Novel Synthetic Routes to the Anionic Alkylidene Complex [Cp*Mo(NO)(CH$_2$SiMe$_3$)(=CHSiMe$_3$)]$^-$ from Its Neutral Dialkyl Precursor

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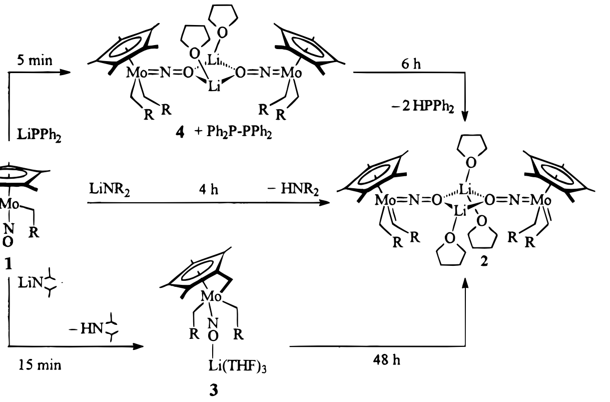
*Summary: Conversion of the dialkyl nitrosyl complex Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$ (**1**) to the lithium salt of the anionic alkylidene complex [Cp*Mo(NO)(CH$_2$SiMe$_3$)(=CHSiMe$_3$)]$_2$[Li$_2$(THF)$_3$] (**2**) may be effected with each of the lithium reagents LiN(SiMe$_3$)$_2$, LDA, or LiPPh$_2$. Interestingly, each transformation follows a different mechanistic pathway.*

Since the discovery by Schrock of nonstabilized alkylidene ligands bound to transition-metal centers,[1] numerous such complexes containing M=C linkages have been synthesized,[2] and some have been utilized as specific reactants or selective catalysts.[3] Despite all this research, very few anionic alkylidene complexes have been isolated to date,[4] even though deprotonation of an alkyl ligand in a neutral organometallic precursor would appear to be an attractive synthetic route to such species.[5] We now report that an anionic alkylidene complex of molybdenum can be synthesized by exposing the 16e dialkyl complex Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$ (**1**)[6] to various lithium reagents and that the mechanistic pathway followed by these reactions is dependent on the lithium reagent employed. The chemistry that forms the basis of this report is summarized in Scheme 1 in which R = SiMe$_3$ throughout.

Scheme 1



Treatment of **1** with 1 equiv of LiN(SiMe$_3$)$_2$ in THF effects a deprotonation at the α-carbon of one alkyl ligand and forms the alkylidene complex [Cp*Mo(NO)(CH$_2$SiMe$_3$)(=CHSiMe$_3$)]$_2$[Li$_2$(THF)$_3$] (**2**), which is isolable as analytically pure, colorless plates in 62% yield from pentane. No intermediate complexes are detectable when this conversion is effected in THF-d_8 and is monitored by ^{1}H NMR spectroscopy over the course of 4 h at 20 °C. Complex **2** in C$_6$D$_6$ exhibits signals diagnostic of an alkylidene complex in both its ^{1}H (at δ 11.7) and ^{13}C (at δ 257, $^1J_{CH}$ = 143 Hz) NMR spectra in addition to other peaks consistent with its formulation.[7] The IR spectrum of **2** as a Nujol mull displays a very low nitrosyl-stretching frequency of 1352 cm^{-1}, which is indicative of a Lewis acid being coordinated to the nitrosyl oxygen atom.[8] This inference is confirmed by the solid-state structure of **2** which has been determined by an X-ray crystallographic analysis.[9] An ORTEP plot of **2** is shown in Figure 1. The alkyl and alkylidene carbon atoms are clearly differentiated by their Mo−C bond lengths and by their Mo−C−Si bond angles.[10] The Mo−NO linkages in the molecule are essentially linear, and the bond lengths within the Mo−NO fragment indicate a considerable degree of Mo→NO back-bonding consistent with the electron-rich nature of the metal center.[11] The orientation of the alkylidene ligand (such that its principal constituents and the Mo−NO fragment are virtually coplanar)[12] is that which is predicted from orbital overlap considerations.[13] Complex **2** is isoelec-

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(1) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796.

(2) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1 and references therein.

(3) Several transition-metal alkylidene complexes are efficient olefin metathesis catalysts; see: Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100 and references cited therein.

(4) (a) The anionic alkylidene complex Lu(CH$_2$SiMe$_3$)$_3$(=CHSiMe$_3$)-Li has been reported, but definitive NMR spectroscopic evidence for its formulation has not been obtained; see: Schumann, H.; Muller, J. *J. Organomet. Chem.* **1979**, *169*, C1. (b) The [CpW(CO)$_2$(=CHPh)]$^-$ anion has been postulated as a reaction intermediate, but it has not been isolated; see: Winter, M. J.; Woodward, S. *J. Organomet. Chem.* **1989**, *361*, C18. (c) The "ate" complex, Li(DME)Mo(=NAd)(=CHCMe$_2$Ph)(OCH(CF$_3$)$_2$)$_3$, has been fully characterized; see: Schrock, R. R.; Luo, S.; Lee, J. C.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883.

(5) Deprotonation of an alkyl ligand in an organometallic cation is a known route to neutral alkylidene complexes; see, for instance: (a) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577. (b) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(6) Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991.

(7) Anal. Calcd for C$_{18}$H$_{36}$LiMoNOSi$_2$ (**2**, desolvated by exposure to high vacuum overnight at 20 °C): C, 48.99; H, 8.16; N, 3.17. Found: C, 48.62; H, 8.46; N, 2.94. IR (Nujol): ν_{NO} 1352 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 11.7 (s, 1H, =CHSiMe$_3$), 1.89 (s, 15H, C$_5$Me$_5$), 0.49 (s, 9H, SiMe$_3$), 0.35 (s, 9H, SiMe$_3$), −0.74 (s, 2H, CH$_2$SiMe$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 257 (=CHSiMe$_3$), 107 (C$_5$Me$_5$), 68.6 (THF), 25.9 (THF), 10.9 (CMe$_5$), 7.60 (CH$_2$SiMe$_3$), 3.17 (SiMe$_3$), 2.45 (SiMe$_3$). ^{7}Li NMR (C$_6$D$_6$): δ −3.0 (s).

(8) (a) Legzdins, P.; Richter-Addo, G. B. *Metal Nitrosyls*; Oxford University Press: New York, 1992; p 276. (b) Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 2885.

(9) Crystal data for [Cp*Mo(NO)(CH$_2$SiMe$_3$)(=CHSiMe$_3$)]$_2$[Li$_2$(THF)$_3$] (**2**) at T = 208 K: triclinic, space group $P\bar{1}$, Z = 2, a = 13.535(6) Å, b = 13.753(4) Å, c = 18.543(7) Å, α = 108.31(3)°, β = 110.35(4)°, γ = 90.45(3)°, V = 3045.7 Å^3, R_F = 0.055 for 4828 reflections with $I_o \geq 2.5\sigma(I_o)$ and 571 variables. Full details of this structure determination will be published elsewhere.

(10) See caption to Figure 1.

(11) For comparison, the neutral Cp*Mo(NO)(CH$_2$SiMe$_3$)(CH$_2$Ph) exhibits bond lengths of Mo−N = 1.760 (2) Å and N−O = 1.217 (2) Å; see: Dryden, N. H.; Legzdins, P.; Phillips, E. C.; Trotter, J.; Yee, V. C. *Organometallics* **1990**, *9*, 882.

(12) Torsion angle N(1)−Mo(1)−C(2)−Si(2) = 5.1°.

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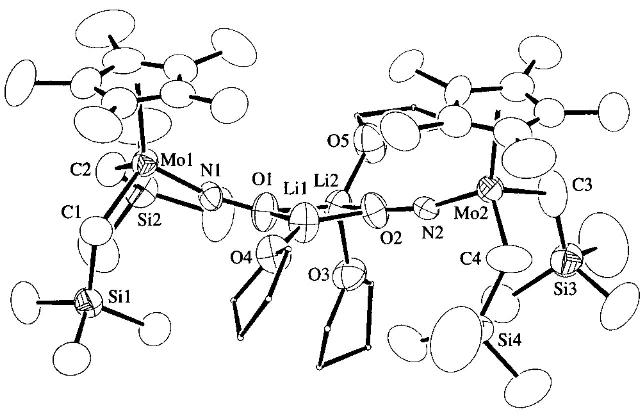

Figure 1. ORTEP diagram of [Cp*Mo(NO)(CH_2SiMe_3)($CHSiMe_3$)]$_2$[$Li_2(THF)_3$] (**2**) at 208 K. Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; for clarity the THF C atoms are represented as small spheres of arbitrary radius. Selected interatomic distances (Å) and angles (deg): Mo(1)−N(1) = 1.711(8), Mo(2)−N(2) = 1.738(8), N(1)−O(1) = 1.314(12), N(2)−O(2) = 1.282(11), Mo(1)−C(1) = 2.207(9), Mo(2)−C(3) = 2.208(11), Mo(1)−C(2) = 1.960(11), Mo(2)−C(4) = 1.940(11), O(1)−Li(1) = 1.849(22), O(1)−Li(2) = 1.937(18), Mo(1)−C(1)−Si(1) = 117.6(5), Mo(2)−C(3)−Si(3) = 122.4(6), Mo(1)−C(2)−Si(2) = 132.9(5), Mo(2)−C(4)−Si(4) = 136.3(8), Mo(1)−N(1)−O(1) = 164.0(5), Mo(2)−N(2)−O(2) = 165.7(5), Li(1)−O(1)−Li(2) = 91.3(9), O(1)−Li(1)−O(2) = 92.2(9).

tronic with known neutral alkylidene nitrosyl compounds of the type Cp′Mo(NO)(=CHR)(L).[14]

In contrast to the conversion considered in the preceding paragraph, reaction of **1** with 1 equiv of LDA in THF for 15 min results in deprotonation of the Cp* ligand and formation of the lithium salt of the "tucked-in" anionic complex, [(η^5,η^1-$C_5Me_4CH_2$)Mo(NO)(CH_2SiMe_3)$_2$][Li(THF)$_3$] (**3**), in 40% isolated yield.[15,16] The identity of **3** is established unequivocally by its NMR spectra which exhibit six different methylene-proton resonances and four inequivalent Cp* methyl-group signals, features similar to those which we have observed previously in the spectra of the related 18e neutral complex (η^5,η^1-$C_5Me_4CH_2$)Mo(NO)(CH_2CMe_3)(PMe_3).[17] The Nujol-mull IR spectrum of **3** exhibits a ν_{NO} at 1478 cm^{-1}, thereby indicating that the lithium counterion is coordinated to the nitrosyl ligand of **3** but in a manner different than in **2**. Elemental analysis and ^{1}H NMR spectral data indicate a four-coordinate Li^+ ion with its other coordination sites being occupied by three THF molecules (Scheme 1). Complex **3** spontaneously converts to the thermodynamically more stable **2** when left in THF or C_6D_6 at ambient temperatures for 48 h.[18]

Finally, the primary reaction pathway when **1** is treated with 1 equiv of $LiPPh_2$ in THF below 0 °C for 5 min is one-electron reduction and production of {[Cp*Mo(NO)(CH_2SiMe_3)$_2$][Li(THF)]}$_2$ (**4**) which is isolable as red crystals (ν_{NO} (Nujol) 1350 cm^{-1}) in 15% yield.[19] Monitoring of this fast reaction by ^{1}H and ^{31}P NMR spectroscopies (THF-d_8, 20 °C) also reveals the production of signals attributable to the Ph_2P-PPh_2 coproduct. However, this reaction proceeds further, and over the course of 6 h at ambient temperatures these signals give way to resonances assignable to **2** and $HPPh_2$ as the 17e dialkyl anion, **4**, is converted to the 18e alkylidene anion, **2**, by the Ph_2P-PPh_2 which effects the requisite hydrogen-atom abstraction.[20] The overall reaction of **1** with $LiPPh_2$ in THF thus results in the formation of **2** and $HPPh_2$. Cyclic voltammetry studies have suggested that addition of electrons to Cp′M(NO)R$_2$ compounds should afford the 17e anions. However, treatment of the dialkyls with reducing agents has previously resulted in either no chemical transformation (with Cp_2Co) or decomposition (with CpFe(η^6-C_6Me_6)).[21] The red crystals of **4** are extremely air sensitive,[22] reconverting rapidly on exposure to air to purple **1** (ν_{NO} (Nujol) 1595 cm^{-1}).

Complex **4** has been subjected to an X-ray crystallographic analysis,[23] and an ORTEP diagram of its solid-state molecular structure is shown in Figure 2. Unlike **2**, the dimeric structure of **4** possesses a C_2 axis passing through the center of the essentially planar (dihedral angle Li_2O planes = 3.15°) Li_2O_2 square (internal angles of the square = 90.0(5) ± 1°). Each lithium atom is three coordinate and is sterically shielded by the alkyl ligands of the complex,[24] with some of the Li−H(alkyl) distances being as short as 2.22 Å. Like **2**, the Mo−NO linkages in the molecule are essentially linear (169.6(8)°), and the bond lengths within the MoNO fragment (i.e. Mo−N = 1.713(5) Å and N−O 1.323(6) Å) indicate a considerable degree of Mo→NO back-bonding.[11] The X-band ESR spectrum of **4** exhibits coupling of the unpaired electron to the ^{14}N nucleus of the nitrosyl ligand, the four ^{1}H nuclei of the methylene

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(13) (a) Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1994**, 1607. (b) Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978. (c) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(14) (a) Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 6922. (b) Legzdins, P.; Rettig, S. J.; Veltheer, J. E.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 3575.

(15) Anal. Calcd for $C_{30}H_{60}LiMoNO_4Si_2$ (**3**): C, 54.81; H, 9.13; N, 2.13. Found: C, 54.66; H, 9.26; N, 2.33. IR (Nujol): ν_{NO} 1478 cm$^{-1.}$ ^{1}H NMR (C_6D_6): δ 3.53 (br, 12H, THF), 3.08 (s, 1H, $C_5Me_4CH_2$), 3.07 (s, 1H, $C_5Me_4CH_2$), 1.88 (s, 3H, $C_5Me_4CH_2$), 1.74 (s, 3H, $C_5Me_4CH_2$), 1.63 (s, 3H, $C_5Me_4CH_2$), 1.44 (br, 12H, THF), 1.42 (s, 3H, $C_5Me_4CH_2$), 0.51 (s, 9H, $SiMe_3$), 0.47 (s, 9H, $SiMe_3$), 0.32 (d, J_{HH} = 12.0 Hz, 1H, CH_2SiMe_3), −0.32 (d, J_{HH} = 12.0 Hz, 1H, CH_2SiMe_3), −0.51 (d, J_{HH} = 12.0 Hz, 1H, CH_2SiMe_3), −0.76 (d, J_{HH} = 12.0 Hz, 1H, CH_2SiMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 132 (C_5Me_4), 114 (C_5Me_4), 105 (C_5Me_4), 104 (C_5Me_4), 101 (C_5Me_4), 68.3 (THF), 60.4 (C_5CH_2), 25.5 (THF), 16.9 (CH_2SiMe_3), 16.5 (CH_2SiMe_3), 10.8 (C_5Me_4), 10.4 (C_5Me_4), 9.59 (C_5Me_4), 9.34 (C_5Me_4), 5.05 ($SiMe_3$), 4.56 ($SiMe_3$). ^{7}Li NMR (C_6D_6): δ −3.5 (s).

(16) Other examples of (η^5,η^1-$C_5Me_4CH_2$)-containing complexes are known; see: (a) Huber, S. R.; Baldwin, T. C.; Wigley, D. E. *Organometallics* **1993**, *12*, 91. (b) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232.

(17) Debad, J. D.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1993**, *12*, 2714.

(18) Bercaw and co-workers have previously invoked the reverse conversion of a neutral alkylidene complex (i.e. Cp*$_2$Hf=CHPh) to its "tucked-in" isomer; see: Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219.

(19) The Ph_2P-PPh_2 coproduct has also been isolated from the final reaction mixture and characterized by its mass spectral and NMR spectroscopic data.

(20) Similar conversions of cationic 17e alkyl complexes to cationic 18e alkylidene complexes by hydrogen-atom abstraction have been documented; see: (a) Hayes, J. C.; Jernakoff, P.; Miller, G. A.; Cooper, N. J. *Pure Appl. Chem.* **1984**, *56*, 25. (b) Jernakoff, P.; Cooper, N. J. *Organometallics* **1986**, *5*, 747.

(21) Herring, F. G.; Legzdins, P.; Richter-Addo, G. B. *Organometallics* **1989**, *8*, 1485.

(22) Due to its extreme air sensitivity, a satisfactory elemental analysis of **4** could not be obtained.

(23) Crystals of {[Cp*Mo(NO)(CH_2SiMe_3)$_2$][Li(THF)]}$_2$ (**4**) are monoclinic, *C*2 (No. 5), with a = 29.194(3) Å, b = 9.877(3) Å, c = 10.569(2) Å, β = 108.13(2)°, and Z = 2. Data were corrected for a 10.3% linear decay, absorption (empirical, azimuthal scans for three reflections), and Lorentz and polarization effects. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to R = 0.036 and R_w = 0.031 for 1939 reflections with $I \geq 3\sigma(I)$. Full details of this structure determination will be published elsewhere.

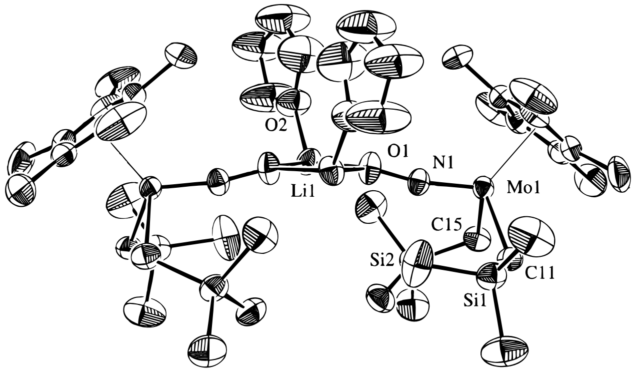

Figure 2. ORTEP diagram of {[Cp*Mo(NO)(CH_2SiMe_3)$_2$][Li(THF)]}$_2$ (**4**). Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms. Selected interatomic distances (Å) and angles (deg): Mo(1)−N(1) = 1.713(5), N(1)−O(1) = 1.323(6), Mo(1)−CP = 2.09, Mo(1)−C(11) = 2.207(9), Mo(1)−C(15) = 2.212(8), O(1)−Li(1) = 1.86(1), Li(1)−O(2) = 1.92(1), C(11)−Mo(1)−N(1) = 102.0(4), C(15)−Mo(1)−N(1) = 101.8(3), Mo(1)−N(1)−O(1) = 169.6(8), N(1)−O(1)−Li(1) = 135.5(5), Li(1)−O(1)−Li(1)′ = 91.0(5), O(1)−Li(1)−O(1)′ = 88.9(5), O(1)−Li(1)−O(2) = 123.3(8).

groups, the ^{7}Li nucleus, and the molybdenum center.[25] Hence, the unpaired electron density in **4** appears to be delocalized over not only the Mo atom and the atoms immediately surrounding it but also over the central Li_2O_2 square to some extent. The ready solubility of **4** in nonpolar solvents suggests that the association established for this complex in the solid state is also maintained in solutions. It may also be noted that complexes **2**−**4** are rare examples of anionic transition-metal nitrosyl complexes that contain alkyl ligands.[26,27]

The deprotonation of an alkyl ligand to form an alkylidene ligand necessarily results in a formal increase of two valence electrons at the metal center. Consequently, for such a conversion to be successful, it is imperative that the starting complex be either electronically unsaturated or contain labile ligands which may be readily lost during the transformation. The metal center in **1** is ideally suited for the chemistry described in this communication since it has a 16-valence-electron configuration. In addition, it also bears a strongly π-acidic nitrosyl ligand which can both stabilize the charge on the anionic product and facilitate its interaction with the cationic counterion. We are currently endeavoring to apply these principles during the synthesis of other anionic alkylidene complexes. We are also investigating the characteristic chemistry of complexes **2**−**4**, focusing in particular on their behavior toward representative electrophiles since we expect the alkylidene ligand in **2** to be very nucleophilic in nature.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L., and we thank Professor F. G. Herring of this Department for his assistance with obtaining and interpreting the ESR spectrum of complex **4**. We also acknowledge Drs. R. J. Batchelor and F. W. B. Einstein of Simon Fraser University and Dr. S. J. Rettig of this Department for solving the crystal structures of complexes **2** and **4**, respectively.

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(24) For examples of similar three-coordinate lithium centers see: (a) Hvoslef, J.; Hope, H.; Murray, B. D.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1438. (b) Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *J. Cryst. Spectrosc.* **1984**, *14*, 541. (c) Becker, G.; Hartmann, H.-M.; Munch, A.; Riffel, H. *Z. Anorg. Allg. Chem.* **1985**, *29*, 530. (d) Engelhardt, L. M.; Harrowfield, J. M.; Lappert, M. F.; MacKinnon, I. A.; Newton, B. H.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 846. (e) Weese, K. H.; Bartlett, R. A.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 2409. (f) Askham, F. R.; Carroll, K. M.; Alexander, S. J.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1993**, *12*, 4810. [Obtained from the Cambridge Structural Data Base: Allen, F. H.; Kennard, O. *Chem. Design Automation News* **1993**, *8*, 31.]

(25) X-Band ESR spectrum of **4** in C_6D_6 at 25 °C: $a_{CH_2} = 5.5$ G, $a_N = 5.9$ G, $a_{Li} = 2.5$ G; $g_{iso} = 1.998\ 00$.

(26) For leading references on a variety of transition-metal nitrosyl anions see: (a) Weiner, W. P.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7462. (b) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110. (c) Weng, W.; Bartic, T.; Brady, M.; Bartik, B; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922. (d) McCleverty, J. A.; Seddon, D. *J. Chem. Soc., Dalton Trans.* **1972**, 2526. (e) Cerveau, G.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *J. Organomet. Chem.* **1987**, *321* (3), 327. (f) Jesús, E.; Miguel, A. V.; Royo, P; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1990**, 2779.

(27) (a) Reference 8a, Chapter 4. (b) Legzdins, P.; Wassink, B. *Organometallics* **1984**, *3*, 1811.