Synthesis, characterization, and properties of some cyclopentadienyl molybdenum nitrosyl benzyl complexes

Peter Legzdins, Kevin M. Smith, and Steven J. Rettig

Abstract: Reaction of $CpMo(NO)(CH_2Ph)Cl$ with Me_2Mg, Ph_2Mg, or PhCCLi reagents in THF affords the corresponding alkyl, aryl, or alkynyl $CpMo(NO)(CH_2Ph)R$ (R = hydrocarbyl) complexes as orange powders in good yields. Unlike related 16-electron $CpMo(NO)R_2$ complexes, these 18-electron species exhibit good thermal stability due to their η^2-benzyl-Mo interactions. Treatment of $CpMo(NO)(CH_2Ph)Cl$ with Na(DME)Cp provides dark green $Cp_2Mo(NO)(CH_2Ph)$, whose solid-state molecular structure has been established by a single-crystal X-ray crystallographic analysis. The two Cp rings display different binding modes to the Mo atom, while the benzyl ligand is coordinated to the metal centre in an η^1 fashion. The triflate complex, $CpMo(NO)(CH_2Ph)(OTf)$, is obtained by addition of AgOTf to the benzyl chloride precursor. The covalent Mo—OTf bond in this compound can be disrupted by the addition of Lewis bases (L) such as PPh_3 or pyridine, leading to the corresponding $[CpMo(NO)(CH_2Ph)(L)][OTf]$ salts. Attempts to generate neutral benzylidene complexes by deprotonation of $[CpMo(NO)(CH_2Ph)(PPh_3)][OTf]$ have not yet been successful.

Key words: nitrosyl, molybdenum, benzyl, hydrocarbyl, triflate.

Résumé : La réaction du $CpMo(NO)(CH_2Ph)Cl$ avec les réactifs Me_2Mg, Ph_2Mg et PhCCLi dans le THF conduit aux complexes alkyles, aryles ou alkynyles correspondants, $CpMo(NO)(CH_2Ph)R$ (R = hydrocarbyle), des poudres oranges obtenues avec des bons rendements. Contrairement à ce qui se produit avec les complexes à seize électrons du type $CpMo(NO)R_2$, ces espèces à dix-huit électrons présentent une bonne stabilité thermique en raison de leurs interactions η^2-benzyl-Mo. Le traitement du $CpMo(NO)(CH_2Ph)Cl$ par du Na(DME)Cp conduit au $Cp_2Mo(NO)(CH_2Ph)$ vert foncé dont on a déterminé la structure moléculaire à l'état solide par une analyse cristallographique réalisée par diffraction des rayons X par un cristal unique. Les deux noyaux Cp présentent des modes de liaison avec le Mo qui sont différents alors que le ligand benzyle est coordiné au centre métallique de façon η^1. On a obtenu le complexe au triflate, $CpMo(NO)(CH_2Ph)(OTf)$ en additionnant du AgOTf au précurseur avec du chlorure de benzyle. La liaison covalente Mo—OTf de ce composé peut être perturbée par l'addition de bases de Lewis (L), telles que la PPh_3 ou la pyridine, qui conduisent à la formation des sels $[CpMo(NO)(CH_2Ph)(L)][OTf]$ correspondants. Les essais effectués en vue de générer des complexes benzylidènes neutres par déprotonation de $[CpMo(NO)(CH_2Ph)(PPh_3)][OTf]$ se sont avérés infructueux jusqu'à maintenant.

Mots clés : nitrosyle, molybdène, benzyle, hydrocarbyle, triflate.

Introduction

We (1) recently reported the intermolecular C—H bond activation of alkane substrates by thermolysis of the 16-electron (16e) bis(hydrocarbyl) complexes, $Cp^*W(NO)(CH_2CMe_3)_2$ and $Cp^*W(NO)(CH_2CMe_3)(CH_2Ph)$. Labeling and kinetic studies established that these reactions proceed via initial elimination of CMe_4 to form the unsaturated alkylidene complexes, $Cp^*W(NO)(=CHCMe_3)$ and $Cp^*W(NO)(=CHPh)$, respectively. However, the generation of these reactive alkylidene species requires reaction temperatures in the range of 70–80°C, and little control can be exerted on the steps following the initial, rate-determining α-hydrogen abstraction step. This practical limitation could be avoided by either lowering the activation barrier of the neopentane elimination process or by finding an alternative route to the reactive alkylidene compounds.

Previous studies in these laboratories have demonstrated that the related $CpMo(NO)(=CHCMe_3)$ fragment is readily produced by the *room temperature* transformation of the 16e $CpMo(NO)(CH_2CMe_3)_2$ compound (2), or by the facile loss of pyridine (py) from the 18e adduct $CpMo(NO)(=CHCMe_3)(py)$ (3). Like the Cp*W analogues, $CpMo(NO)(=CHCMe_3)$ can also activate element—hydrogen bonds. Thus, isolable $CpMo(NO)(CH_2CMe_3)(ER)$ complexes are obtained when the ER group can act as a π-donor

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This paper is dedicated to Professor Brian R. James on the occasion of his 65th birthday.

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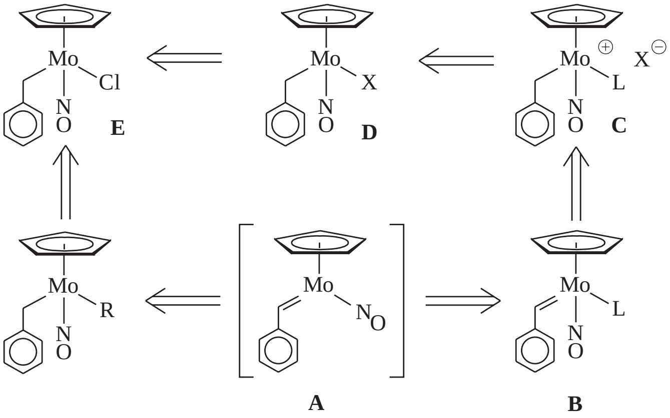
ligand (e.g., HER = HOPh, H_2NCMe_3, $HSCMe_3$), thereby resulting in 18e products (3). However, stable $CpMo(NO)(CH_2CMe_3)R$ compounds resulting from activation of hydrocarbon RH substrates have not yet been observed, and this may well be a manifestation of the marked thermal instability of 16e $CpMo(NO)(R)_2$ complexes. For instance, diaryl species can be observed in situ when $[CpMo(NO)Cl_2]_2$ is treated with $(aryl)_2Mg$ reagents at low temperature, but these 16e complexes decompose at ambient temperatures even in the presence of trapping agents (4). The differing reactivities of Mo and W cyclopentadienyl nitrosyl alkyl complexes have recently been analyzed using density functional theoretical techniques (5).

The current study was undertaken with a view to developing a non-thermolytic route to an electronically unsaturated alkylidene species, specifically the benzylidene fragment [CpMo(NO)(=CHPh)] (**A**). As shown in the retrosynthetic strategy outlined below in Scheme 1, the reactive 16e species **A** should be accessible by loss of a labile, neutral ligand L from the 18e CpMo(NO)(=CHPh)(L) complex (**B**). The neutral benzylidene compound could be formed by deprotonation of the cationic complex $[CpMo(NO)(CH_2Ph)(L)]^+$ (**C**). The cationic complex could, in principle, be synthesized by nucleophilic displacement of a weakly bound anionic ligand X from $CpMo(NO)(CH_2Ph)(X)$ (**D**), which in turn would be derived by salt metathesis from the known $CpMo(NO)(CH_2Ph)(Cl)$ compound (**E**) (6).

Scheme 1.



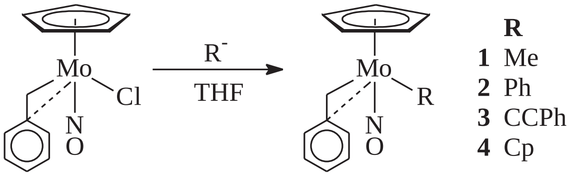
Benzyl chloro complex **E** also provides a metathetical route to the benzyl hydrocarbyl complexes expected to result from the C—H bond activation of RH substrates by the [CpMo(NO)(=CHPh)] target species. Indeed, the prototypal complex, $CpMo(NO)(CH_2Ph)(CH_2SiMe_3)$, has previously been synthesized using just this methodology (6). The independent synthesis of additional $CpMo(NO)(CH_2Ph)R$ compounds was thus undertaken to assess their thermal stability and to establish their diagnostic spectroscopic properties. It was anticipated that these alkyl complexes, as well as compounds **C** and **D**, might well be stabilized as 18e species by the η^2-benzyl-metal interactions characteristic of other $Cp'M(NO)(CH_2Ph)(X)$ complexes (Cp′ = Cp or Cp*, M = Mo or W) (6, 7), some of which are analogues of those depicted above in Scheme 1.

This paper describes the synthesis of several $CpMo(NO)(CH_2Ph)R$ compounds by salt metathesis and outlines their spectroscopic and physical properties. The solid-state molecular structure of one of these compounds, namely $Cp_2Mo(NO)(CH_2Ph)$, as determined by X-ray crystallography is described. The synthesis and characterization of CpMo(NO)(CH$_2$Ph)(OTf), (OTf = triflate, OSO_2CF_3) and $[CpMo(NO)(CH_2Ph)(L)]^+[OTf]^-$, corresponding to target molecules **D** and **C** in Scheme 1, respectively, are also presented. Finally, the various attempts to generate alkylidene complexes from these precursors are summarized.

Results and discussion

Direct synthesis of $CpMo(NO)(CH_2Ph)R$ complexes

[1]



As shown in eq. [1] above, $CpMo(NO)(CH_2Ph)Cl$ is a useful precursor to a range of $CpMo(NO)(CH_2Ph)R$ complexes, where R is methyl **1**, phenyl **2**, phenylalkynyl **3**, or cyclopentadienyl **4**. The metathesis reactions proceed cleanly in THF as determined by monitoring the change in ν (NO) during the course of the reaction by solution IR spectroscopy. The conversions can be accomplished using a diverse range of hydrocarbylating reagents, including organolithium and organosodium species as well as the more typical organomagnesium reagents. Analytically pure, crystalline samples of the $CpMo(NO)(CH_2Ph)R$ complexes may be obtained by chromatography of the crude products on Alumina I using toluene as eluant, followed by recrystallization from toluene:hexanes solvent mixtures. The colour, yield, and elemental analysis data for the new compounds are listed in Table 1. Their IR and mass spectral data are collected in Table 2, and Table 3 contains their ^1H and ^{13}C NMR data.

The replacement of the electronegative Cl ligand with more covalently bound hydrocarbyl groups has the expected effect on the electron density at the metal centres. This is indicated by the ν(NO) bands in the Nujol mull IR spectra of the $CpMo(NO)(CH_2Ph)R$ compounds which are from 14 to 44 cm^{-1} lower in energy than the 1620 cm^{-1} value exhibited by $CpMo(NO)(CH_2Ph)Cl$ (6). The magnitude of this decrease in ν (NO) follows the trend $C\equiv CPh < Cp \sim Ph \sim CH_2Ph < CH_2SiMe_3 \sim Me$, which is consistent with the electron-donating abilities of these hydrocarbyl ligands. The IR spectrum of **3** also displays a ν(C≡C) band at 2091 cm^{-1} (8).

In their ^1H NMR (C_6D_6) spectra, the C_5H_5 signals of compounds **1**–**4** lie in the 4.80–5.20 ppm region and are diagnostic indicators of these complexes. Also useful is the signal at –0.88 ppm characteristic of a Me ligand in the ^1H NMR (C_6D_6) spectrum of **1**. The ^{13}C NMR spectra of complexes **1**–**3** are important chiefly for the ipso carbon signals of the CH_2Ph ligands which fall in the 110–113 ppm range indicative of η^2-benzyl-molybdenum interactions (6, 7). In contrast, complex **4** does not appear to possess a η^2-benzyl ligand according to its ^1H and ^{13}C NMR spectra. The benzyl methylene ^1H NMR signal appears as a singlet at room

Table 1. Numbering scheme, colour, yield, and elemental analysis data for the new complexes.

			Anal. found (calcd.)		
Complex	Cmpd no.	Colour (yield, %)[a]	C	H	N
$CpMo(NO)(CH_2Ph)(CH_3)$	**1**	orange (63)	52.67 (52.54)	5.11 (5.09)	4.78 (4.71)
$CpMo(NO)(CH_2Ph)(Ph)$	**2**	orange (72)	60.03 (60.18)	4.75 (4.77)	3.89 (3.90)
$CpMo(NO)(CH_2Ph)(C\equiv CPh)$	**3**	orange (68)	62.73 (62.67)	4.45 (4.47)	3.66 (3.65)
$Cp_2Mo(NO)(CH_2Ph)$	**4**	dark green (65)	58.29 (58.80)	4.84 (4.93)	3.91 (4.03)
$CpMo(NO)(CH_2Ph)(OTf)$	**5**	orange (83)	36.35 (36.21)	2.81 (2.80)	3.16 (3.25)
$[CpMo(NO)(CH_2Ph)(PPh_3)][OTf]$	**6**	yellow (79)	53.31 (53.69)	3.95 (3.92)	1.89 (2.02)
$[CpMo(NO)(CH_2Ph)(py)][OTf]$	**7**	yellow (82)	42.51 (42.36)	3.29 (3.36)	5.22 (5.49)

[a] Yield calculated from crude isolated product.

Table 2. Infrared ν(NO) and mass spectral data for the new complexes.

		IR (ν(NO) cm^{-1})		FAB-MS (*m*/*z*)
Complex	Cmpd no.	Nujol	CH_2Cl_2	P+
$CpMo(NO)(CH_2Ph)(CH_3)$	**1**	1576	1591	299
$CpMo(NO)(CH_2Ph)(Ph)$	**2**	1592	1603	361
$CpMo(NO)(CH_2Ph)(C\equiv CPh)$	**3**	1604	1620	385
$Cp_2Mo(NO)(CH_2Ph)$	**4**	1592	1607	349
$CpMo(NO)(CH_2Ph)(OTf)$	**5**	1654	1657	284
$[CpMo(NO)(CH_2Ph)(PPh_3)][OTf]$	**6**	1655	1655	546

temperature, and the ipso carbon signal occurs at 152.3 ppm in the ^{13}C NMR spectrum of **4**. There is also only a single ^1H NMR peak for the two Cp ligands at room temperature. Consequently, a single-crystal X-ray crystallographic analysis of **4** was undertaken to establish definitively its solid-state molecular structure. The results of this analysis are discussed in the next section.

Solid-state molecular structure of $Cp_2Mo(NO)(CH_2Ph)$

The nature of the Cp—Mo bonds in $Cp_2Mo(NO)X$ complexes has been the subject of debate since their initial synthesis over 30 years ago (9, 10). If these compounds possessed two η^5-Cp groups and a linear nitrosyl ligand, they would have a formal valence electron count of 20 (11*e*). Early suggestions that this unfavourable situation might be avoided by the complexes adopting an asymmetric η^5-Cp/η^3-Cp binding mode (11*a*, *b*) were *not* supported by subsequent X-ray crystallographic studies. The solid-state molecular structures of $Cp_2Mo(NO)(\eta^1\text{-Cp})$ (11*c*), $Cp_2Mo(NO)(CH_3)$ (11*d*), and $Cp^*(Cp)Mo(NO)(CH_3)$ (11*f*) all exhibit linear Mo-N-O angles (>172°) and essentially planar but skewed Cp′ groups with all 10 multihapto ring C atoms lying within bonding distance of the Mo centres. This observation contrasts with the situation in $Cp_2W(CO)_2$ which possesses distinct η^5-Cp and η^3-Cp ligands (12). The η^3-Cp group contains a localized C—C double bond, with the two unique C atoms bent 20° away from the plane containing the three Cs bound to the W centre. Calhorda and co-workers (13) have recently investigated via DFT calculations the phenomenon of ring slippage in Cp_2MoL_2 species and related Cp and indenyl complexes of Mo(II).

The solid-state molecular structure of $Cp_2Mo(NO)(CH_2Ph)$ **4** (Fig. 1) exhibits features intermediate between those displayed by $Cp_2W(CO)_2$ and the previously reported $Cp_2Mo(NO)R$ structures. All 10 Cp carbons in **4** are within 2.336–2.700 Å (avg = 2.475 Å) of the Mo centre, and the

Fig. 1. The solid-state molecular structure of $Cp_2Mo(NO)(CH_2Ph)$ (**4**); 50% probability thermal ellipsoids are shown.

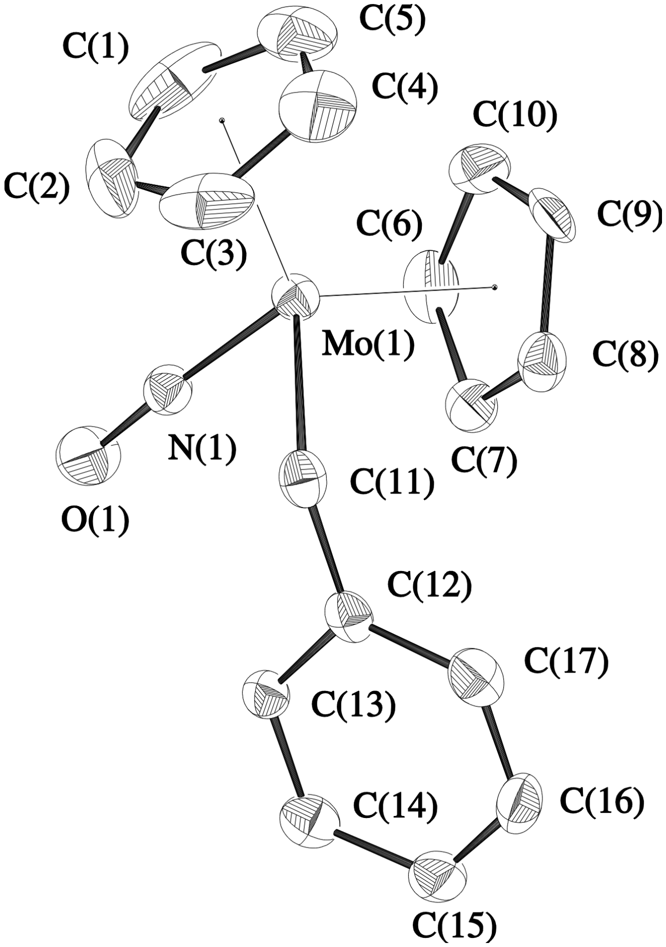


Table 3. ^{1}H and ^{13}C NMR data for the new complexes.

Compound (solvent)	^{1}H NMR (δ)[a]	^{13}C NMR (δ)
1	7.5–6.8 (m, 5H, Ph)	131.0–127.5 (Ph)
(C_6D_6)	4.99 (s, 5H, C_5H_5)	112.2 (*C* ipso)
	3.19 (d, 1H C*H*H)	99.3 ($C_5\mathrm{H}_5$)
	2.21 (d, 1H, CH*H*)	37.8 ($C\mathrm{H}_2$)
	–0.88 (s, 3H, CH_3)	1.34 ($C\mathrm{H}_3$)
2	7.2–6.4 (m, 10H, Ph)	196.9 (*C* ipso Ph)
(C_6D_6)	5.04 (s, 5H, C_5H_5)	140.4–124.2 (Ph)
	3.12 (d, 1H C*H*H)	112.1 (*C* ipso Bz)
	2.83 (d, 1H, CH*H*)	100.1 ($C_5\mathrm{H}_5$)
		40.1 ($C\mathrm{H}_2$)
3	7.6–7.0 (m, 10H, Ph)	136.1–131.4 (Ph)
(C_6D_6)	5.13 (s, 5H, C_5H_5)	112.7 (*C* ipso Bz)
	3.19 (d, 1H C*H*H)	108.8 ($C{\equiv}\mathrm{C}$)
	2.66 (d, 1H, CH*H*)	106.1 ($C_5\mathrm{H}_5$)
		42.8 ($\mathrm{C}H_2$)
4	7.6–7.0 (m, 5H, Ph)	152.3 (*C* ipso Bz)
(C_6D_6)	5.17 (s, 10H, C_5H_5)	128.0, 127.7, 123.8 (*C* Ph)
	3.45 (s, 2H $\mathrm{C}H_2$)	109.0 ($C_5\mathrm{H}_5$)
		25.1 ($\mathrm{C}H_2$)
5	7.5–6.8 (m, 5H, Ph)	137.2–127.7 (Ph)
(C_6D_6)	5.04 (s, 5H, C_5H_5)	112.4 (*C* ipso)
	3.12 (d, 1H C*H*H)	102.7 ($C_5\mathrm{H}_5$)
	2.83 (d, 1H, CH*H*)	50.5 ($C\mathrm{H}_2$)
6	7.8–6.5 (m, 20H, Ph)	136.3–126.8 (Ph)
(CD_3NO_2)	5.78 (s, 5H, C_5H_5)	110.1 (*C* ipso)
	3.92 (d, 1H C*H*H)	103.1 ($C_5\mathrm{H}_5$)
	3.63 (d, 1H, CH*H*)	44.7 ($C\mathrm{H}_2$)
7	7.9–7.0 (m, 10H, Ph, NC_5H_5)	156.1–127.8 (Ph, $\mathrm{N}C_5\mathrm{H}_5$)
(CD_3NO_2)	6.18 (s, 5H, C_5H_5)	112.7 (*C* ipso)
	3.95 (d, 1H C*H*H)	104.9 ($C_5\mathrm{H}_5$)
	3.78 (d, 1H, CH*H*)	50.2 ($C\mathrm{H}_2$)

[a] The H—H coupling constants of the diastereotopic benzyl hydrogens, while not specifically measured, appear to be in the normal 4.5–7.0 Hz range expected for these complexes (6).

difference between the two Cp groups is not as marked as in the $Cp_2W(CO)_2$ structure. However, the C(1)-C(5) ring exhibits characteristics more typical of an η^3-Cp ligand than previously observed for any other structurally characterized $Cp_2Mo(NO)R$ species. The C(4) and C(5) atoms are 2.700(3) and 2.667(3) Å away from the Mo atom, respectively, and the C(4)—C(5) bond length of 1.317(5) Å is significantly shorter than the other C—C distances in the ring (1.392(5)–1.407(5) Å, avg = 1.401 Å). The C(1)-C(2)-C(3)-C(4) and C(3)-C(2)-C(1)-C(5) torsion angles of 7.0(4)° and 8.0(4)°, respectively, are also reminiscent of, if less pronounced than, those found in $Cp_2W(CO)_2$. The crystallographic and experimental data for **4** are presented in Table 4. Table 5 lists the positional and thermal parameters of its constituent atoms, while selected bond lengths and angles are collected in Tables 6 and 7, respectively.

Stabilizing effects of η^2-CH_2Ph ligands

The coordinative and electronic saturation imparted by their η^2-benzyl ligands is deemed to be responsible for the thermal stability of compounds **1**–**3**. Of the known Cp′M(NO)R_2 (Cp′ = Cp, Cp*; M = Mo, W) complexes, the CpMo-containing species are the most Lewis acidic, the most prone to M—C bond hydrolysis, and the most thermally sensitive (14). The general fragility of the 16e CpMo(NO)R_2 species is in marked contrast to the robust 18e complexes shown below.

These latter compounds achieve a saturated electronic configuration via additional σ-donor ligation (15), lower oxidation state (9), or multihapto ancillary ligand bonding (11, 14). All of the species shown above are thermally stable at ambient temperature, and several are remarkably tolerant of air and (or) water. The range of hydrocarbyl ligands available to these 18e complexes extends to groups which are difficult to synthesize (e.g., Me, Ph) or entirely unknown

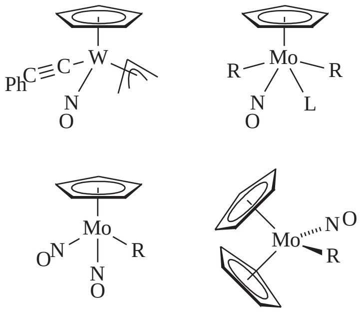


Table 4. Crystallographic and experimental data for $Cp_2Mo(NO)(CH_2Ph)$ (**4**).

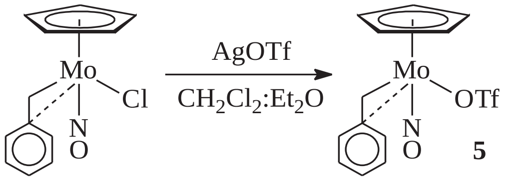
Colour	Green-black
Formula	$C_{17}H_{17}MoNO$
Formula weight	347.27
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	11.120(2)
b (Å)	15.2821(3)
c (Å)	16.8371(6)
V (Å^3)	2861.4(3)
Z	8
d_{calcd}(g cm^{-1})	1.612
F(000)	1408.00
μ (Mo Kα) (cm^{-1})	9.09
T (K)	180(1)
Crystal dimensions (mm^3)	0.50 × 0.40 × 0.10
Scan type	(ω and ϕ) 0.5°
2θ (max)(deg)	60.1
Total reflections	26 363
Unique reflections	3639
Reflections with $I \geq 3\sigma(I)$	2083
No. of variables	181
R_1 (on F, $I \geq 3\sigma(I)$)	0.030
R_2 (on F^2, all data)	0.021
Goodness of fit	1.53
Max Δ/σ (final cycle)	0.0003
Residual density (e Å^{-3})	–0.83 to 1.09

(e.g., Et, *i*-Bu, C≡CR, C_6F_5) for the 16e Cp′M(NO)(R)(R′) compounds.

Synthesis of [CpMo(NO)(CH$_2$Ph)(L)][OTf]

The stabilizing influence of the η^2-benzyl ligand is also of critical importance to the target molecule $CpMo(NO)(CH_2Ph)(OTf)$ **5** which can be synthesized in high yields as illustrated below in eq. [2].

[2]

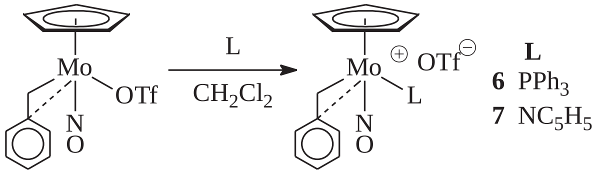


Silver salts have been previously utilized to abstract halide ligands from Cp′M(NO)$_x$-containing complexes. For instance, if the abstraction from $CpMo(NO)(CH_2Ph)Cl$ is performed using $AgBF_4$ in acetonitrile, NCMe-solvated organometallic cations can be isolated (16). Furthermore, treatment of Cp′M(NO)$_2$Cl with $AgBF_4$ in CH_2Cl_2 generates the reactive Cp′M(NO)$_2$(FBF$_3$) species (17) which have been used to synthesize lactones (17*b*) and pyrones (17*c*). Halide-abstraction reactions with AgO_2CR (R = 2-phenylbutyrate) (16e) or AgO_3SR (R = *p*-tolyl, camphor) (18) in CH_2Cl_2 afford neutral nitrosyl complexes with covalent M—O bonds.

As shown in eq. [2], the synthesis of **5** is best accomplished in a 1:1 solvent mixture of CH_2Cl_2 and Et_2O. The thermal stability of $CpMo(NO)(CH_2Ph)(OTf)$, which is isolable as a orange powder that can even be handled briefly in air without deleterious effects, can be contrasted with that of CpMo(NO)(η^3-(*Z*)-crotyl)(OTs) (which was not isolated, but was generated at low temperature and used in situ) (18*a*) and that of $Cp^*W(NO)(CH_2SiMe_3)(OTf)$ (which decomposes upon being generated in non-coordinating arene or chlorinated solvents).[4] The existence of a covalent Mo—OSO_2CF_3 bond in **5** is inferred from its solubility in poor ion-supporting solvents such as toluene, C_6D_6 and Et_2O, and by its IR spectrum (Nujol) (19). The highly electron-withdrawing nature of the OTf group in **5** is evidenced by the ν(NO) (Nujol) value of 1654 cm^{-1} which is much higher in energy than that exhibited by the hydrocarbyl products **1**–**4** or the benzyl chloride starting material.

As shown above in eq. [3], reaction of isolated or in situ generated $CpMo(NO)(CH_2Ph)(OTf)$ with PPh_3 or pyridine results in the formation of complexes **6** and **7**, respectively. As expected, these [CpMo(NO)(CH$_2$Ph)(L)][OTf] salts display decreased solubility as compared to the neutral complexes **1**–**5**. Thus, **6** and **7** are only moderately soluble even in THF, and dissolve readily only in good ion-supporting solvents such as CH_2Cl_2 and CH_3NO_2. As solids, **6** and **7** appear to be relatively inert with respect to O_2 and water, since the yellow powders may be handled briefly in air without noticeable decomposition. The decrease in the highest frequency ν(SO) band of the triflate group from 1321 cm^{-1} in the IR spectrum of **5** to ~1260 cm^{-1} in **6** and **7** is consistent with the displacement of the OTf group from the Mo centre (19). The ^{1}H and ^{13}C NMR spectra of **6** and **7** help demonstrate that only one L ligand is present in each molecule and that the η^2-benzyl-molybdenum interaction is preserved in each complex.

[3]



Attempted deprotonation of [CpMo(NO)(CH$_2$Ph)(PPh$_3$)][OTf]

In an attempt to form a benzylidene compound such as $CpMo(NO)(=CHPh)(PPh_3)$ or $[CpMo(NO)(=CHPh)]_2$, cationic complex **6** was treated with a variety of Brønsted bases (e.g., KO-*t*-Bu, LiN(SiMe$_3$)$_2$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), NEt$_3$, HN-*i*-Pr$_2$) in THF and CH_2Cl_2. In each case, monitoring of the reaction by solution IR spectroscopy revealed the complete consumption of starting material and the formation of a broad band at ~1600 cm^{-1}. However, ^{1}H NMR spectra of the crude reaction mixtures resulting from these reactions were devoid of signals characteristic of alkylidene Hs. None of the attempts to purify, chromatograph, crystallize, or precipitate the products from

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[4] P. Legzdins and S.F. Sayers. Unpublished results.

Table 5. Positional and thermal parameters, with esds in parentheses, for $Cp_2Mo(NO)(CH_2Ph)$ (**4**).

Atom	*x*	*y*	*z*	*B*(eq)
Mo(1)	0.08242(2)	0.174875(14)	0.10364(2)	1.677(5)
O(1)	0.2723(2)	0.04584(12)	0.06261(13)	3.26(6)
N(1)	0.1903(2)	0.09618(13)	0.07689(14)	1.91(6)
C(1)	0.0288(3)	0.2235(3)	–0.0257(2)	4.54(11)
C(2)	–0.0204(4)	0.1401(2)	–0.0150(3)	4.80(12)
C(3)	–0.1140(4)	0.1501(2)	0.0392(3)	4.26(11)
C(4)	–0.1299(3)	0.2401(2)	0.0532(2)	3.94(10)
C(5)	–0.0468(4)	0.2833(2)	0.0135(2)	3.82(10)
C(6)	0.2373(3)	0.2644(2)	0.1512(2)	2.64(8)
C(7)	0.1964(3)	0.2139(2)	0.2146(2)	2.23(7)
C(8)	0.0807(3)	0.2434(2)	0.2347(2)	2.25(7)
C(9)	0.0539(3)	0.3156(2)	0.1863(2)	2.35(7)
C(10)	0.1470(3)	0.3265(2)	0.1333(2)	2.71(7)
C(11)	–0.0068(3)	0.0705(2)	0.1781(2)	2.00(7)
C(12)	0.0635(3)	0.03364(15)	0.2457(2)	1.79(7)
C(13)	0.1632(3)	–0.0209(2)	0.2334(2)	1.93(7)
C(14)	0.2284(3)	–0.0541(2)	0.2959(2)	2.31(8)
C(15)	0.1970(3)	–0.0354(2)	0.3735(2)	2.47(8)
C(16)	0.0975(3)	0.0163(2)	0.3869(2)	2.66(7)
C(17)	0.0320(3)	0.0494(2)	0.3248(2)	2.45(8)

Table 6. Selected bond lengths (Å) for $Cp_2Mo(NO)(CH_2Ph)$ (**4**).[a]

Bond lengths (Å)			
Mo(1)—CP(1)	2.23	Mo(1)—CP(2)	2.12
Mo(1)—N(1)	1.757(2)	C(2)—C(3)	1.392(5)
Mo(1)—C(1)	2.377(4)	C(3)—C(4)	1.407(5)
Mo(1)—C(2)	2.362(4)	C(4)—C(5)	1.317(5)
Mo(1)—C(3)	2.469(3)	C(6)—C(7)	1.394(4)
Mo(1)—C(4)	2.700(3)	C(6)—C(10)	1.414(4)
Mo(1)—C(5)	2.667(3)	C(7)—C(8)	1.404(4)
Mo(1)—C(6)	2.340(3)	C(8)—C(9)	1.404(4)
Mo(1)—C(7)	2.336(3)	C(9)—C(10)	1.377(4)
Mo(1)—C(8)	2.442(3)	C(11)—C(12)	1.492(4)
Mo(1)—C(9)	2.581(3)	O(1)—N(1)	1.217(3)
Mo(1)—C(10)	2.477(3)	C(1)—C(2)	1.398(5)
Mo(1)—C(11)	2.258(3)	C(1)—C(5)	1.407(5)

[a] CP(1) and CP(2) refer to the unweighted centroids of the C(1–5) and C(6–10) rings, respectively.

Table 7. Selected bond angles (°) for $Cp_2Mo(NO)(CH_2Ph)$ (**4**).[a]

Bond angles (°)			
N(1)-Mo(1)-C(11)	87.7(1)	N(1)-Mo(1)-CP(1)	116.8
N(1)-Mo(1)-CP(2)	115.3	C(11)-Mo(1)-CP(1)	103.5
C(11)-Mo(1)-CP(2)	106.6	CP(1)-Mo(1)-CP(2)	119.8
Mo(1)-N(1)-O(1)	174.1(2)	C(2)-C(1)-C(5)	107.3(3)
C(1)-C(2)-C(3)	106.1(3)	C(2)-C(3)-C(4)	108.1(3)
C(3)-C(4)-C(5)	108.5(4)	C(1)-C(5)-C(4)	109.3(3)
C(7)-C(6)-C(10)	107.7(3)	C(6)-C(7)-C(8)	107.8(3)
C(7)-C(8)-C(9)	107.9(3)	C(8)-C(9)-C(10)	108.1(3)
C(6)-C(10)-C(9)	108.3(3)	Mo(1)-C(11)-C(12)	117.4(2)
C(11)-C(12)-C(13)	121.8(3)	C(11)-C(12)-C(17)	122.0(3)

[a] CP(1) and CP(2) refer to the unweighted centroids of the C(1–5) and C(6–10) rings, respectively.

the attempted deprotonation reactions resulted in any tractable material.

Related attempts to form alkylidene complexes by deprotonation of neutral $Cp^*M(NO)(CH_2CMe_3)(PMe_3)Cl$ (M = Mo, W) (16*a*) or $Cp^*Mo(NO)(CH_2SiMe_3)_2$ (20) complexes with $LiNR_2$ reagents have been shown to result in metallated η^5,η^1-$C_5Me_4CH_2$ species due to attack on the Cp* methyl groups. From the reaction of LiN-*i*-Pr_2 with $Cp^*Mo(NO)(CH_2SiMe_3)_2$, the anionic "tucked-in" compound goes on to rearrange to $[Cp^*Mo(NO)(=CHSiMe_3)(CH_2SiMe_3)]_2[Li_2(THF)_3]$ (20).

Experimental

Methods

All reactions and subsequent manipulations were conducted under anaerobic conditions using an atmosphere of N_2. $CpMo(NO)(CH_2Ph)Cl$ (6) and the $R_2Mg{\cdot}x$(dioxane) (6) and Na(DME)Cp (21) reagents were prepared according to the published procedures. All other reagents were used as received from commercial suppliers. Filtrations were performed through Celite (1 × 2 cm) supported on a medium-porosity glass frit unless specified otherwise. For the low-temperature alkylation reactions, solvents were transferred via trap-to-trap distillation from the drying reagent directly onto the reactants contained in a flask cooled by a liquid nitrogen bath.

Synthesis of $CpMo(NO)(CH_2Ph)R$ (R = Me (1), Ph (2), C≡CPh (3), Cp (4))

All four complexes were prepared in a similar manner, and the synthesis of $CpMo(NO)(CH_2Ph)Me$ (**1**) is described as a representative example.

THF (~25 mL) was vacuum transferred onto $CpMo(NO)(CH_2Ph)Cl$ (0.186 g, 0.59 mmol) and $Me_2Mg{\cdot}x$(dioxane) (0.089 g, 0.59 mmol). The mixture was stirred while being allowed to warm slowly to room temperature. After ~1 h, the solvent was removed from the final red solution in vacuo. The residue was extracted with a 2:1 solvent mixture of $Et_2O:CH_2Cl_2$, and the extracts were filtered. The solvent was again removed from the filtrate in vacuo, and the residue was triturated with Et_2O twice to obtain CpMo(NO)(CH_2Ph)Me (**1**) as an orange powder (0.110 g, 63% yield). Analytically pure samples of **1** were obtained by extraction of the crude powder with a 1:1 solvent mixture of THF:toluene, followed by chromatography using an Alumina I column with toluene as eluant. The resulting orange eluate was then reduced in volume in vacuo, hexanes were added, and the solution was chilled to –30°C overnight to induce the deposition of orange crystals.

CpMo(NO)(CH_2Ph)Ph (**2**), CpMo(NO)(CH_2Ph)(C≡CPh) (**3**), and Cp_2Mo(NO)(CH_2Ph) (**4**) were synthesized from CpMo(NO)(CH_2Ph)(Cl) in an analogous manner, using $Ph_2Mg\cdot x$(dioxane), LiC≡CPh, and Na(DME)Cp, respectively, instead of $Me_2Mg\cdot x$(dioxane) as the hydrocarbylating reagent.

Synthesis of CpMo(NO)(CH_2Ph)(OTf) (5)

First CH_2Cl_2 (20 mL) and then Et_2O (20 mL) were added via syringe to CpMo(NO)(CH_2Ph)Cl (0.433 g, 1.36 mmol) and AgOTf (0.350 g, 1.36 mmol). After ~10 min, a flocculent white precipitate had formed in the orange solution. The mixture was filtered, and the Celite plug was washed with Et_2O (3 × 5 mL). The combined filtrates were taken to dryness in vacuo, and the residue was triturated twice with Et_2O (10 mL) to obtain CpMo(NO)(CH_2Ph)(OTf) (**5**) as an orange powder (0.529 g, 83% yield).

Synthesis of [CpMo(NO)(CH_2Ph)(L)][OTf] (L = PPh_3 (6), NC_5H_5 (7))

Both triflate salts **6** and **7** may be obtained from either isolated or in situ generated **5**. The two-step synthesis of [CpMo(NO)(CH_2Ph)(PPh_3)][OTf] from CpMo(NO)(CH_2Ph)Cl is described as a representative example.

First CH_2Cl_2 (10 mL) and then Et_2O (10 mL) were added to CpMo(NO)(CH_2Ph)Cl (0.115 g, 0.36 mmol) and AgOTf (0.092 g, 0.36 mmol). After ~10 min, the mixture was filtered through Celite onto solid PPh_3 (0.096 g, 0.36 mmol). The solution was stirred briefly, and then hexanes (10 mL) were added. The total volume of the solution was reduced to ~25 mL, and it was chilled to –30°C overnight to obtain [CpMo(NO)(CH_2Ph)(PPh_3)][OTf] **6** as a yellow powder (0.198 g, 79% yield).

X-ray crystallographic analysis of Cp_2Mo(NO)(CH_2Ph) (4)

A green/black plate of **4** having approximate dimensions of 0.50 × 0.40 × 0.10 mm was mounted in a glass capillary. All measurements were made on a Rigaku/ADSC CCD area detector with graphite monochromated Mo Kα radiation. Data were collected in 0.50° oscillations with 60.0 s exposures. A sweep of data was done using ϕ oscillations from 0.0 to 190.0° at $\chi = -90°$ and a second sweep was performed using ω oscillations between –23.0 and 18.0° at $\chi = -90°$. The crystal-to-detector distance was 39.20(3) mm. The detector swing angle was –10°. The data were corrected for Lorentz and polarization effects.

The structure was solved by heavy-atom Patterson methods (22) and expanded using Fourier techniques (23). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions with C—H = 0.98 Å. Neutral atom scattering factors were taken from Cromer and Waber (24). Anomalous dispersion effects were included in *F*calc (25); the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley (26). The values for the mass attenuation coefficients are those of Creagh and Hubbell (27). All calculations were performed using the teXsan (28) crystallographic software package of Molecular Structure Corp.

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References

1. (*a*) E. Tran and P. Legzdins. J. Am. Chem. Soc. **119**, 5071 (1997); (*b*) C.S. Adams, P. Legzdins, and E. Tran. J. Am. Chem. Soc. **123**, 612 (2001).
2. P. Legzdins, S.J. Rettig, J.E. Veltheer, R.J. Batchelor, and F.W.B. Einstein. Organometallics, **12**, 3575 (1993).
3. P. Legzdins, J.E. Veltheer, M.A. Young, R.J. Batchelor, and F.W.B. Einstein. Organometallics, **14**, 407 (1995).
4. N.H. Dryden, P. Legzdins, S.J. Rettig, and J.E. Veltheer. Organometallics, **11**, 2583 (1992).
5. R. Poli and K.M. Smith. Organometallics, **19**, 2850 (2000).
6. N.H. Dryden, P. Legzdins, J. Trotter, and V.C. Yee. Organometallics, **10**, 2857 (1991).
7. P. Legzdins, R.H. Jones, E.C. Phillips, V.C. Yee, J. Trotter, and F.W.B. Einstein. Organometallics, **10**, 986 (1991).
8. J. Ipaktschi, F. Mirzaei, G.J. Demuth-Eberle, J. Beck, and M. Serafin. Organometalics, **16**, 3965 (1997).
9. J.K. Hoyano, P. Legzdins, and J.T. Malito. J. Chem. Soc. Dalton Trans. 1022 (1975).
10. (*a*) M.W. Hunt, W.G. Kita, B.E. Mann, and J.A. McCleverty. J. Chem. Soc. Dalton Trans. 467 (1978); (*b*) M.W. Hunt, W.G. Kita, and J.A. McCleverty. J. Chem. Soc. Dalton Trans. 474 (1978); (*c*) M.W. Hunt and J.A. McCleverty. J. Chem. Soc. Dalton Trans. 480 (1978).
11. (*a*) R.B. King. Inorg. Chem. **7**, 90 (1968); (*b*) F.A. Cotton and P. Legzdins. J. Am. Chem. Soc. **90**, 6232 (1968); (*c*) J.L. Calderon, F.A. Cotton, and P. Legzdins. J. Am. Chem. Soc. **91**, 2528 (1969); (*d*) F.A. Cotton and G.A. Rusholme. J. Am. Chem. Soc. **94**, 402 (1972); (*e*) J.W. Lauher and R. Hoffmann. J. Am. Chem. Soc. **98**, 1729 (1976); (*f*) E. de Jesús, A. Vázquez de Miguel, P. Royo, A.M.M. Lanfredi, and A. Tiripicchio. J. Chem. Soc. Dalton Trans. 2779 (1990).
12. G. Huttner, H.H. Brintzinger, L.G. Bell, P. Friedrich, V. Bejenke, and D. Neugebauer. J. Organomet. Chem. **145**, 329 (1978).
13. (*a*) M.J. Calhorda and L.F. Veiros. Coord. Chem. Rev. **185–186**, 37 (1999); (*b*) M.J. Calhorda, C.A. Gamelas, C.C. Romão, and L.F. Veiros. Eur. J. Inorg. Chem. 331 (2000).
14. P. Legzdins and J.E. Veltheer. Acc. Chem. Res. **26**, 41 (1993).
15. B. Alegre, E. de Jesús, A. Vázquez de Miguel, P. Royo, A.M.M. Lanfredi, and A. Tiripicchio. J. Chem. Soc. Dalton Trans. 819 (1988).
16. (*a*) J.D. Debad, P. Legzdins, S.J. Rettig, and J.E. Veltheer. Organometallics, **12**, 2714 (1993); (*b*) P. Legzdins and C.R. Nurse. Inorg. Chem. **21**, 3110 (1982); (*c*) T.T. Chin, P. Legzdins, J. Trotter, and V.C. Yee. Organometallics, **11**, 913 (1992); (*d*) P. Legzdins, S.J. Rettig, and S.F. Sayers. J. Am.

Chem. Soc. **116**, 12 105 (1994); (*e*) N.H. Dryden, P. Legzdins, S.F. Sayers, J. Trotter, and V.C. Yee. Can. J. Chem. **73**, 1035 (1995); (*f*) J.A. McCleverty and A.J. Murray. Transition Met. Chem. **4**, 273 (1979).

17. (*a*) P. Legzdins and D.T. Martin. Organometallics, **2**, 1785 (1983); (*b*) P. Legzdins, G.B. Richter-Addo, F.W.B. Einstein, and R.H. Jones. Organometallics, **9**, 431 (1990); (*c*) P. Legzdins, W.S. McNeil, E.G. Vessey, R.J. Batchelor, and F.W.B. Einstein. Organometallics, **11**, 2718 (1992).
18. (*a*) J.W. Faller, M.J. DiVerdi, and J.A. John. Tetrahedron Lett. **32**, 1271 (1991); (*b*) J.W. Faller, J.T. Nguyen, and M.R. Mazzieri. Organometallics, **12**, 1434 (1993); (*c*) J.W. Faller, K.J. Chase, and M.R. Mazzieri. Inorg. Chim. Acta, **229**, 39 (1995).
19. G.A. Lawrance. Chem. Rev. **86**, 17 (1986).
20. (*a*) P. Legzdins and S.F. Sayers. Organometallics, **15**, 3907 (1996); (*b*) P. Legzdins and S.F. Sayers. Chem. Eur. J. **3**, 1579 (1997).
21. J.C. Smart and C.J. Curtis. Inorg. Chem. **16**, 1788 (1977).
22. P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, and C. Smykalla. PATTY: The DIRDIF program system. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands. 1992.
23. P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, and J.M.M. Smits. DIRDIF94: The DIRDIF-94 program system. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands. 1994.
24. D.T. Cromer and J.T. Waber. International tables for X-ray crystallography. Vol. IV. Kynoch Press, Birmingham, U.K. 1974. Table 2.2A.
25. J.A. Ibers and W.C. Hamilton. Acta Crystallogr. **17**, 781 (1964).
26. D.C. Creagh and W.J. McAuley. International tables for crystallography. Vol. C. *Edited by* A.J.C. Wilson. Kluwer Academic Publishers, Boston. 1992. Table 4.2.6.8, pp. 219–222.
27. D.C. Creagh and J.H. Hubbell. International tables for crystallography. Vol. C. *Edited by* A.J.C. Wilson. Kluwer Academic Publishers, Boston. 1992. Table 4.2.4.3, pp. 200–206.
28. teXsan: Crystal structure analysis package. Molecular Structure Corp. 1985 and 1992.