and ^{13}C NMR spectra of the other η^4-diene-containing complexes **1-14** can be interpreted in a similar manner.

The ^1H and ^{13}C NMR properties of the cyclopentadienyl groups present in compounds **1-9** and **13** are as expected. Their ^1H NMR resonances are sharp singlets (δ 4.9–5.6 ppm, Table III) which integrate for less than five protons when normal pulse delays (0–5 s) are used. This fact simply reflects the relatively long relaxation times of the cyclopentadienyl protons,[10] a fairly common property of compounds containing CpM(NO) (M = Mo or W) groups.[15] The ^{13}C NMR signals of the cyclopentadienyl carbons of complexes **1-9** and **13** consist of doublets having normal chemical shift (Table V) and $^1J_{^{13}C^{-1}H}$ (Table VI) values.[30]

The signals due to the constituent atoms of the diene ligands of **1-14** provide the chemically most interesting information. Particular aspects worthy of note include the following:

(1) The configurations of the diene ligands in **1-14** can be reliably established from their NMR spectra. For instance, complexes **13** and **14** contain a symmetrically substituted diene (i.e. 2,3-dimethylbutadiene) complexed to the CpMo(NO) fragment in a cis fashion. Consequently, the ^1H and ^{13}C NMR spectra of these compounds reflect the fact that their molecular structures possess mirror symmetry. In contrast, complexes **1-12** contain dienes (both symmetrically and unsymmetrically substituted) coordinated to the metal center in a twisted, transoidal manner. Accordingly, the two ends of the diene ligands are inequivalent, the inequivalence being readily apparent

in their NMR spectra. Thus, $\delta_{C_2} \ll \delta_{C_3}$ in the ^{13}C NMR spectra and the geminal ($^2J_{^1H^{-1}H}$) and vicinal ($^3J_{^1H^{-1}H}$) coupling constants are larger and smaller, respectively, at C_4 and C_3 than at C_1 and C_2 as evident in the ^1H NMR spectra. In other words, the NMR spectral parameters indicate that compounds **1-12** possess solution molecular structures similar to that established for **8** in the solid state[9a] whereas complexes **13** and **14** in solution possess structures analogous to that established for **13** by single-crystal X-ray crystallography.[9b]

(2) As noted earlier for complex **7**, each compound which contains an unsymmetrically substituted diene ligand (i.e. **2**, **4**, **5**, **7**, and **11**) exists in solutions as a mixture of diastereomers. Their NMR spectra confirm that these diastereomers simply have opposite orientations of the diene ligand facing the molybdenum center.

(3) In forming complexes **6** and **7**, the hexadienes involved retain their E,E and E,Z geometries, respectively, throughout. Furthermore, once formed, **7** does not isomerize to **6** even after being maintained at 30 °C for extended periods of time. This behavior contrasts with that exhibited by $Cp_2Zr(\eta^4\text{-}trans\text{-}(E,Z)\text{-}2,4\text{-hexadiene})$ which rapidly converts to its E,E isomer at temperatures above 0 °C.[7]

(4) Most importantly, the ^1H and ^{13}C NMR spectra of **1-14** provide valuable information about the nature of the molybdenum–diene bonding extant in these compounds. In valence-bond terms, the metal–diene bonding in cis-diene complexes can be represented by a resonance hybrid involving forms Ia (the π, π form) and Ib (the σ, π, σ form)[7] shown. Most η^4-cis-diene complexes of the later transition

metals [e.g. $(\eta^4\text{-}cis\text{-}C_4H_6)Fe(CO)_3$][32] are best described as being classically π-bonded diene complexes (i.e. mainly form Ia) while those of earlier transition metals [e.g. $Cp_2Zr(\eta^4\text{-}cis\text{-diene})$] adopt principally the σ, π, σ mode of interaction (i.e. Ib).[7] By analogy to these cis-diene complexes, a similar bonding description may be invoked for the trans-diene compounds, i.e.

IIa now being the π, π form and IIb the σ, π, σ form. In principle, the differences between the a and b resonance forms in both cases I and II should be readily detectable by NMR spectroscopy since the terminal carbons in forms a are sp²-hybridized whereas in b they are sp³-hybridized.

The protons on the terminal carbon atoms of the diene ligand in the cis-diene complex **13** exhibit a geminal proton-proton coupling constant ($^2J_{11-12} = {^2}J_{41-42}$) of 5.04 Hz, a value intermediate to those observed for $(\eta^4\text{-}cis\text{-}C_4H_6)$-$Fe(CO)_3$ ($^2J = 2.4$ Hz; π, π)[32] and $Cp_2Zr(\eta^4\text{-}cis\text{-}C_4H_6)$ ($^2J = 10.0$ Hz; σ, π, σ).[7] In addition, the one-bond carbon-13-proton coupling constants evident in the NMR spectra of **12** (i.e. $^1J_{^{13}C^{-1}H} = 146.5$ and 162.5 Hz) are similar in magnitude to what is expected for an sp²-hybridized carbon (i.e. 155–160 Hz)[28,31] and somewhat larger than that found for $Cp_2Zr(\eta^4\text{-}cis\text{-}C_4H_6)$ (i.e. 144 Hz).[33] It thus appears that

(30) The magnitudes of $^1J_{^{13}C^{-1}H}$ are diagnostic of the valence-bond hybridization extant at carbon.[28,31]

(31) (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, England, 1981. (b) Becker, E. B. *High Resolution NMR: Theory and Chemical Applications*, 2nd ed.; Academic Press: New York, 1980.

(32) Bachmann, K.; von Philipsborn, W. *Org. Magn. Reson.* **1976**, *8*, 648.

(33) Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300.

the molybdenum–diene linkage in **13** more closely resembles those extant in later transition-metal complexes. Certainly, resonance form Ia makes a larger contribution to the metal–diene bonding in the CpMo(NO) system than in the Cp$_2$Zr systems.

The *trans*-diene complexes **1–12** exhibit very small geminal coupling constants ($^2J_{11-12} \simeq {}^2J_{41-42}$ = 2–4 Hz, Table IV) which approach those of free butadiene (^2J = 1.7 Hz)[34] and are somewhat smaller than those exhibited by Cp$_2$Zr(η^4-*trans*-diene) compounds (^2J = 4–6 Hz).[7] Furthermore, the vicinal coupling constants displayed by **1–12** (i.e. $^3J_{trans} = {}^3J_{12-21}$ and $^3J_{32-41} \simeq$ 11–15 Hz) are smaller than those exhibited by the zirconocene *trans*-diene complexes ($^3J_{trans} \simeq$ 16 Hz)[7] or free butadiene ($^3J_{trans}$ = 16.9 Hz).[34] Finally, the coupling constants across C$_2$–C$_3$ for **1–12** ($^3J_{21-32} \simeq$ 10–12 Hz) are similar in magnitude to that of free butadiene (^3J = 10.3 Hz)[34] but smaller than that measured for the zirconocene systems ($^3J \simeq$ 15–16 Hz).[7] Taken together, these spectral properties indicate that resonance form IIb contributes more to the molybdenum–diene bonding in compounds **1–12** than it does in the analogous Cp$_2$Zr(η^4-*trans*-diene) species.

In summary, the ^{1}H and ^{13}C NMR data suggest that the *cis*- and *trans*-diene ligands are bonded to the Cp'Mo(NO) groups of **1–14** in a similar manner, resonance hybrids a and b making approximately equal contributions to the metal–diene bonding in each case (either I or II). This conclusion is supported by the fact that the diene carbon–carbon bond lengths are approximately equivalent (at 1.401–1.418 Å) in the solid-state molecular structures of both **8** (containing a *trans*-diene ligand)[9a] and **13** (containing a *cis*-diene ligand).[9b] This fact contrasts with the intramolecular dimensions of the related zirconocene systems, as might be expected on the basis of their different NMR properties (vide supra). In the zirconium compounds, the *cis*-diene ligands exhibit long–short–long diene carbon–carbon bond alternations (i.e. principally Ib) while their *trans*-diene analogues display the short–long–short alternation (i.e. IIa) similar to that of free butadiene.[7]
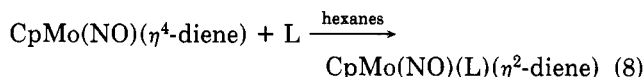
Electronic Consequences of Coordinating Butadienes to the CpMo(NO) Group. As outlined earlier, the two isomeric complexes, CpMo(NO)(η^4-*cis*-2,3-dimethylbutadiene) (**13**) and CpMo(NO)(η^4-*trans*-2,3-dimethylbutadiene) (**3**), are preparable by reaction 1 in isolated yields of 13% and 37%, respectively. However, **13** is thermodynamically unstable and isomerizes irreversibly to **3** in solutions at 20 °C, i.e.

CpMo(NO)(η^4-*cis*-2,3-dimethylbutadiene) $\underset{\mathbf{13}}{\overset{20\ °C}{\rightleftharpoons\!\!\!\!\!\!\times\!\!\!\!\!\!\rightleftharpoons}}$

$$\text{CpMo(NO)}(\eta^4\text{-}trans\text{-2,3-dimethylbutadiene)} \quad (7)$$
$$\mathbf{3}$$
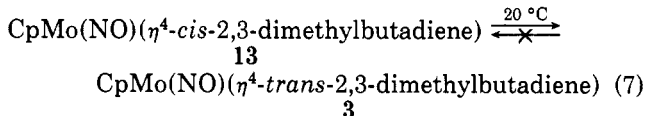
The unprecedented stability of **3** over **13** can be rationalized in terms of their electronic structures. Fenske–Hall MO calculations on the model systems containing *cis*- and *trans*-butadiene bound to CpMo(NO)[9b] reveal that in both complexes there is substantial electron donation from the diene π_2 orbital to the metal and backdonation from metal to the diene π_3* orbital. This result is in accord with the interpretation of the NMR properties of the complexes **1–14** presented in the previous section. Furthermore, the *cis*-diene is calculated to be both a weaker donor and stronger acceptor than the *trans*-diene. In spite of this, the NO 2π population is greater in the cis complex (1.57e) than in the trans complex (1.51e).[9b] Consistent with this

calculation is the fact that the nitrosyl-stretching frequency evident in the IR spectrum of **13** (1552 cm^{-1} in CH$_2$Cl$_2$) is lower in energy than that for **3** (1590 cm^{-1} in CH$_2$Cl$_2$, Table I). Finally, the MO calculations suggest that the greater stability of the trans complex (i.e. a HOMO energy ca. 0.9 eV lower than that of the cis complex) results from the asymmetry of the *trans*-diene ligand which is better able to stabilize the high-lying occupied orbitals of the CpMo(NO) fragment.[9b] In other words, the principal factors responsible for the preferential attachment of butadienes to CpMo(NO) in a twisted, transoidal fashion are electronic in nature. That the resulting Mo–(η^4-*trans*-diene) linkages are relatively strong is indicated by the representative chemical properties of CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene) (**8**) outlined in the next section.

Reactions of CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene) (8) with Phosphines and Carbon Monoxide. Our preliminary studies of the characteristic reactivities of some of the η^4-*trans*-diene complexes have afforded some interesting results. For instance, treatment of CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene) (**8**, a representative member of this class of compounds) with neutral Lewis bases, L, such as phosphines or carbon monoxide leads to novel η^2-diene complexes, i.e.

$$\text{CpMo(NO)}(\eta^4\text{-diene)} + \text{L} \xrightarrow{\text{hexanes}}$$
$$\text{CpMo(NO)(L)}(\eta^2\text{-diene)} \quad (8)$$

where diene = 2,5-dimethyl-2,4-hexadiene. The various η^2-diene product complexes [i.e. L = PMePh$_2$ (**18**), PMe$_3$ (**19**), or CO (**20**)] are isolable in good yields as yellow, crystalline solids. The NMR spectra of these compounds are presented in the Experimental Section and are indicative of their possessing "piano-stool" molecular structures, i.e.
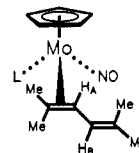
Thus, when L = PMePh$_2$ or PMe$_3$, the proton on the coordinated double bond of the diene ligand (i.e. H$_A$) exhibits substantial coupling to the phosphorus ($J_{^1H-^{31}P}$ = 9.4 Hz). Molecular structures similar to that depicted above have been established for related CpMo(NO)(CO)(η^2-olefin) complexes.[35]

For L = PMePh$_2$, conversion 8 requires 12 h at 20 °C to go to completion. It is thus somewhat more sluggish than previously reported displacements of η^4-dienes from a metal's coordination sphere by stronger Lewis bases.[36] Interestingly, further reaction between the η^2-diene product complex and another equivalent of phosphine to form the known[15] CpMo(NO)(PMePh$_2$)$_2$ compound is even slower, requiring an additional 8 days. This reluctance of the η^2-diene complex to liberate the diene is probably a manifestation of increased Mo→η^2-diene back-bonding caused by the presence of the phosphine ligand. As expected, the electron density at the metal center in the η^2-diene complex [ν_{NO} (CH$_2$Cl$_2$) 1553 cm^{-1}] is intermediate between that of the η^4-*trans*-diene species [ν_{NO} (CH$_2$Cl$_2$) 1584 cm^{-1}, Table I] and the bis(phosphine) complex [ν_{NO} (CH$_2$Cl$_2$) 1539 cm^{-1}].[15]

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Finally, it should be noted that the η^2-diene-carbonyl complex (20) requires somewhat more forcing conditions for its preparation than do the related phosphine compounds (18 and 19). Thus, when L = CO in reaction 8, a hexanes solution of the organometallic reactant must be subjected to 60 psig of carbon monoxide at room temperature for 5 days in order to effect complete conversion. This observation again gives a clear indication of the relatively high inertness of the Mo–η^4-*trans*-diene linkage in 8 to undergo substitution reactions. Even more surprising is the fact that no CpMo(NO)(CO)$_2$, the disubstituted product, is formed during this transformation.

Clearly, further studies of the characteristic reactivities of compounds 1–14 must be effected so that their chemical properties can be discussed in the proper context. Such studies are currently in progress.

New Types of Organometallic Oxo Complexes Containing Molybdenum and Tungsten

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Treatment of solutions of the 16-electron dialkyl compounds Cp′M(NO)R$_2$ (Cp′ = Cp (η^5-C$_5$H$_5$) or Cp* (η^5-C$_5$Me$_5$); M = Mo or W; R = CH$_2$SiMe$_3$, CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$Ph, or Me) with either dioxygen or aqueous hydrogen peroxide in Et$_2$O at ambient temperatures and pressures produces novel dioxo alkyl complexes Cp′M(O)$_2$R which can be isolated in moderate yields (45–60%). The results of labeling studies with ^{18}O$_2$ are consistent with the first steps of the reactions involving O$_2$ proceeding via the coordination of the diatomic molecule to the metal centers in the organometallic reactants. The preferred sites of reactivity in the dioxo alkyl complexes are their M=O linkages. Thus, exposure to 30% H$_2$O$_2$ in Et$_2$O converts them cleanly to the oxo peroxo derivatives Cp′M(O)(η^2-O$_2$)R and treatment of representative Cp′W(O)$_2$R species with HCl (or PCl$_5$ or Me$_3$SiCl) in Et$_2$O produces the corresponding Cp′W(O)(Cl)$_2$R compounds in high yields. These dichloro oxo complexes are very useful synthetic precursors in their own right, undergoing metathesis with alkyllithium or alkyl Grignard reagents to produce the oxo trialkyl compounds Cp′W(O)R$_n$R′$_{3-n}$ in which R and R′ represent selected alkyl groups. Sterically crowded members of this class of compounds are not isolable under ambient conditions since they spontaneously convert to the corresponding oxo alkylidene species, presumably via intramolecular α-H abstraction. The isolable oxo trialkyl complexes can be induced to undergo the same conversions simply by gentle warming of their solutions. All the new oxo complexes isolated during this work have been fully characterized by conventional spectroscopic techniques. Their physical properties indicate that they are all monomeric 16-valence-electron species possessing piano-stool molecular structures and containing the metal in its highest oxidation state of +6.

Introduction

The first examples of organometallic oxo complexes were the vanadium-containing species CpV(O)X$_2$ (Cp = η^5-C$_5$H$_5$; X = Cl or Br), obtained by Fischer and Vigoureux in the late 1950s.[2] Shortly thereafter, Cousins and Green described some cyclopentadienyl oxo compounds of molybdenum,[3] but this area of research then remained relatively dormant until recently. During the past 5 years, many research groups have shown a renewed interest in the synthesis and chemistry of higher oxidation state organometallic oxo complexes, this interest being manifested by the appearance of reports describing such diverse complexes as CpRe(O)$_3$,[4] Cp*Re(O)$_3$ (Cp* = η^5-C$_5$Me$_5$),[4,5] CpReOMe$_2$,[4b] Re(O)I(MeC=CMe)$_2$,[6] W$_2$O$_3$(CH$_2$CMe$_3$)$_6$,[7] CpW(O)(C$_2$H$_4$)Me,[8] CpW(O)(C$_2$H$_4$)COMe,[8] MeReO$_3$,[9] and

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