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Synthesis and Characterization of Chiral Molybdenum and Tungsten Neutral Complexes Containing η^2-Benzyl Ligands[1,2]

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Reaction of $Cp'M(NO)Cl_2$ (Cp' = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5); M = Mo or W) with 2 equiv of *p*-XylMgCl (*p*-Xyl = *p*-$MeC_6H_4CH_2$) affords the corresponding bis(*p*-xylyl) complexes in good yields. Subsequent treatment of the $Cp'M(NO)(CH_2Ar)_2$ compounds (CH_2Ar = CH_2Ph or *p*-Xyl) with HCl produces the new isolable $Cp'M(NO)(CH_2Ar)Cl$ species. These, in turn, undergo metathesis reactions with RMgCl or $R_2Mg(dioxane)_2$ reagents and convert to $Cp'M(NO)(CH_2Ar)R$ (R = CH_2SiMe_3, CH_2CMe_3 (Npt), or $C_6H_4CH_3$ (*p*-Tol)). All new complexes isolated during this work have been fully characterized by conventional spectroscopic methods. Single-crystal X-ray crystallographic analyses have been performed on two prototypal complexes, namely $Cp^*Mo(NO)(CH_2Ph)Cl$ and $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$. Crystal data for $Cp^*Mo(NO)(CH_2Ph)Cl$: $a = 9.3451\ (16)$ Å, $b = 11.8954\ (9)$ Å, $c = 15.6511\ (17)$, $\beta = 100.176\ (9)°$, $Z = 4$, space group $P2_1/n$, number of unique reflections 6159, number of variables 218, $R_F = 0.033$, $R_{wF} = 0.047$. Crystal data for $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$: $a = 8.3901\ (10)$ Å, $b = 9.3937\ (17)$ Å, $c = 14.9556\ (19)$, $\alpha = 74.017\ (11)°$, $\beta = 98.009\ (9)°$, $\gamma = 86.849\ (12)°$, $Z = 2$, space group $P1$, number of unique reflections 5092, number of variables 358, $R_F = 0.023$, $R_{wF} = 0.031$. Both compounds possess normal three-legged piano-stool molecular geometries, the most chemically interesting features involving their η^2-benzyl ligands. The intramolecular dimensions of the $Mo(\eta^2$-$CH_2Ph)$ groupings in both structures are essentially identical and indicate that the η^2-benzyl groups in these diamagnetic complexes function as three-electron ligands via C–Mo σ bonds involving their methylene and ipso carbon atoms. All evidence points to the presence of the η^2-benzyl ligands as being the principal factor responsible for the stability of the 18-electron $Cp'M(NO)(CH_2Ar)X$ (X = Cl or R) complexes. In solutions these complexes are stereochemically nonrigid, and $Cp^*Mo(NO)(CH_2Ph)Cl$ has been subjected to a variable-temperature ^1H NMR study.

Introduction

The family of the formally 16-electron bis(alkyl) complexes, $Cp'M(NO)R_2$ (Cp' = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5); M = Mo or W; R = alkyl), has to date exhibited many novel chemical transformations. Most notable among these are the conversions that occur when the complexes are treated with O_2,[3] S_8,[4] Se_8,[4] and CO.[5] Reactions such as (1)–(3) are believed to proceed via the incoming Lewis bases forming initial 1:1 adducts at the metal centers. These adducts then undergo subsequent intramolecular transformations involving at least one of the metal–alkyl bonds to form the product complexes indicated above. Consequently, it became of interest to us to prepare mixed bis(alkyl) species, $Cp'M(NO)(R)(R')$, so that a direct comparison of reactivity of two different alkyl groups on the same $Cp'M(NO)$ fragment could be effected.

$$Cp^*W(NO)(CH_2CMe_2Ph)_2 \xrightarrow{O_2} Cp^*W(O)_2(CH_2CMe_2Ph) \quad (1)$$

$$CpW(NO)R_2 \xrightarrow{E_8} CpW(NO)(ER)(R) \xrightarrow{E_8} CpW(NO)(\eta^2\text{-}E_2R)(R) \rightarrow CpW(NO)(ER)_2 \quad (2)$$

$$R = CH_2SiMe_3;\ E = S \text{ or } Se$$

$$CpW(NO)R_2 \xrightarrow{CO} CpW(NO)(\eta^2\text{-}COR)(R) \xrightarrow{CO} CpW(NO)(\eta^2\text{-}COR)(\eta^1\text{-}COR) \quad (3)$$

$$R = CH_2CMe_3$$

Prior to the successful syntheses described in this paper, there had been other attempts to prepare mixed-alkyl complexes of the $Cp'M(NO)(R)(R')$ type. Although these attempts were unsuccessful, it is instructive to consider the observations collected during these attempts in order to analyze the possible sources of failure. For instance, an attempt to form a mixed bis(alkyl) species via stepwise alkylation employed a first reaction having a 1:1 stoichiometry of the Grignard reagent Me_3SiCH_2MgCl and $CpW(NO)I_2$. Surprisingly, this reaction did not result in the simple metathesis of one alkyl for one halide to form the expected $CpW(NO)(CH_2SiMe_3)(I)$ product. Instead, the well-known bis(alkyl) species was formed.[6]

$$CpW(NO)I_2 + Me_3SiCH_2MgCl \rightarrow \tfrac{1}{2}CpW(NO)I_2 + \tfrac{1}{2}CpW(NO)(CH_2SiMe_3)_2 \quad (4)$$

Subsequent studies on the electrochemical properties of the dihalo nitrosyl precursor complexes suggested that reaction 4 might possibly proceed through an organometallic radical-anion intermediate formed by initial single-electron transfer from the Grignard reagent.[7] If this radical-anion intermediate had reacted with a second equivalent of Grignard reagent faster than did the diiodo nitrosyl starting material, it would then explain the observed selectivity in alkylation resulting in the bis(alkyl) product complex.

Subsequent attempts to form these mixed-alkyl species by treatment of the diiodo nitrosyl complexes with a 1:1 mixture of Grignard reagents

$$CpW(NO)I_2 + Me_3SiCH_2MgCl + PhCH_2MgCl \rightarrow \tfrac{1}{2}CpW(NO)(CH_2Ph)_2 + \tfrac{1}{2}CpW(NO)(CH_2SiMe_3)_2 \quad (5)$$

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[2] Taken in part from: (a) Dryden, N. H. Ph.D. Dissertation, The University of British Columbia, 1990. (b) Yee, V. C. Ph.D. Dissertation, The University of British Columbia, 1990.

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were also unsuccessful, the known bis(alkyl) species being the only isolable products.[6] This particular lack of success can be attributed to various possible complications. The first could be that the desired $CpW(NO)(CH_2Ph)(CH_2SiMe_3)$ compound is inherently unstable with respect to disproportionation into its symmetrically substituted products

$$2Cp'M(NO)(CH_2Ph)(CH_2SiMe_3) \rightarrow Cp'M(NO)(CH_2Ph)_2 + Cp'M(NO)(CH_2SiMe_3)_2 \quad (6)$$

thereby explaining its lack of formation from the mixture of alkylating agents. This type of organic ligand exchange has been observed previously for a mixed bis(hydrocarbyl) zirconocene species:[8]

$$2Cp_2Zr(CH_2Ph)(CH{=}CHPh) \rightarrow Cp_2Zr(CH_2Ph)_2 + Cp_2Zr(\eta^4\text{-}PhCH{=}CHCH{=}CHPh) \quad (7)$$

A second possible problem associated with the mixture of Grignard reagents utilized in reaction 5 may be due to the relative rates of reaction of the two alkylating agents. If one Grignard reagent is much more reactive than the other, then the selective nature of the metathesis observed may well be a manifestation of this kinetic effect.

Only one mixed-alkyl species of the type $Cp'M(NO)(R)(R')$ was known prior to the beginning of this work, namely $CpW(NO)(CH_2SiMe_3)(CH_2CPh_3)$.[9] It had been formed serendipitously by the reaction of $[Ph_3C]^+PF_6^-$ with $CpW(NO)(CH_2SiMe_3)_2$:

$$CpW(NO)(CH_2SiMe_3)_2 + [Ph_3C]^+PF_6^- \rightarrow CpW(NO)(CH_2SiMe_3)(CH_2CPh_3) + PF_5 + Me_3SiF \quad (8)$$

Unfortunately, this synthetic route has proved to be of minimal utility since the product complex is difficult to isolate and is only obtainable in relatively low yields. Furthermore, reaction 8 is only successful for the case portrayed and lacks general applicability since it cannot be extended to encompass the synthesis of other $Cp'M(NO)(R)(R')$ species.

This paper presents complete details concerning the successful synthesis and characterization of particular examples of the general class of compounds having the composition $Cp'M(NO)(\eta^2\text{-}CH_2Ar)Cl$ (Ar = aryl) and their subsequent alkylation to form the previously elusive mixed-alkyl species $Cp'M(NO)(\eta^2\text{-}CH_2Ar)R$. The unusual spectroscopic and structural properties of this whole range of complexes are discussed in detail, especially with regard to the insight that they provide regarding the nature of the metal–η^2-benzyl interaction.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous and anaerobic conditions with use of conventional Schlenk-tube techniques under an atmosphere of dinitrogen.[10,11] General procedures routinely employed in these laboratories have been described in detail previously.[12] Reagent chemicals were obtained from commercial sources (e.g., anhydrous HCl, Matheson; Me_3SiCH_2MgCl in Et_2O, Aldrich) and were used as received. The organometallic starting materials $Cp^*M(NO)Cl_2$ (M = Mo or W)[13] were synthesized by treating the appropriate $Cp^*M(NO)(CO)_2$ precursor complex with an equimolar amount of PCl_5 in Et_2O,[15b] and the $Cp'M(NO)(CH_2Ph)_2$ reagents (Cp′ = Cp or Cp*; M = Mo or W) were prepared by known routes.[16] The purities of the organometallic reagents were established by elemental analyses.

General Preparation of $R_2Mg(dioxane)_2$ (R = *p*-Tol[17] or Npt).[17] These dialkylmagnesium reagents were synthesized by using a modification of a published procedure for the preparation of unsolvated dialkylmagnesium complexes.[18] The method outlined below seems to be of general applicability, the reagents $(p\text{-}MeC_6H_4)_2Mg(dioxane)_2$ [i.e., $(p\text{-}Tol)_2Mg(dioxane)_2$] and $(Me_3CCH_2)_2Mg(dioxane)_2$ [i.e., $(Npt)_2Mg(dioxane)_2$] having been successfully prepared by this route.

Solutions of the Grignard reagents (Npt)MgCl in Et_2O[19] and (*p*-Tol)MgCl in THF[20] at concentrations of 0.5–1.0 N were prepared, and the solutions were treated with 1,4-dioxane (ca. 4 equiv). This treatment resulted in the deposition of a thick white slurry of insoluble $[MgCl_2(dioxane)]_n$ in the reaction mixture. The supernatant solution containing $R_2Mg(dioxane)_2$ was isolated by centrifugation of portions of the slurry and cannulation of the clear supernatant solutions out of the centrifuge tubes into a flask. The solvent was removed from the combined supernatant solutions under reduced pressure to obtain either a white solid or a tarry residue. These residues were then triturated with hexanes, the hexanes were carefully removed by cannulation, and the remaining solid was dried in vacuo to obtain the desired organomagnesium products as free-flowing white powders. The compositions of the solids were established by hydrolysis of weighed solid samples and titration of the resulting solutions with 0.100 N HCl using phenolpthalein as indicator. In both cases, hydrolysis of these powders gave an amount of base approximately equal to that calculated for a complex having the composition $R_2Mg(dioxane)_2$.

Preparation of $Cp^*W(NO)(p\text{-}Xyl)_2$. A stirred suspension of $Cp^*W(NO)Cl_2$ (6.0 g, 14.3 mmol) in Et_2O (100 mL) was cooled to 0 °C in an ice–water bath. An aliquot of (*p*-Xyl)MgCl[17,21] in Et_2O (33 mL, 0.86 N, 28.6 mmol) was added to the light green solution/brown suspension via a syringe. An immediate reaction occurred as evidenced by the formation of a light orange flocculant suspension. After being stirred for 1 h, the reaction mixture was treated with CH_2Cl_2 (50 mL) to dissolve the suspended solids. Deaerated water (3 mL) was then added, causing the solution to become a darker red-orange and a white gel to form on the sides of the flask. After being stirred for a further 15 min, the solvents were removed from the final reaction mixture under reduced pressure to obtain a red-orange solid residue. The residue was extracted with CH_2Cl_2 (30 mL), and the extract was transferred to the top of an alumina column (Fisher neutral, Activity III, 200 × 30 mm) made up in CH_2Cl_2 and supported on a glass frit. The

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[13] The dihalo nitrosyl complexes $Cp'M(NO)X_2$ (Cp′ = Cp or Cp*; M = Mo or W; X = Cl, Br, or I) possess either monomeric[14] or halide-bridged dimeric[15] molecular structures in the solid state. However, the physical and chemical properties of these compounds in solutions are most consistent with their existing as solvated monomers.[7] Consequently, in this paper the dichloro complexes are represented exclusively by their monomeric formulae.

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[17] The following abbreviations are used throughout this paper: *p*-Tol = *p*-tolyl = $p\text{-}MeC_6H_4$, Npt = neopentyl = CH_2CMe_3, and *p*-Xyl = *p*-xylyl = *p*-methylbenzyl = $p\text{-}MeC_6H_4CH_2$.

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[21] A solution of (*p*-Xyl)MgCl was prepared by slow addition of α-chloro-*p*-xylene (20 mL, 148 mmol) to a suspension of Mg turnings (5.0 g, 200 mmol) in Et_2O (200 mL). After 2 h the supernatant solution was filtered through Celite and was determined to be 0.86 N by standardization with 0.100 M HCl/phenolphthalein.

Table I. Infrared and Analytical Data for the New Benzyl Alkyl, Bis(benzyl), and Benzyl Chloro Complexes

compound	IR (ν_{NO}, cm^{-1})		anal. found (calcd)		
	Nujol mull	solution	C	H	N
CpW(NO)(CH$_2$Ph)Cl[a]	1597	1597[b]	35.29 (35.54)	2.95 (2.98)	3.41 (3.45)
Cp*W(NO)(CH$_2$Ph)Cl[c]	1580	1582[b]	42.92 (42.92)	4.63 (4.66)	2.88 (2.94)
CpMo(NO)(CH$_2$Ph)Cl	1620	1627[b]	45.11 (45.38)	3.96 (3.81)	4.39 (4.41)
Cp*Mo(NO)(CH$_2$Ph)Cl	1609	1611[b]	52.89 (52.66)	5.78 (5.72)	3.66 (3.61)
Cp*W(NO)(*p*-Xyl)$_2$	1561, 1541[d]	1550[b]	55.74 (55.82)	5.93 (5.94)	2.51 (2.50)
Cp*W(NO)(*p*-Xyl)Cl	1568	1578[b]	43.95 (44.15)	4.92 (4.94)	2.82 (2.86)
Cp*Mo(NO)(*p*-Xyl)$_2$	1580, 1562[d]	1575[b]	66.06 (66.23)	6.96 (7.05)	3.04 (2.97)
Cp*Mo(NO)(*p*-Xyl)Cl	1612	1607[b]	53.68 (53.81)	5.90 (6.02)	3.60 (3.48)
CpW(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)	1554	1593[e]	41.76 (42.02)	5.07 (5.07)	3.09 (3.06)
Cp*W(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)	1549	1576[e]	48.00 (47.82)	6.29 (6.31)	2.70 (2.65)
CpMo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)	1578	1613[e]	51.88 (52.02)	6.35 (6.28)	3.83 (3.79)
Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)	1570	1597[e]	57.15 (57.39)	7.60 (7.57)	3.22 (3.19)
Cp*W(NO)(*p*-Xyl)(Npt)	1541	1578[e]	52.38 (52.58)	6.84 (6.72)	2.71 (2.66)
Cp*Mo(NO)(*p*-Xyl)(Npt)	1599, 1560[d]	1595[e]	62.95 (63.14)	8.22 (8.06)	3.30 (3.20)
Cp*Mo(NO)(*p*-Xyl)(*p*-Tol)	1590	1603[e]	65.64 (65.64)	6.86 (6.83)	2.94 (3.06)

[a] Cl: found, 8.86; calcd; 8.74. [b] CH$_2$Cl$_2$. [c] Cl: found, 7.37; calcd, 7.45. [d] Two bands, presumably corresponding to the mull spectrum and a Nujol solution spectrum of the complex, are observed. [e] Et$_2$O.

column was eluted with CH$_2$Cl$_2$ to remove a single orange band. The volume of the eluate was reduced in vacuo to about 100 mL. An equal volume of hexanes was added, and the resulting solution was slowly concentrated under reduced pressure to initiate crystallization. Overnight cooling at −25 °C completed the crystallization of an orange microcrystalline solid, which was collected by cannulating away the mother liquor and washing the remaining solid with pentane (20 mL). This solid was then dried in vacuo at room temperature to obtain 2.38 g of Cp*W(NO)(*p*-Xyl)$_2$. Concentration and cooling of the mother liquor afforded two additional crops of product (total 3.28 g) for an overall yield of 72%.

The analogous Cp*Mo(NO)(*p*-Xyl)$_2$ complex was obtained in a similar manner in 76% overall yield starting from 19 mmol of Cp*Mo(NO)Cl$_2$. The analytical and spectroscopic data for both Cp*M(NO)(*p*-Xyl)$_2$ complexes are collected in Tables I and II.

Preparation of Cp*W(NO)(CH$_2$Ph)Cl. An orange solution of Cp*W(NO)(CH$_2$Ph)$_2$ (6.70 g, 12.6 mmol) in CH$_2$Cl$_2$ (100 mL) was prepared in a 300-mL three-necked flask at ambient temperature. The reaction flask was partially evacuated and then filled with dry HCl gas. The progress of the subsequent reaction was periodically monitored by IR spectroscopy, the diminution of the starting ν_{NO} at 1548 cm^{-1} occurring concomitantly with the appearance of a new band (ν_{NO} = 1582 cm^{-1}). When the IR spectrum recorded showed no qualitative difference from the preceding one, the reaction was deemed complete. There was no appearance of any spectral features attributable to Cp*W(NO)Cl$_2$ (ν_{NO} = 1624 cm^{-1}) in any of the IR spectra obtained.

The final solution was then treated with hexanes (100 mL) and concentrated in vacuo until an orange precipitate began to form. The reaction mixture was cooled (−25 °C) to complete the crystallization of the orange product complex, which was isolated by cannulation of the supernate into another flask. The orange solid was washed with hexanes (20 mL), and the wash solution was added to the supernate. The solid was dried in vacuo for 2 h at 20 °C under dynamic vacuum (5 × 10^{-3} mm) to obtain 4.10 g (69% yield) of Cp*W(NO)(CH$_2$Ph)Cl as a red-orange crystalline solid. The combined solutions were concentrated and cooled to give an additional 1.08 g of product (86% overall yield).

The other congeners were prepared in a similar manner to obtain Cp*Mo(NO)(CH$_2$Ph)Cl (66% yield), CpMo(NO)(CH$_2$Ph)Cl (87% yield), CpW(NO)(CH$_2$Ph)Cl (60% yield), and Cp*Mo(NO)(*p*-Xyl)Cl (85% yield) as microcrystalline solids. The analytical and spectroscopic properties of these compounds are presented in Tables I and II. There was no evidence for the formation of any Cp′M(NO)Cl$_2$ complexes during these preparations; i.e., no nitrosyl absorptions attributable to these dichloro complexes were detectable in any of the IR spectra of the various reaction solutions.

Preparation of Cp*W(NO)(*p*-Xyl)Cl. A sample of Cp*W(NO)(*p*-Xyl)$_2$ (2.38 g, 4.26 mmol) was dissolved in toluene (80 mL). A gas reaction bulb containing HCl (475 mL at STP, ca. 20 mmol) was then attached to the reaction flask and opened to the reaction solution. The reaction mixture was stirred for 18 h at room temperature, during which time the solution became darker red. The final solution was taken to dryness in vacuo to obtain an orange-yellow solid, which was redissolved in 1:1 hexanes/CH$_2$Cl$_2$. The volume of this solution was slowly diminished under reduced pressure until a precipitate had formed and the supernatant liquid was pale orange. The supernatant solution was removed by cannulation, and the remaining residue was dried under vacuum to obtain the desired Cp*W(NO)(*p*-Xyl)Cl complex as an orange, feathery solid (1.86 g, 89% yield). Characterization data for this compound are also collected in Tables I and II.

Preparation of Cp′M(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) Complexes. The four congeners were prepared in a similar fashion, the specific procedure for Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) being given below as a representative example.

A suspension of Cp*Mo(CH$_2$Ph)Cl (1.45 g, 3.75 mmol) in Et$_2$O (100 mL) was prepared, and an IR spectrum of the supernatant solution was recorded (ν_{NO} = 1626 cm^{-1}). The mixture was treated with an aliquot of Me$_3$SiCH$_2$MgCl in Et$_2$O (5.0 mL, 0.75 N, 3.75 mmol) whereupon an instantaneous reaction occurred as evidenced by the disappearance of the suspension and the formation of a clear red solution (single ν_{NO} at 1597 cm^{-1}). The MgCl$_2$ product was precipitated by the addition of a small quantity of deaerated water (ca. 0.1 mL), and the reaction mixture was taken to dryness under reduced pressure. The residue was extracted with 2:5 CH$_2$Cl$_2$/hexanes (2 × 70 mL), and the extracts were filtered through a short column of Celite (50 × 20 mm) supported on a medium-porosity frit. The volume of the combined filtrates was reduced in vacuo to obtain a saturated solution, which was cooled (−25 °C) for several hours to induce the deposition of large red crystals (e.g., 2 × 2 × 3 mm) of Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) (0.730 g) that were isolated by first removing the supernatant solution via cannula and then washing the crystals with a small amount of hexanes (10 mL). The supernatant solution was again concentrated in vacuo, and an additional two crops of crystals were collected (1.345 g, 82% overall yield).

The analogous CpW(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) (65%), Cp*W(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) (86%), and CpMo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) (31%) complexes were synthesized and isolated similarly as large red crystals in the yields indicated. The characterization data for all these complexes are collected in Tables I and III.

Preparation of Cp*M(NO)(*p*-Xyl)(Npt). The complexes Cp*Mo(NO)(*p*-Xyl)(Npt)[17] and Cp*W(NO)(*p*-Xyl)(Npt)[17] were prepared in a similar manner. The procedure for the tungsten complex is presented below as a representative example.

A sample of (Npt)$_2$Mg(dioxane)$_2$ (0.54 g, 170 mg/mmol of Npt$^-$, 3.2 mmol) was weighed into a Schlenk tube in a glovebox. The solid was dissolved in Et$_2$O (20 mL), and the resulting solution was then cannulated into an orange suspension of Cp*W(NO)(*p*-Xyl)Cl (2.4 g, 2.5 mmol) in Et$_2$O (60 mL). The reaction mixture was stirred for 2 h at ambient temperature, during which time the suspended organometallic reactant was consumed. The final orange reaction solution was treated with H$_2$O (0.4 mL), stirred for 10 min, and then taken to dryness in vacuo to a solid residue.

Table II. Mass Spectral and ^{1}H and ^{13}C{^{1}H} NMR Data for the Bis(benzyl) and Benzyl Chloro Complexes

low-resolution mass spectrum,[a] m/z[b]	^{1}H NMR (C_6D_6) δ	^{13}C{^{1}H} NMR ($CDCl_3$) δ[c]	low-resolution mass spectrum,[a] m/z[b]	^{1}H NMR (C_6D_6) δ	^{13}C{^{1}H} NMR ($CDCl_3$) δ[c]
	CpW(NO)(CH$_2$Ph)Cl			Cp*W(NO)(*p*-Xyl)Cl[f]	
405, [P]$^+$ 375, [P − NO]$^+$	7.57 (t, 1 H, *p*-ArH, $^3J_{HH}$ = 7.5 Hz) 6.88 (d, 2 H, *o*-ArH, $^3J_{HH}$ = 7.5 Hz) 6.73 (t, 2 H, *m*-ArH, $^3J_{HH}$ = 7.5 Hz) 5.00 (s, 5 H, C$_5$H$_5$)[d] 3.15 (d, 1 H, CH_AH$_B$, $^2J_{HH}$ = 6.0 Hz) 2.70 (d, 1 H, CH$_A\mathit{H}_B$, $^2J_{HH}$ = 6.0 Hz)	137.62 (C_{para}, d, [164]) 135.35 (C_{arom}, d, [163]) 129.68 (C_{arom}, d, [164]) 109.62 (C_{ipso}) 101.14 (C_5H$_5$, d, [180]) 42.89 (CH$_2$, t, [149])	489, [P]$^+$ 459, [P − NO]$^+$	6.84 (d, 2 H, ArH_AH$_B$, $^3J_{HH}$ = 7.5 Hz) 6.68 (d, 2 H, ArH$_A\mathit{H}_B$, $^3J_{HH}$ = 7.5 Hz) 3.21 (d, 1 H, CH_AH$_B$, $^2J_{HH}$ = 7.3 Hz) 2.20 (s, 3 H, ArCH_3) 2.18 (d, 1 H, CH$_A\mathit{H}_B$, $^2J_{HH}$ = 7.3 Hz) 1.64 (s, 15 H, C$_5$(CH_3)$_5$)	145.89 (C_{para}) 138.09 (C_{ortho}) 130.39 (C_{meta}) 109.47 (C_{ipso}) 109.20 (C_5(CH$_3$)$_5$) 47.83 (CH$_2$) 22.26 (ArCH$_3$) 10.26 (C$_5$(CH$_3$)$_5$)
	Cp*W(NO)(CH$_2$Ph)Cl			Cp*Mo(NO)(*p*-Xyl)Cl[f]	
475, [P]$^+$ 445, [P − NO]$^+$	7.55 (t, 1 H, *p*-ArH, $^3J_{HH}$ = 7.5 Hz) 6.88 (d, 2 H, *o*-ArH, $^3J_{HH}$ = 7.7 Hz) 6.76 (t, 2 H, *m*-ArH, $^3J_{HH}$ = 7.5 Hz) 3.20 (d, 1 H, CH_AH$_B$, $^2J_{HH}$ = 6.0 Hz) 2.14 (d, 1 H, CH$_A\mathit{H}_B$, $^2J_{HH}$ = 6.0 Hz) 1.58 (s, 15 H, C$_5$(CH_3)$_5$)	137.83 (C_{arom}, d, [161]) 133.62 (C_{para}, d, [161]) 129.33 (C_{arom}, d, [161]) 112.63 (C_{ipso}) 110.08 (C_5(CH$_3$)$_5$) 48.20 (CH$_2$, t, [147], $^1J_{WC}$ = 53 Hz) 10.49 (C$_5$(CH$_3$)$_5$, q, [128])	403, [P]$^+$ 373, [P − NO]$^+$	6.80 (d, 2 H, ArH_AH$_B$, $^3J_{HH}$ = 8.1 Hz) 6.66 (br s, 2 H, ArH$_A\mathit{H}_B$) 3.30 (d, 1 H, CH_AH$_B$, $^2J_{HH}$ = 5.0 Hz) 2.20 (s, 3 H, ArCH_3) 2.10 (d, 1 H, CH$_A\mathit{H}_B$, $^2J_{HH}$ = 5.0 Hz) 1.55 (s, 15 H, C$_5$(CH_3)$_5$)	146.14 (C_{para}) 137.80 (C_{ortho}) 130.16 (C_{meta}) 111.11 (C_{ipso}) 111.00 (C_5(CH$_3$)$_5$) 51.70 (CH$_2$) 22.18 (ArCH$_3$) 10.38 (C$_5$(CH$_3$)$_5$)
	CpMo(NO)(CH$_2$Ph)Cl			Cp*W(NO)(*p*-Xyl)$_2$[f]	
319, [P]$^+$ 289, [P − NO]$^+$	7.54 (t, 1 H, *p*-ArH, $^3J_{HH}$ = 7.5 Hz) 6.83 (t, 2 H, *m*-ArH, $^3J_{HH}$ = 7.5 Hz) 6.70 (br s, 2 H, *o*-ArH) 5.03 (s, 5 H, C$_5\mathit{H}_5$)[d] 3.25 (d, 1 H, CH_AH$_B$, $^2J_{HH}$ = 5.0 Hz) 2.73 (d, 1 H, CH$_A\mathit{H}_B$, $^2J_{HH}$ = 5.0 Hz)	136.70 (C_{ortho})[e] 135.45 (C_{arom}, d, [161]) 129.40 (C_{arom}, d, [161]) 111.27 (C_{ipso}) 102.45 (C_5H$_5$, d, [179]) 47.51 (CH$_2$, t, [149])	559, [P]$^+$ 529, [P − NO]$^+$	6.98 (d, 4 H, ArH_AH$_B$, $^3J_{HH}$ = 6.9 Hz) 6.79 (d, 4 H, ArH$_A\mathit{H}_B$, $^3J_{HH}$ = 6.9 Hz) 2.31 (d, 2 H, CH_AH$_B$, $^2J_{HH}$ = 9.0 Hz) 2.02 (s, 6 H, ArCH_3) 1.54 (s, 15 H, C$_5$(CH_3)$_5$) 0.74 (d, 2 H, CH$_A\mathit{H}_B$, $^2J_{HH}$ = 9.0 Hz)	137.40 (C_{para}) 132.49 (C_{arom}) 130.32 (C_{ipso}) 129.18 (C_{arom}) 107.06 (C_5(CH$_3$)$_5$) 42.46 (CH$_2$) 21.50 (ArCH$_3$) 9.96 (C$_5$(CH$_3$)$_5$)
	Cp*Mo(NO)(CH$_2$Ph)Cl			Cp*Mo(NO)(*p*-Xyl)$_2$[f]	
389, [P]$^+$ 359, [P − NO]$^+$	7.51 (t, 1 H, *p*-ArH, $^3J_{HH}$ = 6.1 Hz) 6.88 (t, 2 H, *m*-ArH, $^3J_{HH}$ = 6.1 Hz) 6.68 (br s, 2 H, *o*-ArH) 3.29 (d, 1 H, CH_AH$_B$, $^2J_{HH}$ = 4.6 Hz) 2.07 (d, 1 H, CH$_A\mathit{H}_B$, $^2J_{HH}$ = 4.6 Hz) 1.41 (s, 15 H, C$_5$(CH_3)$_5$)	137.18 (C_{ortho}, br d, [152]) 133.84 (C_{para}, d, [153]) 129.30 (C_{meta}, d, [160]) 114.78 (C_{ipso}) 111.29 (C_5(CH$_3$)$_5$) 51.78 (CH$_2$, dd, [147, 151]) 10.61 (C$_5$(CH$_3$)$_5$, q, [127])	473, [P]$^+$ 443, [P − NO]$^+$	6.81 (m, 8 H, ArH) 2.38 (d, 2 H, CH_AH$_B$, $^2J_{HH}$ = 7.2 Hz) 2.09 (s, 6 H, ArCH_3) 1.51 (s, 15 H, C$_5$(CH_3)$_5$) 0.57 (d, 2 H, CH$_A\mathit{H}_B$, $^2J_{HH}$ = 7.2 Hz)	137.20 (C_{para}) 131.55 (C_{ipso}) 131.44 (C_{arom}) 128.81 (C_{arom}) 108.00 (C_5(CH$_3$)$_5$) 43.93 (CH$_2$) 21.40 (ArCH$_3$) 10.08 (C$_5$(CH$_3$)$_5$)

[a] Probe temperatures 120 °C. [b] m/z values are for the highest intensity peak of the calculated isotopic cluster. [c] Values of $^1J_{CH}$ (Hz) were determined by a gated decoupled pulse sequence. [d] Relaxation delays (10–20 s) were required to observe full integrations of Cp proton signals. [e] The low solubility of CpMo(NO)(CH$_2$Ph)Cl in CDCl$_3$ and the very broad nature of this signal make its assignment tentative at best. [f] ^{13}C{^{1}H} NMR spectrum of this complex recorded in C$_6$D$_6$.

The residue was taken up in 1:1 CH$_2$Cl$_2$/hexanes (30 mL) and filtered through a column of alumina (Fisher neutral, Activity III, 20 × 70 mm) supported on a medium-porosity frit. An orange filtrate was collected by washing the column with a 1:1 CH$_2$Cl$_2$/hexanes mixture (60 mL). The filtrate was concentrated under reduced pressure until precipitation began and was then cooled (−25 °C) to complete the crystallization. The supernatant solution was removed by cannulation, and the remaining orange solid was washed with hexanes (20 mL). The solid was dried at 20 °C (5 × 10^{-3} mm) for 2 h to obtain 0.45 g (34% yield) of Cp*W(NO)(*p*-Xyl)(Npt). The supernatant and washing solutions were combined, reduced in volume, and returned to the freezer to induce the deposition of an additional 0.14 g of product (0.59 g total, 45% overall yield).

The preparation of the molybdenum congener on a similar scale afforded Cp*Mo(NO)(*p*-Xyl)(Npt) as a feathery, orange solid in 54% yield. The characterization data for both complexes can be found in Tables I and III.

Preparation of Cp*Mo(NO)(*p*-Xyl)(*p*-Tol). Solid samples of Cp*Mo(NO)(*p*-Xyl)Cl (0.40 g, 1.0 mmol) and (*p*-Tol)$_2$Mg(dioxane)$_2$ (0.26 g, 175 mg/mmol of *p*-Tol$^-$, 0.75 mmol) were weighed into a Schlenk tube in a drybox. The tube was removed from the box and cooled at 10 °C for 10 min. Then Et$_2$O (45 mL) was rapidly syringed into the tube, and the resulting mixture was stirred overnight at ambient temperature. The final orange reaction solution was then treated with water (0.1 mL) and stirred for 5 min to destroy the excess Grignard reagent. The reaction mixture was taken to dryness in vacuo to obtain a sticky, orange residue, which was dissolved in 2:1 hexanes/CH$_2$Cl$_2$ (60 mL) and filtered through an alumina column (Fisher neutral, Activity III, 20 × 70 mm). The column was then washed with 1:1 hexanes/CH$_2$Cl$_2$ to complete the removal of a single orange band. Solvent was removed from the combined filtrates in vacuo to obtain an orange glass, which was redissolved in hexanes (20 mL). Cooling of this hexanes solution to −78 °C resulted in the deposition of an orange solid. The cooling bath was taken away, and the solvent

Table III. Mass Spectral and ^{1}H and ^{13}C{^{1}H} NMR Data for the Chiral Benzyl Alkyl Complexes

low-resolution mass spectrum,[a] *m/z*[b]	^{1}H NMR (C$_6$D$_6$) δ	^{13}C{^{1}H} NMR (CDCl$_3$) δ[c]
	CpW(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)	
457, [P]$^+$ 442, [P − CH$_3$]$^+$ 427, [P − NO]$^+$	7.58 (t, 1 H, *p*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 6.65 (d, 2 H, *o*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz) 6.51 (t, 2 H, *m*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 5.01 (s, 5 H, C$_5$*H*$_5$)[d] 3.09 (d, 1 H, ArC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 5.8 Hz) 2.60 (d, 1 H, ArCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 5.8 Hz) 0.22 (s, 9 H, Si(C*H*$_3$)$_3$) −0.19 (d, 1 H, SiC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 12.9 Hz) −3.68 (d, 1 H, SiCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 12.9 Hz)	135.27 (C_{ortho}, d, [161]) 132.00 (C_{para}, d, [161]) 129.44 (C_{meta}, d, [161]) 111.51 (C_{ipso}) 99.46 (*C*$_5$H$_5$, d, [179]) 38.91 (Ar*C*H$_2$, t, [147], $^{1}J_{\mathrm{WC}}$ = 46 Hz) 13.84 (Si*C*H$_2$, t, [112], $^{1}J_{\mathrm{WC}}$ = 77 Hz) 2.59 (Si(*C*H$_3$)$_3$, q, [118])
	Cp*W(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)	
527, [P]$^+$ 512, [P − CH$_3$]$^+$ 497, [P − NO]$^+$	7.50 (t, 1 H, *p*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 6.62 (t, 2 H, *m*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 6.54 (d, 2 H, *o*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 3.25 (d, 1 H, ArC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 5.0 Hz) 2.10 (d, 1 H, ArCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 5.0 Hz) 1.55 (s, 15 H, C$_5$(C*H*$_3$)$_5$) 0.32 (s, 9 H, Si(C*H*$_3$)$_3$) −0.73 (d, 1 H, SiC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 13.5 Hz) −4.06 (d, 1 H, SiCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 13.5 Hz)	134.65 (C_{arom}) 130.41 (C_{para}) 129.52 (C_{arom}) 115.54 (C_{ipso}) 108.27 (*C*$_5$(CH$_3$)$_5$) 47.05 (Ar*C*H$_2$) 20.02 (*C*H$_2$Si) 10.51 (C$_5$(*C*H$_3$)$_5$) 3.05 (Si(*C*H$_3$)$_3$)
	CpMo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)	
371, [P]$^+$ 356, [P − CH$_3$]$^+$ 341, [P − NO]$^+$	7.39 (t, 1 H, *p*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz) 6.62 (t, 2 H, *m*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz) 6.26 (br s, 2 H, *o*-ArH) 5.00 (s, 5 H, C$_5$*H*$_5$)[d] 3.11 (d, 1 H, ArC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 4.5 Hz) 2.60 (d, 1 H, ArCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 4.5 Hz) 0.26 (s, 9 H, Si(C*H*$_3$)$_3$) 0.14 (d, 1 H, SiC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 12.8 Hz) −4.15 (d, 1 H, SiCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 12.8 Hz)	134.10 (C_{ortho}) 131.87 (C_{para}) 128.56 (C_{meta}) 112.57 (C_{ipso}) 99.89 (*C*$_5$H$_5$) 39.16 (Ar*C*H$_2$) 15.93 (Si*C*H$_2$) 2.40 (Si(*C*H$_3$)$_3$)
	Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)[e]	
441, [P]$^+$ 426, [P − CH$_3$]$^+$ 411, [P − NO]$^+$	7.36 (t, 1 H, *p*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 6.66 (t, 2 H, *m*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 6.20 (d, 2 H, *o*-ArH, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 3.23 (d, 1 H, ArC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 4.5 Hz) 2.00 (d, 1 H, ArCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 4.5 Hz) 1.53 (s, 15 H, C$_5$(C*H*$_3$)$_5$) 0.30 (s, 9 H, Si(C*H*$_3$)$_3$) −0.64 (d, 1 H, SiC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 13.1 Hz) −4.49 (d, 1 H, SiCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 13.1 Hz)	133.84 (C_{ortho}) 130.54 (C_{para}) 128.63 (C_{meta}) 115.72 (C_{ipso}) 108.39 (*C*$_5$(CH$_3$)$_5$) 46.09 (Ar*C*H$_2$) 19.52 (Si*C*H$_2$) 10.60 (C$_5$(*C*H$_3$)$_5$) 3.77 (Si(*C*H$_3$)$_3$)
	Cp*W(NO)(*p*-Xyl)(Npt)[e]	
525, [P]$^+$ 493, [P − NO − 2 H]$^+$	6.63 (s, 4 H, Ar*H*) 3.24 (d, 1 H, ArC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 7.0 Hz) 2.17 (d, 1 H, ArCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 7.0 Hz) 2.03 (s, 3 H, ArC*H*$_3$) 1.58 (s, 15 H, C$_5$(C*H*$_3$)$_5$) 1.35 (d, 1 H, CC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 13.7 Hz) 1.20 (s, 9 H, C(C*H*$_3$)$_3$) −2.41 (d, 1 H, CCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 13.7 Hz)	140.44 (C_{para}) 133.76 (C_{arom}) 130.59 (C_{arom}) 118.32 (C_{ipso}) 107.72 (*C*$_5$(CH$_3$)$_5$) 65.50 (C*C*H$_2$) 48.51 (Ar*C*H$_2$) 37.57 (C_{quat}) 34.81 (C(*C*H$_3$)$_3$) 21.88 (Ar*C*H$_3$) 10.29 (C$_5$(*C*H$_3$)$_5$)
	Cp*Mo(NO)(*p*-Xyl)(Npt)[e]	
439, [P]$^+$ 407, [P − NO − 2 H]$^+$	6.59 (d, 2 H, Ar*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz) 6.18 (d, 2 H, ArH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz) 3.33 (d, 1 H, ArC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 4.8 Hz) 2.13 (s, 3 H, ArCH$_3$) 2.00 (d, 1 H, ArCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 4.8 Hz) 1.58 (s, 15 H, C$_5$(C*H*$_3$)$_5$) 1.17 (s, 9 H, C(C*H*$_3$)$_3$) 0.94 (d, 1 H, CC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 12.5 Hz) −2.88 (d, 1 H, CCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 12.5 Hz)	142.10 (C_{para}) 133.76 (C_{ortho}) 129.85 (C_{meta}) 114.07 (C_{ipso}) 108.12 (*C*$_5$(CH$_3$)$_5$) 57.66 (C*C*H$_2$) 45.70 (Ar*C*H$_2$) 37.06 (C_{quat}) 34.64 (C(*C*H$_3$)$_3$) 21.78 (Ar*C*H$_3$) 10.55 (C$_5$(*C*H$_3$)$_5$)
	Cp*Mo(NO)(*p*-Xyl)(*p*-Tol)[e]	
459, [P]$^+$ 429, [P − NO]$^+$	6.88 (d, 2 H, Ar*H*, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz) 6.2–6.7 (m, 6 H, Ar*H*) 3.42 (d, 1 H, ArC*H*$_{\mathrm{A}}$H$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 4.5 Hz) 2.23 (s, 3 H, ArC*H*$_3$) 2.12 (d, 1 H, ArCH$_{\mathrm{A}}$*H*$_{\mathrm{B}}$, $^{2}J_{\mathrm{HH}}$ = 4.5 Hz) 1.88 (s, 3 H, ArC*H*$_3$) 1.54 (s, 15 H, C$_5$(C*H*$_3$)$_5$)	173.14 (C_{ipso}, *p*-Tol) 142.77 (C_{para}, *p*-Xyl) 138.70 (C_{ortho}, *p*-Xyl)) 134.69 (C_{meta}, *p*-Xyl) 132.94 (C_{para}, *p*-Tol) 129.58 (C_{arom}, *p*-Tol) 127.19 (C_{arom}, *p*-Tol) 112.12 (C_{ipso}, *p*-Xyl) 109.02 (*C*$_5$(CH$_3$)$_5$) 47.65 (Ar*C*H$_2$) 21.71 (Ar*C*H$_3$) 21.39 (Ar*C*H$_3$) 10.53 (C$_5$(*C*H$_3$)$_5$)

[a] Probe temperatures 120 °C. [b] *m/z* values are for the highest intensity peak of the calculated isotopic cluster. [c] Values of $^{1}J_{\mathrm{CH}}$ (Hz) were determined by a gated decoupled pulse sequence. [d] Relaxation delays (10–20 s) were required to observe full integrations of Cp proton signals. [e] ^{13}C{^{1}H} NMR spectrum of this complex recorded in C$_6$D$_6$.

was slowly removed under reduced pressure as the solution warmed to obtain 0.365 g (80% yield) of analytically pure Cp*Mo(NO)(*p*-Xyl)(*p*-Tol) as an orange, microcrystalline solid. The physical and spectroscopic properties of this complex can also be found in Tables I and III.

X-ray Crystallographic Analyses of Cp*Mo(NO)(CH$_2$Ph)Cl and Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$). Both X-ray structure determinations were performed in a similar manner. As described above, a suitable X-ray-quality crystal of each complex was obtained by slow crystallizations from CH$_2$Cl$_2$ hexanes solutions at −25 °C effected overnight. After preliminary photographic investigation, each crystal was mounted in a thin-walled glass capillary under N$_2$ and transferred to an Enraf-Nonius CAD4-F diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda_{K\alpha_1}$ = 0.709 30, $\lambda_{K\alpha_2}$ = 0.713 59 Å). Final unit cell parameters for each complex were obtained by least-squares analysis of 2(sin θ)/λ values for 25 well-centered high-angle reflections; i.e., 16.4 ≤ θ ≤ 20.5° for Cp*Mo(NO)(CH$_2$Ph)Cl and 17.5 ≤ θ ≤ 20.1° for Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$). The intensities of three standard reflections were measured every hour

Table IV. Crystallographic and Experimental Data[a] for the Complexes Cp*Mo(NO)(CH$_2$Ph)Cl and Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)

	Cp*Mo(NO)-(CH$_2$Ph)Cl	Cp*Mo(NO)-(CH$_2$Ph)-(CH$_2$SiMe$_3$)
formula	$C_{17}H_{22}NOClMo$	$C_{21}H_{33}NOSiMo$
fw	387.76	439.52
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	9.3451 (16)	8.3901 (10)
b, Å	11.8954 (9)	9.3937 (17)
c, Å	15.6511 (17)	14.9556 (19)
α, deg	90	74.017 (11)
β, deg	100.176 (9)	98.009 (9)
γ, deg	90	86.849 (12)
V, Å^3	1712.5 (4)	1116.7 (3)
Z	4	2
D_{calcd}, Mg/m^3	1.51	1.31
$F(000)$	792	460
μ(Mo Kα), cm^{-1}	9.05	6.35
temp, K	293	293
cryst dimens, mm^3	0.21 × 0.30 × 0.50	0.23 × 0.33 × 0.34
Mo Kα radiation (λ, Å)	0.710 69	0.710 69
transmissn factors	0.74–0.83	0.81–0.89
scan type	coupled ω–2θ	coupled ω–2θ
scan range, deg	0.75 + 0.35 tan θ	0.75 + 0.35 tan θ
scan speed, deg/min	1.68–20.12	1.55–20.12
2θ limits, deg	$0 \leq 2\theta \leq 65$	$0 \leq 2\theta \leq 55$
data collected	$\pm h,-k,-l$	$\pm h,\pm k,l$
no. of unique rflns	6159	5092
no. of rflns with $I > 3\sigma(I)$	4361	4328
no. of variables	218	358
R_F[b]	0.033	0.023
R_{wF}[c]	0.047[d]	0.031[d]
goodness of fit[e]	1.858	1.107
max Δ/σ (final cycle)	0.046	0.007
residual density, e/Å^3	0.67	0.22

[a] Enraf-Nonius CAD4-F diffractometer, Mo Kα radiation, graphite monochromator. [b] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o{}^2]^{1/2}$. [d] $w = [\sigma^2(F)]^{-1}$. [e] GOF = $[R_w(|F_0| - |F_c|)^2/(\text{no. of degrees of freedom})]^{1/2}$.

of X-ray exposure time during the data collection of both complexes and showed no appreciable variations in intensity (ca. 0.5% isotropic) with time. The data were corrected for Lorentz and polarization effects and for absorption by the Gaussian integration method.[22-24] Pertinent crystallographic and experimental parameters for both complexes are summarized in Table IV.

Interpretation of the Patterson function yielded the coordinates of the heaviest atoms in each structure [Mo and Cl in Cp*Mo(NO)(CH$_2$Ph)Cl and Mo and Si in Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$)]. The structures of both compounds were solved by conventional electron density methods and were refined by full-matrix least-squares methods on F, minimizing the function $\sum w(|F_o| - k|F_c|)^2$, where w was calculated from $w = [\sigma^2(F)]^{-1}$. The variable k was used to scale the calculated to the observed structure factors. Most hydrogen atoms were located in difference Fourier maps and were included in the refinement. Final refinement for Cp*Mo(NO)(CH$_2$Ph)Cl was carried out with non-hydrogen atoms being permitted anisotropic thermal motion, benzyl hydrogen atoms with isotropic thermal parameters, and methyl hydrogens on the Cp* group placed in idealized positions that were recalculated before each cycle. Final convergence was reached at $R = 0.033$; the maximum parameter shift during the last cycle of refinement was 0.046σ. Final cycles of refinement for Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) were performed with anisotropic thermal motion for non-hydrogen atoms and isotropic thermal motion for hydrogen atoms. Final convergence was reached at $R = 0.023$; the maximum parameter shift during the last cycle of refinement was 0.007σ.

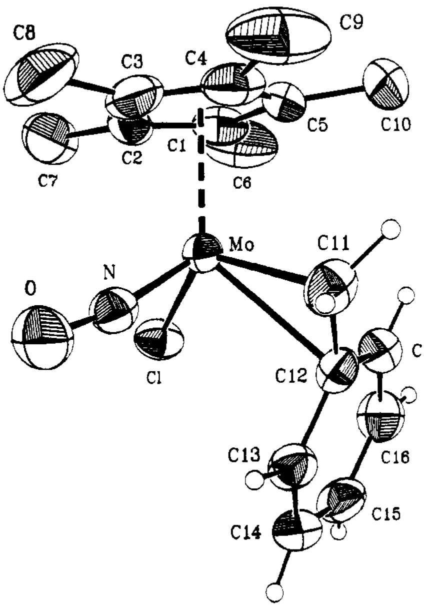

Figure 1. View of the solid-state molecular structure of Cp*Mo(NO)(CH$_2$Ph)Cl, hydrogen atoms having been omitted for clarity.

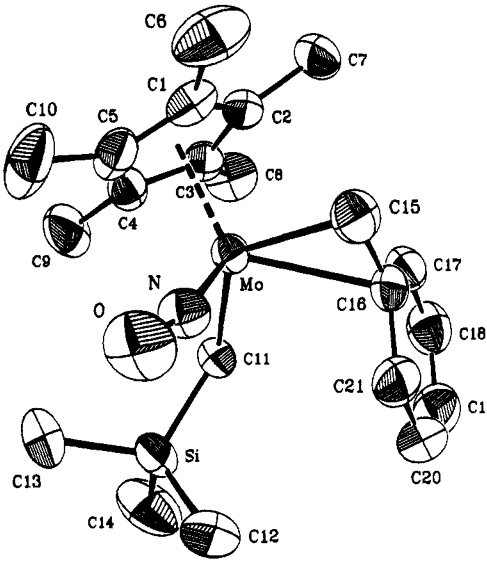

Figure 2. View of the solid-state molecular structure of Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$), hydrogen atoms having been omitted for clarity.

Complex neutral atom scattering factors were taken from ref 25. Final positional and equivalent isotropic thermal parameters (U_{eq} = $^1/_3$ × trace diagonalized U) for the complexes are given in Table V. Selected bond lengths (Å) and bond angles (deg) for the compounds are listed in Tables VII and VIII, respectively. Anisotropic thermal parameters (Table VI), the remaining molecular dimensions, and tables of calculated and observed structure factors for Cp*Mo(NO)(CH$_2$Ph)Cl and Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) are provided as supplementary material. Views of the solid-state molecular structures of Cp*Mo(NO)(CH$_2$Ph)Cl and Cp*Mo(NO)(CH$_2$Ph)(CH$_2$SiMe$_3$) are displayed in Figures 1 and 2, respectively.

Results and Discussion

Preparation and Physical Properties of the Cp*M(NO)(*p*-Xyl)$_2$ Complexes. These organometallic com-

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[22] The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEPII, illustrations, by C. K. Johnson.

[23] Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

[24] Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1967**, *22*, 457.

[25] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England 1974; Vol. IV, Tables 2.2B and 2.3.1.

Table V. Final Positional (Fractional $\times 10^4$; Mo, Cl, and Si $\times 10^5$; H $\times 10^3$) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq}/U_{iso}	atom	x	y	z	U_{eq}/U_{iso}
				$Cp^*Mo(NO)(CH_2Ph)Cl$					
Mo	51612 (2)	41035 (1)	25678 (1)	33	H6a	199	509	74	122
Cl	43253 (8)	58810 (5)	30347 (4)	47	H6b	287	601	137	122
O	8034 (2)	4028 (2)	3730 (2)	68	H6c	305	596	38	122
N	6820 (2)	4069 (2)	3325 (1)	43	H7a	535	671	127	124
C1	4153 (3)	4700 (3)	1108 (2)	53	H7b	679	636	193	124
C2	5665 (3)	4995 (3)	1350 (2)	56	H7c	676	631	91	124
C3	6469 (3)	4017 (3)	1452 (2)	61	H8a	852	473	169	141
C4	5542 (4)	3110 (3)	1327 (2)	59	H8b	846	354	216	141
C5	4096 (3)	3513 (3)	1098 (2)	53	H8c	846	360	114	141
C6	2907 (6)	5508 (4)	879 (2)	98	H9a	708	185	148	132
C7	6190 (6)	6196 (4)	1368 (3)	100	H9b	553	144	167	132
C8	8125 (4)	3968 (5)	1626 (3)	113	H9c	577	163	69	132
C9	6021 (6)	1899 (4)	1287 (3)	105	H10a	307	200	87	104
C10	2788 (4)	2792 (4)	807 (2)	83	H10b	205	296	116	104
C11	4606 (3)	2419 (2)	2974 (2)	51	H10c	239	295	20	104
C12	3718 (3)	3081 (2)	3467 (2)	41	H11a	524 (3)	198 (3)	326 (2)	55 (9)
C13	4240 (3)	3447 (2)	4318 (2)	45	H11b	406 (3)	188 (2)	248 (2)	45 (7)
C14	3411 (3)	4116 (2)	4757 (2)	51	H13	513 (4)	328 (3)	453 (2)	58 (9)
C15	2053 (3)	4450 (3)	4347 (2)	54	H14	373 (3)	429 (2)	532 (2)	46 (8)
C16	1512 (3)	4117 (3)	3517 (2)	56	H15	145 (3)	503 (3)	457 (2)	62 (9)
C17	2340 (3)	3440 (2)	3076 (2)	47	H16	48 (3)	434 (2)	317 (2)	53 (8)
					H17	192 (4)	330 (3)	252 (2)	72 (10)
				$Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$					
Mo	23822 (2)	156 (2)	79675 (1)	36 (0)	H7a	−12 (4)	−235 (4)	959 (2)	87 (10)
Si	31252 (8)	28380 (7)	59945 (5)	57 (0)	H7b	−69 (4)	−340 (4)	910 (2)	91 (10)
O	5866 (2)	458 (2)	8280 (2)	83 (0)	H7c	−132 (6)	−163 (6)	877 (4)	160 (18)
N	4408 (2)	420 (2)	8128 (1)	51 (0)	H8a	−148 (4)	−164 (4)	650 (3)	104 (11)
C1	2498 (3)	−2562 (2)	8651 (2)	54 (0)	H8b	−190 (5)	−46 (5)	710 (3)	131 (15)
C2	809 (2)	−2127 (2)	8377 (1)	47 (0)	H8c	−109 (5)	−11 (4)	629 (3)	112 (12)
C3	485 (2)	−1541 (2)	7395 (1)	45 (0)	H9a	176 (5)	−44 (5)	567 (3)	101 (13)
C4	1967 (3)	−1648 (2)	7040 (2)	50 (0)	H9b	321 (4)	−147 (4)	604 (2)	90 (11)
C5	3212 (2)	−2292 (2)	7824 (2)	59 (0)	H9c	166 (6)	−190 (6)	565 (4)	163 (19)
C6	3302 (6)	−3359 (4)	9640 (3)	94 (0)	H10a	565 (4)	−256 (4)	829 (2)	88 (10)
C7	−443 (4)	−2449 (3)	9014 (2)	71 (0)	H10b	519 (5)	−211 (5)	720 (3)	117 (16)
C8	−1165 (3)	−998 (4)	6818 (2)	70 (0)	H10c	503 (5)	−356 (5)	775 (3)	114 (13)
C9	2083 (6)	−1363 (5)	6015 (3)	85 (0)	H11a	91 (3)	253 (3)	678 (2)	49 (6)
C10	4930 (4)	−2732 (5)	7768 (4)	98 (0)	H11b	88 (3)	151 (3)	620 (2)	58 (6)
C11	1605 (2)	1791 (2)	6622 (1)	44 (0)	H12a	490 (5)	471 (4)	632 (3)	105 (11)
C12	4084 (5)	4072 (4)	6657 (3)	84 (0)	H12b	455 (6)	347 (5)	725 (3)	142 (18)
C13	4800 (5)	1642 (5)	5779 (4)	96 (0)	H12c	329 (5)	489 (4)	656 (3)	103 (12)
C14	2106 (6)	4054 (7)	4804 (3)	109 (0)	H13a	535 (5)	78 (5)	642 (3)	120 (14)
C15	2132 (3)	149 (3)	9380 (2)	59 (0)	H13b	442 (5)	129 (4)	532 (3)	99 (13)
C16	1227 (3)	1565 (2)	8861 (1)	48 (0)	H13c	555 (4)	240 (4)	544 (3)	105 (11)
C17	−398 (3)	1621 (3)	8475 (2)	55 (0)	H14a	277 (7)	462 (6)	445 (4)	160 (19)
C18	−1262 (3)	2936 (3)	7937 (2)	70 (0)	H14b	155 (7)	343 (7)	454 (4)	176 (27)
C19	−520 (4)	4227 (3)	7750 (2)	78 (0)	H14c	172 (7)	496 (6)	485 (4)	160 (23)
C20	1081 (4)	4212 (3)	8104 (2)	77 (0)	H15a	302 (4)	15 (3)	972 (2)	75 (9)
C21	1970 (3)	2909 (3)	8640 (2)	61 (0)	H15b	150 (3)	−59 (3)	970 (2)	74 (8)
H6a	429 (5)	−310 (5)	964 (3)	117 (15)	H17	−98 (3)	79 (3)	857 (2)	60 (7)
H6b	288 (6)	−293 (6)	1017 (4)	174 (21)	H18	−235 (4)	301 (4)	765 (2)	99 (11)
H6c	347 (5)	−437 (5)	971 (3)	125 (14)	H19	−106 (4)	517 (4)	737 (2)	91 (9)
					H20	182 (5)	506 (5)	799 (3)	128 (14)
					H21	302 (3)	279 (3)	889 (2)	70 (8)

pounds are preparable by treatment of their dichloro precursors with 2 equiv of the appropriate Grignard reagent:

$$Cp^*M(NO)Cl_2 + 2p\text{-}XylMgCl \xrightarrow[2.\ H_2O]{1.\ Et_2O} Cp^*Mo(NO)(p\text{-}Xyl)_2 + 2MgCl_2 \quad (9)$$

The liberation of the final bis(*p*-xylyl) products from their intermediate $MgCl_2$ adducts in reaction 9 is accomplished with water, methodology that has been used during the preparations of other bis(alkyl) complexes.[4] The bis(*p*-xylyl) complexes are notably more soluble in common organic solvents than are their bis(benzyl) analogues,[1] a property undoubtedly reflecting the presence of the methyl groups on the aromatic rings. As solids, they can be handled in air for short periods of time for the purposes of transfer and weighing without the occurrence of noticeable decomposition. When stored under dinitrogen, the bis(*p*-xylyl) compounds appear to be indefinitely thermally stable, as are the analogous bis(benzyl) complexes.[16] Their characteristic IR and mass spectroscopic data (presented in Tables I and II) are consistent with their monomeric formulations.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of the bis(*p*-xylyl) complexes also reveal just how similar these species are to their bis(benzyl) analogues. Prior to the inception of this work, the series of complexes $Cp'M(NO)(CH_2Ph)_2$ had been structurally characterized and found to be unique members of the larger class of compounds $Cp'M(NO)R_2$. Their uniqueness stems from the fact that they all contain one benzyl ligand coordinated in an η^2 fashion and functions as a formal 3-electron donor to the metal center.[26]

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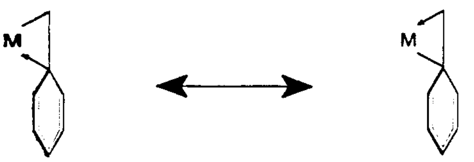
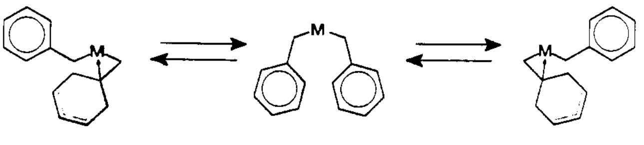
[26] A preliminary account of the solid-state molecular structure of $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ has appeared: Dryden, N. H.; Legzdins, P.; Phillips, E. C.; Trotter, J.; Yee, V. C. *Organometallics* **1990**, *9*, 882.



Hence, unlike the other dialkyls, these original bis(benzyl) complexes, $Cp'M(NO)(CH_2Ph)_2$, are 18-valence-electron species. They are also stereochemically nonrigid in solution at ambient temperatures, the principal fluxionality involving the two benzyl ligands exchanging their modes of atttachment to the metal centers.



This process causes the ^1H and $^{13}C\{^1H\}$ NMR signals of the η^1- and η^2-benzyl ligands to be time-averaged, one set of benzyl resonances being the observable result. Both of the newly prepared $Cp^*M(NO)(p\text{-}Xyl)_2$ species[17] also exhibit signals in their ^1H and $^{13}C\{^1H\}$ NMR spectra for just one type of p-xylyl ligand (Table II). This apparent symmetry is seen most clearly in the ^1H NMR spectra of these complexes, a single distinctive AB doublet pattern diagnostic of a para-disubstituted benzene ring being evident. This pattern is useful for monitoring subsequent chemistry since it simplifies an otherwise crowded aromatic region of the ^1H NMR spectra. The methylene proton resonances of the bis(p-xylyl) complexes also occur at chemical shift values that correspond closely to those observed for the methylene protons of the bis(benzyl) complexes.

Preparation and Physical Properties of the $Cp'M(NO)(CH_2Ar)Cl$ Complexes. At the outset, we had hoped that the demonstrated ability of an η^2-benzyl ligand to provide extra electron density to the metal center would permit the isolation of thermally stable complexes of the type $Cp'M(NO)(\eta^2\text{-}CH_2Ar)Cl$. Our hypothesis was strengthened by the knowledge that similar species involving η^3-allyl ligands, e.g., $CpM(NO)(\eta^3\text{-allyl})I$ (M = W[27a] or Mo[27b,c]), had been prepared previously. The apparently straightforward synthetic route to these complexes, namely selective alkylation of the dichloro precursors with 1 equiv of a Grignard reagent, was not attempted because of the poor results obtained previously from similar reactions (as noted in the Introduction of this paper).[28] Therefore, treatment of the bis(benzyl) complexes with HCl constituted our first attempt to form the benzyl chloro species. Gratifyingly, this method was indeed successful, the desired complexes being prepared most conveniently if an excess of HCl is employed (eq 10). The progress of reaction 10 can be easily monitored by IR spectroscopy since the product benzyl chloro complexes exhibit ν_{NO} absorptions in solution (Table I) approximately 30 cm^{-1} higher in energy than the bis(benzyl) starting materials. This shift in ν_{NO} is consistent with there being a reduced electron density at the metal center available for M dπ → NO π^* backbonding, the result of replacing a benzyl ligand with a more electronegative chlorine atom. Among the $Cp'M(NO)(CH_2Ar)Cl$ complexes, the ν_{NO} bands of the Cp*-containing species are approximately 15 cm^{-1} lower in energy than those for the Cp-containing ones, a property reflective of the greater electron-donating ability of the Cp* ligand. As well, the ν_{NO} bands of the tungsten complexes are about 30 cm^{-1} lower in energy than those for the molybdenum complexes. Similar trends in the observed nitrosyl stretching frequencies have been previously noted for the starting bis(benzyl) complexes and other classes of compounds containing the Cp'M(NO) moieties.[16,30]

$$Cp'M(NO)(CH_2Ar)_2 \xrightarrow{\text{excess HCl}} Cp'M(NO)(CH_2Ar)Cl + ArCH_3 \quad (10)$$

Table VII. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses

	length (A)		length (A)
	$Cp^*Mo(NO)(CH_2Ph)Cl$		
Mo–Cl	2.4117 (6)	C3–C8	1.524 (5)
Mo–N	1.778 (2)	C4–C5	1.419 (4)
Mo–C11	2.193 (3)	C4–C9	1.513 (5)
Mo–C12	2.439 (2)	C5–C10	1.497 (4)
Mo–Cp	2.0404 (12)	C11–C12	1.460 (4)
O–N	1.198 (3)	C12–C13	1.404 (3)
C1–C2	1.440 (4)	C12–C17	1.392 (3)
C1–C5	1.413 (5)	C13–C14	1.376 (4)
C1–C6	1.505 (4)	C14–C15	1.375 (4)
C2–C3	1.379 (5)	C15–C16	1.367 (4)
C2–C7	1.510 (5)	C16–C17	1.383 (4)
C3–C4	1.376 (5)		
	$Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$		
Mo–N	1.760 (2)	C2–C7	1.503 (3)
Mo–C11	2.218 (2)	C3–C4	1.427 (3)
Mo–C15	2.188 (2)	C3–C8	1.506 (3)
Mo–C16	2.473 (2)	C4–C5	1.425 (3)
Mo–Cp	2.058 (1)	C4–C9	1.501 (4)
Si–C11	1.855 (2)	C5–C10	1.498 (3)
Si–C12	1.867 (3)	C15–C16	1.450 (3)
Si–C13	1.869 (3)	C16–C17	1.397 (3)
Si–C14	1.885 (4)	C16–C21	1.417 (3)
O–N	1.217 (2)	C17–C18	1.375 (4)
C1–C2	1.423 (3)	C18–C19	1.372 (4)
C1–C5	1.415 (4)	C19–C20	1.371 (5)
C1–C6	1.503 (4)	C20–C21	1.375 (4)
C2–C3	1.400 (3)		

As noted above, there is no deleterious effect in using excess HCl to effect conversion 10. Selective hydrochlorination of an alkyl ligand has been used previously to prepared other mixed alkyl halo nitrosyl complexes, but, unlike for transformation 10, the stoichiometry of the reactants in reaction 11 must be carefully controlled to avoid the subsequent formation of $Cp^*Ru(NO)Cl_2$.[31]

$$Cp^*Ru(NO)Ph_2 + HCl(aq) \xrightarrow{\text{acetone}} Cp^*Ru(NO)(Ph)Cl + PhH \quad (11)$$

The $Cp'M(NO)(CH_2Ar)Cl$ complexes are orange to red-orange solids that are soluble in polar organic as well as aromatic solvents, but to a lesser degree than are their corresponding bis(benzyl) precursors. The benzyl chloro compounds are markedly less soluble in aliphatic solvents, with only the Cp*-containing members showing any appreciable solubility. All the members of this class of compounds are air-stable as solids for reasonable periods of time, a property that permits them to be handled

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(27) (a) Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *11*, 3268. (b) McCleverty, J. A.; Murray, A. J. *Transition. Met. Chem.* (*Weinheim*) **1979**, *4*, 273. (c) Faller, J. W.; Whitmore, B. C. *Organometallics* **1986**, *5*, 752 and references cited therein.

(28) A similar observation has recently been made concerning unsuccessful attempts to selectively methylate $CpMo(NO)I_2$ with MeLi or MeMgX.[29] These investigators also report that attempted alkylation of $CpMo(NO)I_2$ under heterogeneous conditions with Me_3Al in toluene affords $[CpMo(NO)(I)(Me)]_2$.

(29) Alegre, B.; de Jesús, E.; de Miguel, A. V.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1988**, 819.

(30) Hunter, A. D.; Legzdins, P. *Organometallics* **1986**, *5*, 1001.

(31) Chang, J.; Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3258.

Table VIII. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

	angle (deg)		angle (deg)
	$Cp^*Mo(NO)(CH_2Ph)Cl$		
C1-Mo-N	96.26 (7)	C4-C3-C8	126.1 (4)
C1-Mo-C11	127.42 (8)	C3-C4-C5	108.6 (3)
C1-Mo-C12	91.18 (6)	C3-C4-C9	124.7 (4)
C1-Mo-Cp	112.48 (4)	C5-C4-C9	125.9 (4)
N-Mo-C11	90.50 (11)	C1-C5-C4	107.6 (2)
N-Mo-C12	96.29 (9)	C1-C5-C10	127.1 (3)
N-Mo-Cp	120.19 (8)	C4-C5-C10	125.0 (3)
C11-Mo-C12	36.25 (9)	Mo-C11-C12	81.10 (15)
C11-Mo-Cp	108.34 (9)	Mo-C12-C11	62.65 (13)
C12-Mo-Cp	132.05 (7)	Mo-C12-C13	104.96 (15)
Mo-N-O	170.3 (2)	Mo-C12-C17	99.0 (2)
C2-C1-C5	106.3 (2)	C11-C12-C13	122.3 (2)
C2-C1-C6	126.1 (4)	C11-C12-C17	120.1 (2)
C5-C1-C6	127.6 (3)	C13-C12-C17	117.5 (2)
C1-C2-C3	108.3 (3)	C12-C13-C14	121.4 (2)
C1-C2-C7	122.4 (4)	C13-C14-C15	119.2 (3)
C3-C2-C7	128.9 (4)	C14-C15-C16	121.0 (3)
C2-C3-C4	109.1 (3)	C15-C16-C17	119.8 (3)
C2-C3-C8	124.6 (4)	C12-C17-C16	121.0 (3)
	$Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$		
N-Mo-C11	96.15 (8)	C2-C3-C4	108.0 (2)
N-Mo-C15	90.87 (10)	C2-C3-C8	125.4 (2)
N-Mo-C16	99.34 (8)	C4-C3-C8	126.4 (2)
N-Mo-Cp	121.42 (7)	C3-C4-C5	107.8 (2)
C11-Mo-C15	126.60 (8)	C3-C4-C9	124.1 (3)
C11-Mo-C16	91.18 (7)	C5-C4-C9	127.3 (3)
C11-Mo-Cp	111.82 (6)	C1-C5-C4	107.7 (2)
C15-Mo-C16	35.60 (8)	C1-C5-C10	126.5 (3)
C15-Mo-Cp	108.80 (8)	C4-C5-C10	125.6 (3)
C16-Mo-Cp	128.74 (6)	Mo-C11-Si	120.29 (10)
C11-Si-C12	111.31 (13)	Mo-C15-C16	82.97 (12)
C11-Si-C13	114.39 (14)	Mo-C16-C15	61.43 (11)
C11-Si-C14	109.5 (2)	Mo-C16-C17	97.98 (13)
C12-Si-C13	107.0 (2)	Mo-C16-C21	105.70 (14)
C12-Si-C14	107.7 (3)	C15-C16-C17	120.3 (2)
C13-Si-C14	106.7 (2)	C15-C16-C21	122.3 (2)
Mo-N-O	169.7 (2)	C17-C16-C21	117.2 (2)
C2-C1-C5	108.0 (2)	C16-C17-C18	121.5 (2)
C2-C1-C6	124.5 (3)	C17-C18-C19	120.0 (3)
C5-C1-C6	127.0 (3)	C18-C19-C20	120.2 (3)
C1-C2-C3	108.5 (2)	C19-C20-C21	120.8 (2)
C1-C2-C7	125.6 (2)	C16-C21-C20	120.2 (2)
C3-C2-C7	125.4 (2)		

without an inert atmosphere for the purpose of weighing and transfer. When stored under N_2 at 10 °C in the dark, they remain unchanged over a period of at least 6 months.

The mass spectra of all these complexes (Table II) are relatively simple, each spectrum displaying a highest mass isotopic cluster of signals corresponding to a parent ion of composition $[Cp'M(NO)(CH_2Ar)Cl]^+$. Daughter-ion peaks due to loss of NO are evident for all the compounds, an observation that is ubiquitous during the analysis of the mass spectra of organometallic nitrosyl complexes.[32]

Preparation and Properties of the Complexes $Cp'M(NO)(CH_2Ar)R$ (R = CH_2SiMe_3, Npt, or *p*-Tol). The reactions of the benzyl chloro species with a (trimethylsilyl)methyl Grignard reagent

$$Cp'M(NO)(CH_2Ph)Cl + Me_3SiCH_2MgCl \xrightarrow[2.\ H_2O]{1.\ Et_2O} Cp'M(NO)(CH_2Ph)(CH_2SiMe_3) + MgCl_2 \quad (12)$$

proceed quickly and cleanly, as indicated by the IR spectra of the final reaction solutions, which exhibit a single strong absorbance due to the ν_{NO} of the product complex (Table I). In no case is there any spectral evidence for the formation of a $MgCl_2$ adduct involving the nitrosyl ligand of the product complexes. As noted previously, such adducts, i.e., $[Cp'(R)_2M(NO)]_2MgCl_2$, commonly occur during the preparations of the symmetrical bis(alkyl) analogues from the dihalo nitrosyl starting materials.[4]

The product complexes formed via reaction 12 are thermally stable as solids and can be handled in air without the occurrence of any noticeable decomposition. The $Cp'M(NO)(CH_2Ph)(CH_2SiMe_3)$ compounds all exhibit a single strong nitrosyl absorption in their IR spectra between 1576 and 1613 cm^{-1} (Table I), these values corresponding closely to the ν_{NO} parameters exhibited by their bis(benzyl) analogues. This fact is not surprising since the electron-donating ability of simple σ-alkyls would not be expected to vary widely, thereby leaving the metal with essentially the same electron density in related $Cp'M(NO)(CH_2Ph)_2$ and $Cp'M(NO)(CH_2Ph)R$ complexes. In their low-resolution mass spectra (Table III), all the complexes exhibit a highest mass isotopic cluster of signals assignable to the parent ion peaks of the monomeric $Cp'M(NO)(CH_2Ph)(CH_2SiMe_3)$ species.

During the preparations of the various 16-electron $Cp'M(NO)R_2$ complexes, it has been previously observed that the presence of the (trimethylsilyl)methyl group generally results in higher yields of products and affords the most thermally stable complexes. The $Cp'M(NO)(CH_2Ph)(Npt)$ derivatives[17] have thus been synthesized during this investigation to compare the relative ease of formation and ultimate stability of these neopentyl analogues of the $Cp'M(NO)(CH_2Ph)(CH_2SiMe_3)$ complexes. Reactions to form the neopentyl-substituted products

$$Cp^*M(NO)(p\text{-}Xyl)Cl \xrightarrow[2.\ H_2O]{1.\ 0.65\ (Npt)_2Mg(dioxane)_2\ \text{in}\ Et_2O} Cp^*M(NO)(p\text{-}Xyl)(Npt) \quad (13)$$

result in eventual isolation of the desired complexes in good yields as orange microcrystalline solids. The $Cp^*M(NO)(p\text{-}Xyl)(Npt)$ products[17] are similar in their physical and spectroscopic properties to the analogous benzyl (trimethylsilyl)methyl complexes (vide infra). The only notable difference for the synthesis of the neopentyl derivatives involves the more forcing reaction conditions needed than those used for the preparation of the (trimethylsilyl)methyl analogues. Our initial attempts at forming these non-(trimethylsilyl)methyl-substituted complexes were disappointing, giving intractable oils. We subsequently discovered that utilization of longer reaction times, slight excesses of alkylating agents, and chromatography of the final products on alumina give much better results. Therefore, the preparation of other alkyl benzyl complexes of this type in future is probably best accomplished by using these latter (apparently general) procedures.

The aryl-substituted complex $Cp^*Mo(NO)(p\text{-}Xyl)(p\text{-}Tol)$[17] is also preparable via a route similar to that depicted in eq 13, and its stability mirrors that of the alkyl benzyl complexes. During the attempted preparation of the related 16-electron bis(aryl) complexes $Cp'M(NO)(Ar)_2$, we observed that the bis(aryl) complexes are much less thermally stable than are their bis(alkyl) analogues, with only the $Cp^*W(NO)(Ar)_2$ complexes being isolable.[15b] This thermal instability is not exhibited by $Cp^*Mo(NO)(p\text{-}Xyl)(p\text{-}Tol)$, a manifestation of the influence of the η^2-benzyl linkage that greatly stabilizes this family of mixed-alkyl complexes.

The low-resolution mass spectra of the $Cp^*M(NO)(p\text{-}Xyl)(R)$ complexes (Table III) exhibit highest mass isotopic clusters attributable to $[Cp^*M(NO)(p\text{-}Xyl)(R)]^+$ parent ions, an observation consistent with the formulation of

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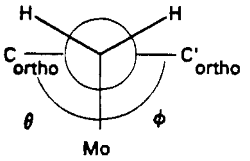
(32) Charalambous, J. In *Mass Spectrometry of Metal Compounds*; Charalambous, J., Ed.; Butterworths: London, England, 1975; p 55.

these compounds as monomeric species.

Solid-State Molecular Structures of $Cp^*Mo(NO)(CH_2Ph)X$ (X = Cl or CH_2SiMe_3). In light of the novel η^2-benzyl linkages found in the parent bis(benzyl) complexes, it was of interest to determine the nature of the metal–benzyl links in these new classes of benzyl-containing complexes. The single-crystal X-ray crystallographic analysis of a prototypal member, namely $Cp^*Mo(NO)(CH_2Ph)Cl$, has been performed, and it confirms the anticipated η^2-coordination mode for the benzyl ligand. An ORTEP diagram of this complex is presented in Figure 1 along with pertinent crystallographic and experimental data in Table IV. The specific details of the molecular structure are discussed below, but for now it is important to note that the $M–CH_2Ph$ unit is isostructural with those found in the other η^2-benzyl structures previously determined.[1]

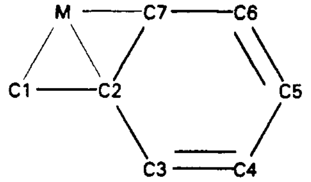
The $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ complex has also been analyzed by single-crystal X-ray crystallography,[26] thereby allowing a comparison of the relative effect on the η^2-benzyl–metal linkage of a (trimethylsilyl)methyl group versus a chlorine atom. The ORTEP plot of this alkyl complex is presented in Figure 2, and its crystallographic data are also presented in Table IV. Basically, the $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ complex contains an η^2-benzyl ligand identical with that extant in its chloro analogue. This fact indicates that the alkyl and chloro groups do not significantly change the nature of the bonding interaction between the metal and the benzyl ligand in spite of the different steric and electronic effects provided by these groups.

The intramolecular dimensions involving the Mo–Cp* portions of both molecules are normal and comparable to those found in related compounds.[3,33] The Mo–N–O linkages in both compounds are essentially linear, the angles at N being 170.3 (2)° for the chloro complex and 169.7 (2)° for the alkyl compound. These features are consistent with the nitrosyl ligands functioning as formal 3-electron donors in both complexes. Furthermore, in both compounds the metal center lies under the CH_2–Ph bond axis in a direction perpendicular to the plane of the benzyl ligand.



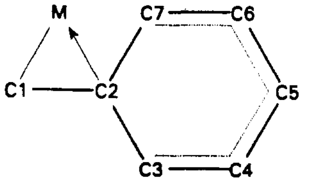
This orientation is best quantified by the dihedral angles $C_{ortho}–C_{ipso}–C1–Mo$ (θ) and $C'_{ortho}–C_{ipso}–C_1–Mo$ (ϕ). For the chloro species these angles are 84.5 (2)° (θ) and 91.0 (2)° (ϕ), respectively, and for the (trimethylsilyl)methyl analogue they are 82.3 (2)° (θ) and 91.2 (2)° (ϕ). For comparison, it should be noted that in $CpMo(\eta^3\text{-}p\text{-}Xyl)(CO)_2$[34] the dihedral angles are quite different (i.e., 60.9° (θ) and 111.59° (ϕ)) and mirror the asymmetric interaction of the benzyl ligand with the metal. The hapticity of the benzyl ligand is also characterized by the metal–carbon bond lengths exhibited by both of these coordination modes. In both η^2-benzyl complexes, the molybdenum atom is within bonding distance of the methylene carbon ($Mo–C_{methylene}$ = 2.193 (3) Å in one and 2.188 (2) Å in the other) and the ipso carbon ($Mo–C_{ipso}$ = 2.439 (2) Å in one and 2.473 (2) Å in the other) of the benzyl ligand. However, the molybdenum atoms are at least 3 Å away from either of the ortho carbons of the η^2-benzyl ligands, a distance that would appear to preclude a significant $Mo–C_{ortho}$ bonding interaction since a Mo–C single bond length is generally estimated to be 2.39 Å.[35] In the η^3-benzyl complex, the $Mo–C_{ortho}$ (2.480 (6) Å), the Mo–C1 (2.269 (7) Å), and the $Mo–C_{ipso}$ (2.364 (5) Å) bond lengths all agree reasonably well with this estimated Mo–C bond length and indicate the existence of strong Mo–C bonding.

The aromatic ring systems are also significantly different structurally in the η^2- and η^3-benzyl cases. In the classic η^3-case (vide infra), π-bond localization is evident in the aromatic ring by virtue of the short C3–C4 and C5–C6 bonds and the long C4–C5 and C6–C7 bonds. Hence, the electronic structure extant in this η^3-grouping is best represented in valence-bond terms in the following manner:



M = $CpMo(CO)_2$

In such a representation, the aromatic ring has a diene-like structure. In contrast, the intramolecular dimensions of the η^2-benzyl ligands in both solid-state molecular structures determined during this work reveal no evidence for the existence of bond localization. Indeed, the four C–C bond lengths in both C3–C4–C5–C6–C7 groups (using the same numbering system as in the η^3-case above) are essentially the same, thereby suggesting the presence of delocalized multiple bonding extending over these carbon atoms. The C2–C3 and C2–C7 bond lengths are noticeably longer, a feature suggesting a reduced bond order between these carbon atoms. Therefore, the overall interaction is best represented in valence-bond terms:



M = $Cp^*Mo(NO)(X)$

X = CH_2SiMe_3, Cl

This representation indicates that there has been a net donation of 2 electrons from the aromatic π-system to the metal center. This results in an overall 3-electron donation from the benzyl ligand to the metal, the benzylic methylene radical supplying the other electron. The η^2-benzyl-containing compounds are formulated in this matter as 18-electron species since they exhibit diamagnetic properties, e.g., unbroadened NMR spectra. It should be noted, however, that there is still a degree of aromatic character to the phenyl ring in these cases since the lengthened C2–C3 and C2–C7 bonds are still reasonably close to the value of 1.395 Å expected for a C–C double bond.[37]

In a molecule of $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$, the methylene group of the (trimethylsilyl)methyl ligand is situated directly over the ring of the benzyl group (Figure 2). A closer examination of the CH_2–Si group shows that

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(33) Malito, J. T.; Shakir, R.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1253 and references cited therein.

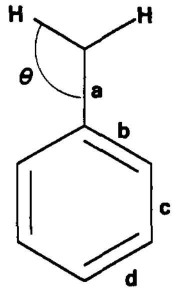
(34) Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418.

(35) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550. This estimated bond length is the sum of the covalent radii for Mo of 1.62 Å [i.e., half of the Mo–Mo single bond length in $Cp_2Mo_2(CO)_6$][36] and for C of 0.77 Å.

(36) Adams, R. D.; Collins, D. M.; Cotton, F. A *Inorg. Chem.* **1974**, *13*, 1086.

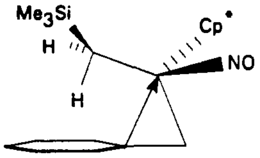
(37) *CRC Handbook of Chemistry and Physics*, 60th ed., Weast, R. Ed.; CRC Press: Boca Raton, FL, 1979; p F-216.

Table IX. Comparison of Bond Lengths (Å) and Angles (deg) Calculated for the Benzyl Radical ($CH_2Ph^{\bullet}$) and Found for the η^2-Benzyl Ligands



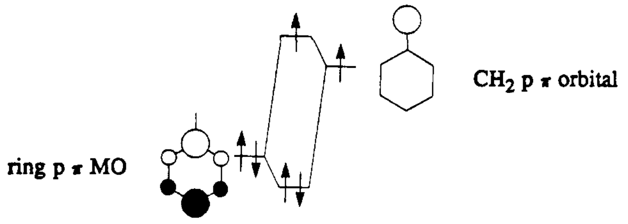
	θ	a	b	c	d
$Cp^*Mo(NO)(CH_2Ph)Cl$	118	1.46	1.40	1.37	1.38
$Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$	117	1.45	1.41	1.37	1.37
$PhCH_2^{\bullet}$	121	1.40	1.43	1.39	1.40

it is oriented so as to place one hydrogen atom over the plane of the benzyl aromatic ring:



Indeed, this proton lies almost exactly over the center of the six ring carbons, 2.50 Å above the plane of the ring. This structural feature will be important in the discussion of the NMR spectroscopic properties of the $Cp'M(NO)(CH_2Ar)R$ (R = Npt or CH_2SiMe_3) complexes (vide infra).

A recent theoretical paper deals, in part, with the rotational barrier of the methylene group in, and the optimized geometry of, the benzyl radical.[38] The rotational barrier is due to a partial double bond resulting from a bonding interaction between the methylene pπ orbital and the aromatic π system. The principal contributor to this interaction can be represented by a simple molecular orbital diagram



where the singly occupied pπ orbital and the filled HOMO of the aromatic ring interact. It is tempting to speculate that the interaction between the η^2-benzyl ligands and the molybdenum centers, as reflected by the crystal structures of $Cp^*Mo(NO)(CH_2Ph)Cl$ and $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$, involves a 3-electron donation from the MO's in the above diagram to the metal center. In other words, the η^2-benzyl–Mo interaction may be viewed as a benzyl radical being stabilized by π-coordination to the metal center. Consistent with this view is the fact that in both of the η^2-benzyl complexes there is some multiple-bond character extant between the methylene and ipso carbons. This is reflected in the C_{ipso}–$C_{methylene}$ bond distances [1.460 (3) Å in one and 1.450 (3) Å in the other] being significantly shorter than a CH_3–$C_{aromatic}$ single bond (1.53 ± 0.01 Å).[37]

It is informative to compare the optimized geometry of a free benzyl radical[38] with the geometry determined for the bound η^2-benzyl ligands during this study. The bond distances found for the η^2-benzyl groups and those calculated for the benzyl radical are listed in Table IX. The general trends calculated for the bond distances are similar to those found in the structures, the C_{ipso}–C_{ortho} bonds being longer than the other ring C–C bonds. However, there is a larger difference in the predicted methylene to ring C–C bond distance for the radical and that found in η^2-benzyl ligands. If the two frontier orbitals of the benzyl radical are indeed donating electrons to the metal, then a reduced methylene–ring interaction would be expected and a lengthened bond should result. In other words, the bonding rationale invoking a metal-stabilized benzyl radical is at least consistent with the observed structural parameters.

Similarly, symmetric benzyl–metal interactions have apparently been observed previously for some group 4[39–42] and actinide[43,44] benzyl complexes, these benzyl–metal interactions having been variously described as η^4,[44] η^n,[43] and η^2.[42] The investigators who invoked the η^2 description for $[Cp_2Zr(\eta^2\text{-}CH_2Ph)]^+$ [42] did not specifically discuss the nature of the benzyl–metal bonding in this cationic complex, but implied it to be the same as that found in the above-mentioned η^4 and η^n cases. In all these cases, the benzyl–metal interactions have been rationalized on the basis of the calculated Hückel MO π-electron density for the benzyl anion. These calculations predict that the negative charge of the benzyl anion lies primarily on the methylene carbon ($^4/_7$) with the rest being on the ortho carbons ($^1/_7$ each) and the para carbon ($^1/_7$).[45] Necessarily, these calculations also predict that no negative charge resides on the ipso and meta carbon atoms. Consequently, for the η^4 and η^n cases, M–C_{ortho} interactions involving benzyl to metal electron donation are invoked. However, this interpretation implicitly assumes that the total electron density donated to the metal is distributed throughout the benzyl anion in the same manner as the net negative charge. This would seem to be an oversimplification. In all of these early-transition-metal and actinide-containing species the molecular structures exhibit M–C_{ortho} distances marginally short enough to imply a bonding interaction. The qualitative metal–benzyl bonding description proposed above, namely a metal-stabilized benzyl radical, eliminates the need to invoke metal–C_{ortho} bonding interactions and gives some indication as to how the η^2-benzyl ligand can be viewed as a 3-electron donor. A reexamination of the other benzyl structures may show that they too can be considered as examples of the same η^2-bonding mode observed for the $Cp'M(NO)(CH_2Ar)(X)$ complexes discussed in this paper. Given the very similar ligand sets of the related $Cp^*Mo(NO)(\eta^2\text{-}CH_2Ph)X$ and $CpMo(CO)_2(\eta^3\text{-}p\text{-}Xyl)$[21] complexes, the factors favoring an η^2- or η^3-benzyl ligand, at least in these cases, appear to be principally electronic in nature. A detailed theoretical

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(38) Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942.

(39) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

(40) Davis, G. R.; Jarvis, J. A. J.; Kilbourn, B. T.; Piols, A. J. P. *J. Chem. Soc. Chem. Common.* **1971**, 677.

(41) Davis, G. R.; Jarvis, J. A. J.; Kilbourn, B. T. *J. Chem. Soc., Chem. Commun.* **1971**, 1511.

(42) (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (b) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539 and references cited therein.

(43) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692.

(44) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293.

(45) These charge distributions simply reflect the relative carbon pπ orbital contributions to the HOMO of the benzyl π system; see: Lowe, J. P. *Quantum Chemistry*; Academic Press: New York, 1978; p 506.

analysis of the bonding extant in these complexes may well reveal the source of this effect.

As a final point, it may be noted that the methylene groups of the η^2-benzyl ligands in Cp*Mo(NO)(CH_2Ph)(CH_2SiMe_3) and Cp*Mo(NO)(CH_2Ph)Cl are approaching a geometry indicative of sp^2 hybridization at their carbon atoms. This fact is best demonstrated by the structurally determined C–C–H bond angles, which approach 120°. This sp^2 hybridization is also manifested by the characteristic NMR spectroscopic values found for the methylene groups, as discussed in the next sections.

NMR Spectroscopic Properties of the Cp′M(NO)(CH_2Ar)Cl Complexes. An examination of the ^1H NMR spectroscopic data (Table II) reveals that all the new benzyl chloro complexes exhibit a set of methylene resonances with similar chemical shifts and $^2J_{HH}$ coupling constants. This similarity indicates that all the Cp′M(NO)(CH_2Ar)Cl compounds are basically isostructural in solution. The chemical shifts of the η^2-benzyl methylene proton signals are located at a lower field than seen for the methylene protons in the related η^1-alkyl complexes studied previously.[1,4] This observation is consistent with the methylene group being more alkenyl in character in the η^2-bonding mode of the benzyl ligand.

The low-temperature ^1H NMR spectrum of CpW(NO)(CH_2Ph)$_2$ exhibits two sets of AB doublets corresponding to the methylene protons of each type of benzyl ligand.[1] The low-field methylene proton signals (δ 3.2, 2.7; $^2J_{HH}$ = 5 Hz) can be assigned to the methylene protons of an η^2-benzyl ligand of the CpW(NO)(η^2-CH_2Ph)(η^1-CH_2Ph) species by virtue of their similarity to the related signals displayed by CpW(NO)(η^2-CH_2Ph)Cl. The pair of high-field AB doublets (δ 1.4, –0.7; $^2J_{HH}$ = 10 Hz) can then be assigned to the η^1-benzyl methylene protons of CpW(NO)(η^2-CH_2Ph)(η^1-CH_2Ph).

A closer examination of the observed methylene $^2J_{HH}$ coupling constants provides further confirmation of the electronic nature of the η^2-benzyl group in all the Cp′M(NO)(CH_2Ar)Cl complexes. This geminal $^2J_{HH}$ coupling constant (i.e., 4–7 Hz) is smaller than observed previously (i.e., 8–12 Hz) for the diastereotopic methylene protons of the 16-electron bis(alkyl) complexes CpM(NO)R_2[4] or for the η^1-benzyl ligands in the low-temperature ^1H NMR spectra of the Cp′M(NO)(CH_2Ph)$_2$ compounds.[1] This smaller coupling corresponds to the η^2-benzyl methylene carbon being predominantly sp^2 hybridized (cf. geminal H–H coupling constants of –3 to +2 Hz for C=CH_2 groups)[46] rather than sp^3 hybridized (cf. geminal H–H coupling constants of 12–15 Hz for R′RCH_2 groups).[47] The similarity in the ^1H NMR parameters of the methylene groups indicates that all the Cp′M(NO)(CH_2Ar)Cl complexes possess structurally similar η^2-benzyl–metal linkages.

The assignments of the ^1H and $^{13}C\{^1H\}$ NMR signals for the η^2-benzyl ligands in the aromatic region are straightforward, particularly for the tungsten-containing complexes. At ambient temperatures, the Cp′W(NO)(CH_2Ar)Cl compounds exhibit ^1H NMR signals for the aromatic ring protons indicative of a symmetrically disposed benzyl ligand. This apparent symmetry is also reflected in the observation of only four ring-carbon resonances in their $^{13}C\{^1H\}$ NMR spectra (Table II). This feature is somewhat surprising since, despite the symmetric η^2-benzyl–tungsten interactions, the tungsten centers are asymmetric and should result in two different ortho and two different meta aromatic proton signals.

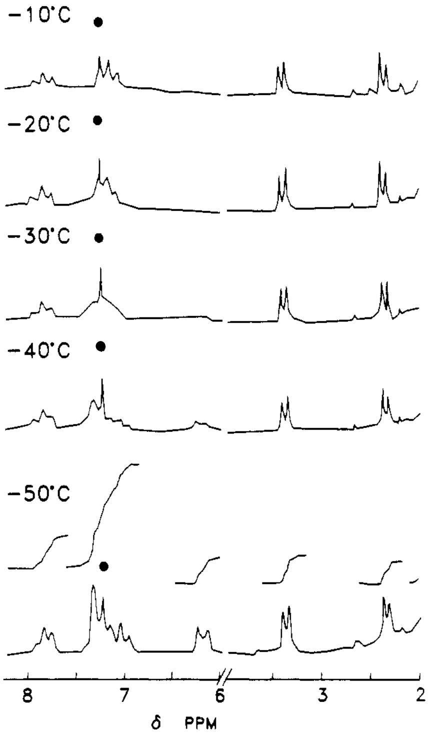

Figure 3. Variable-temperature 80-MHz ^1H NMR spectra of Cp*Mo(NO)(CH_2Ph)Cl in $CDCl_3$ (●).

Although basically similar to the spectra exhibited by their tungsten congeners, the molybdenum complexes display a unique feature, namely a broad singlet for the ortho proton signals (Table II). This broadening effect is also evident in the $^{13}C\{^1H\}$ spectra in which the signals due to the ortho carbon atoms of the Mo complexes have noticeably wider line shapes. Qualitatively similar features are also evident in the spectra of the Mo and W congeners of the Cp*M(NO)(*p*-Xyl)Cl complexes. These observations are indicative of the molybdenum complexes being stereochemically nonrigid, a conclusion that has been substantiated by a variable-temperature ^1H NMR study of Cp*Mo(NO)(CH_2Ph)Cl (the results of which are summarized in Figure 3). As the sample is cooled from room temperature, the aromatic signals first broaden to featureless humps and then begin to sharpen. The signal for the para proton (δ 7.51) does not change significantly. However, the broad signal for the ortho protons in the room-temperature spectrum (δ 6.75) splits into two signals (δ 6.18, 7.30) at –50 °C. These two signals are displaced from the original position of the ortho resonance in equal, but opposite, amounts. A similar change occurs for the meta proton signals (25 °C, δ 7.17; –50 °C, δ 7.07, 7.25). The low-field signals for the ortho and meta protons overlap and are difficult to distinguish, but the higher field signals for both types of protons are unobscured. The observation of broadening for only the ortho proton signals of the Cp′Mo(NO)(CH_2Ar)Cl complexes at room temperature can be explained on the basis of these data. In the ^1H NMR spectrum of Cp*Mo(NO)(CH_2Ph)Cl obtained at –50 °C, the observed difference in chemical shifts ($\Delta\delta$) for the two types of ortho protons is large (>1 ppm) in comparison with the difference in the two meta proton signals (0.17 ppm). Since the temperature of coalescence, T_c, is proportional to $\Delta\delta$, the ortho proton signals coalesce at a much higher temperature than do the meta proton signals. It is probable that a similar fluxional process is operative for the tungsten-containing complexes but that it occurs at faster rates. Such fluxionality would explain the apparently symmetric benzyl environments in these com-

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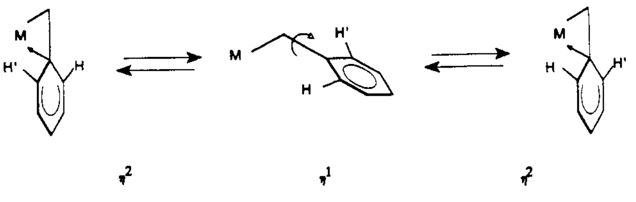
(46) Becker, E. D. *High Resolution NMR, Theory and Chemical Applications*, 2nd ed.; Academic Press: New York, 1980; p 96.

(47) Reference 46, p 95.

plexes and would account for the fact that there is no appreciable broadening of the signals due to the ortho groups in the benzyl ligands.

A fluxional process that would explain the symmetric aromatic environment involves a hapticity change of the benzyl ligand followed by a rotation of the phenyl group.



There is precedent for such a mechanism, a similar fluxionality having been invoked to account for the dynamic NMR behavior of $CpM(CO)_2(\eta^3$-benzyl) (M = Mo or W) complexes.[48] In the carbonyl cases, however, this nonrigidity involves an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ process. Other significant observations concerning the fluxionality of the η^2-benzyl complexes include the following:

(a) There is no observable change in the chemical shift or the coupling constants for the methylene group signals in the variable-temperature ^{1}H NMR spectra of Cp*Mo(NO)(η^2-benzyl)Cl recorded between −50 and +25 °C.

(b) The room-temperature $^{13}C\{^1H\}$ NMR spectra of the new benzyl chloro complexes establish a chemical shift range of 110–113 ppm for the C_{ipso} signals of the fluxional η^2-benzyl ligands. This range corresponds closely with the range of 110–120 ppm found for the η^2-benzyl ligands in low-temperature $^{13}C\{^1H\}$ NMR spectra exhibited by $Cp'M(NO)(CH_2Ph)_2$ complexes and the chemical shift of 113.8 ppm for C_{ipso} found for the η^2-benzyl ligand in the solid-state CP-MAS $^{13}C\{^1H\}$ NMR spectrum of $CpMo(NO)(CH_2Ph)_2$.[1]

(c) The $^1J_{CH}$ (147–151 Hz) and $^2J_{HH}$ (4–7 Hz) ranges for the methylene groups of the benzyl chloro complexes are comparable to those found for the η^2-benzyl ligands ($^1J_{CH}$ = 148–152 Hz; $^2J_{HH}$ = 4–6 Hz) in the low-temperature NMR spectra of $Cp'M(NO)(CH_2Ph)_2$ (M = Mo or W) complexes.[1]

These observations indicate that if the above fluxional mechanism is indeed operative for the η^2-benzyl complexes, the η^1 species (a high-energy intermediate) must be present in very low concentrations[49] since any appreciable amount of this intermediate would cause a shift in the above parameters to values consistent with more η^1-character, i.e. larger C_{ipso} chemical shifts and smaller $^1J_{CH}$ and larger $^2J_{HH}$ values. In addition, there would also be a noticeable temperature dependence of the chemical shifts of the ^{1}H NMR signals due to the methylene protons if the concentration of the η^1 species were significant.[49]

NMR Spectroscopic Properties of the Cp′M(NO)(CH$_2$Ar)R Complexes. Even a cursory examination of the ^{1}H and $^{13}C\{^1H\}$ NMR data of the alkyl benzyl complexes (summarized in Table III) reveals that their benzyl ligands are very similar to those in the corresponding benzyl chloro precursor complexes. The proton–proton coupling constants ($^2J_{HH}$ = 4–7 Hz) for the methylene group and the chemical shifts for the C_{ipso} signal (111–115 ppm) are again diagnostic for an η^2-benzyl–metal link. This similarity is not unexpected, given the close correlation between the solid-state molecular structures of $Cp^*Mo(NO)(CH_2Ph)Cl$ and $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ (vide supra), and again indicates that the ancillary chloro and alkyl ligands have little effect on the metal-benzyl interactions. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the complexes again display symmetric environments for the benzyl ligands and a broadening of the ortho signals for the $CpMo(NO)(CH_2Ph)(CH_2SiMe_3)$ complex. Interestingly, the ^{1}H NMR spectrum of $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ shows no broadening of the ortho proton signals as do the $Cp'Mo(NO)(CH_2Ar)(Cl)$ and $CpMo(NO)(CH_2Ph)(CH_2SiMe_3)$ species. However, in the $^{13}C\{^1H\}$ NMR spectrum of $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ the signals for the ortho aromatic ring carbons do exhibit a noticeable, albeit slight, broadening. A similar situation exists for the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of Cp*Mo(NO)(p-Xyl)(Npt).[17] The ^{1}H NMR spectra of these Cp*Mo-containing complexes show no broadening of the ortho proton signals probably because the rate of fluxionality in these complexes has increased to the point where T_c has become lower than ambient temperature for the ortho proton signals. Since the chemical shift differences (Hz) are much larger for ^{13}C NMR signals than for ^{1}H NMR signals, the T_c values are proportionately higher (vide supra) for the ^{13}C NMR spectra and some broadening is seen. This observation verifies that the T_c values for the fluxionality of these complexes are near room temperature and can vary from one metal-containing complex to another. The T_c for the tungsten complexes is again sufficiently below ambient temperature so that no noticeable broadening of signals occurs.

One final point merits some discussion, namely that there are intriguing ^{1}H NMR chemical shifts for the methylene proton signals of the CH_2SiMe_3 and Npt groups[17] in the benzyl alkyl complexes. Since these CH_2 protons are diastereotopic, they exhibit two different ^{1}H NMR signals and are coupled to one another. However, the observed chemical shifts for the higher field methylene proton in the $Cp'M(NO)(CH_2Ph)(CH_2SiMe_3)$ complexes (δ −3.7 to −4.5) and the Cp*M(NO)(p-Xyl)(Npt) complexes (δ −2.5 to −2.9) are quite unexpected, given the chemical shifts for similar protons exhibited by the previously prepared bis(alkyl) complexes.[3,4] The solid-state molecular structure of $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ provides a clue as to the source of this distinctive chemical shift. The significant shielding of one of the methylene proton signals is simply a manifestation of this proton lying directly over the ring of the benzyl group (vide supra), therefore experiencing a net shielding effect due to the remaining aromatic ring current. The 3.3 ppm upfield shift of the signal in $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ (δ −4.49) from the location of the highest field proton signal in $Cp^*Mo(NO)(CH_2SiMe_3)_2$ (δ −1.17) agrees very well with the theoretically calculated shielding of 3 ppm for a proton situated in such a position over a benzene ring.[50] This good correlation indicates that the molecular structure that exists in solution for $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ is very similar to its solid-state molecular structure. Furthermore, the observation of similar ring current effects for the methylene protons in all the $Cp'M(NO)(CH_2Ar)R$ (R = CH_2SiMe_3 or Npt) complexes is evidence that all these complexes possess a similar molecular geometry in solution and that this geometry corresponds to the solid-state intramolecular dimensions of $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$. The magnitude of this ring-current effect implies that the proximity of the methylene proton and the benzyl ring does not significantly change during the fluxionality of the benzyl ligand in solution. Again,

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[48] Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339.

[49] For an excellent discussion of these issues, see: (a) Brookhart, M.; Buck, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 559. (b) Brookhart, M.; Buck, R. C.; Danielson, E. *J. Am. Chem. Soc.* **1989**, *111*, 567.

[50] Reference 46, p 74.

this is further evidence for only a very small concentration of the η^1-intermediate species during the fluxional processes; otherwise, it would reduce substantially this ring-current effect.

Epilogue

The most interesting result to emanate from this study is the isolation of the desired mixed bis(alkyl) complexes. They do not appear to be particularly unstable in any manner, nor do they show any propensity to undergo disproportionation to symmetric bis(alkyl) complexes. Hence, it can be concluded that the previous attempts to synthesize complexes such as $CpW(NO)(CH_2Ph)(CH_2SiMe_3)$ must have failed due to the synthetic route chosen to prepare them rather than because of the inherent instability of the products. The other bis(alkyl) complexes prepared previously in this research group exhibit a marked reduction in their thermal stability when the metal is changed from tungsten to molybdenum. However, the benzyl-containing compounds are uniformly stable regardless of the metal center involved. This last observation is in accord with the view that it is the extra electron density donated from the benzyl ligand that permits the metal center to attain the favored 18-valence-electron configuration that is the preeminent factor in determining the relative stability of these complexes.

Given the existence of these complexes, it is hoped that a wider ranging investigation of the remarkable transformations observed for the $CpW(NO)(CH_2SiMe_3)_2$ complex[4] can now be extended to encompass these benzyl complexes. For instance, since these new complexes allow variation in their alkyl groups in a systematic manner, this feature could be utilized to probe relative alkyl ligand reactivities. The $Cp'M(NO)(CH_2Ar)X$ species also contain a chiral metal center since the four different ligands are arrayed in a pseudotetrahedral manner about the metal center. Therefore, as well as being possible starting materials for futher reactivity studies, these complexes hold out the promise that detailed mechanistic investigations of any transformations observed could be carried out on their optically active forms. Such reactivity studies are currently in progress.

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Supplementary Material Available: Tables of final anisotropic thermal parameters, bond lengths involving hydrogen atoms, bond angles involving hydrogen atoms, and torsion angles for $Cp^*Mo(NO)(CH_2Ph)Cl$ and $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ (10 pages); listings of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Solution Calorimetric, Equilibrium, and Synthetic Studies of Oxidative Addition/Reductive Elimination of C_5R_5H (R = H, Me, Indenyl) to/from the Complexes $M(CO)_3(RCN)_3/(\eta^5\text{-}C_5R_5)M(CO)_3H$ (M = Cr, Mo, W)

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Equilibrium data are reported for the reaction $CpMo(CO)_3H + 3MeCN \rightleftharpoons Mo(CO)_3(MeCN)_3 + CpH$. Over the temperature range 43–82 °C, $\Delta H = -11.2$ kcal/mol, $\Delta S = -51.3$ cal/(mol °C). Calorimetric data for the enthalpies of displacement of C_5R_5H by nitriles are reported: Cr, R = Me, -0.7 ± 0.7 kcal/mol, M = W, R = H, -5.6 ± 0.7, R = Me, -5.4 ± 0.7 kcal/mol. The enthalpy of reaction of $Na^+(\text{indenyl})^-$ with (p-xylene)$Mo(CO)_3$ forming $Na^+Mo(CO)_3(\text{indenyl})^-$ is -17.3 ± 0.2 kcal/mol, approximately 10 kcal/mol less than the corresponding reaction of $Na^+C_5H_5^-$. The heat of reaction of (indenyl)$W(CO)_3H$ with EtCN forming $W(CO)_3(EtCN)_3$, -20.0 ± 0.8 kcal/mol, is approximately 14 kcal/mol more exothermic than the corresponding reaction of the cyclopentadienyl complex, also in keeping with a reduced M–indenyl ground-state bond energy. Synthetic strategies to the $(C_5R_5)M(CO)_3H$ complexes are summarized.

Introduction

The complexes $CpM(CO)_3H$ (M = Cr, Mo, W) have been widely studied in the 35 years since their discovery by E. O. Fischer.[1] While reports on the unsubstituted cyclopentadienyl hydrides are well-known, data on the substituted complexes are scattered throughout the literature. King and Fronzaglia[2] reported the preparation of $Cp^*W(CO)_3H$ according to eq 1 in 1966. This was one of the

$$W(CO)_3(NCR)_3 + Cp^*H \rightarrow Cp^*W(CO)_3H + 3RCN \quad (1)$$

first Cp* complexes to be synthesized but has been vir-

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(1) Fischer, E. O.; Hafner, W.; Stahl, H. O. *Z. Anorg. Allg. Chem.* **1955**, *282*, 47.

(2) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

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