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Communications

Synthesis of Novel Diamagnetic Chromium(II) Alkyl Complexes[1]

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*Summary: Reaction of $Cr(NO)(N^iPr_2)_3$ with $PhCO_2H$ leads to $Cr(NO)(N^iPr_2)(O_2CPh)_2$ (**1**). The benzoate ligands of **1** may be replaced to form the diamagnetic, structurally-characterized organometallic complexes $CpCr(NO)(N^iPr_2)(OC(O)Ph)$ (**2**), $CpCr(NO)(N^iPr_2)(CH_2SiMe_3)$ (**3**), and $Cr(NO)(N^iPr_2)(CH_2SiMe_3)_2$ (**4**).*

Transition-metal amide complexes are integral to both the foundations of modern inorganic chemistry[2] and the frontiers of current organometallic research.[3] Recent improvements in the scope and selectivity of amine elimination reactions[4] have dramatically increased the utility of metal−amide bonds to synthetic organometallic chemists. We now wish to report the use of the known[5] tris(amido) complex $Cr(NO)(N^iPr_2)_3$ as a synthetic precursor to the first fully-characterized Cr(II) nitrosyl[6] alkyl complexes via amine elimination and salt metathesis reactions. The diamagnetic, low-spin configuration of the formally d^4 products is evidently enforced by the strong, synergic π-bonding interactions present in the $[Cr(NO)(N^iPr_2)]^{2+}$ core.

Scheme 1 summarizes the organometallic complexes we have derived from $Cr(NO)(N^iPr_2)_3$. Convenient access to the chromium monoamido nitrosyl fragment is provided by treatment of the tris(amido) compound with 2 equiv of $PhCO_2H$, which forms the bis(benzoate) complex $Cr(NO)(N^iPr_2)(O_2CPh)_2$ (**1**). Previous research has documented similar reactions of $Cr(NO)(N^iPr_2)_3$[5a,b] (and more recently of $Cr(N)(N^iPr_2)_3$[4b]) with protic reagents which selectively substitute one, two, or three amido ligands. ^1H NMR spectroscopic monitoring in C_6D_6 indicates that the reaction of $Cr(NO)(N^iPr_2)_3$ with less than 2 equiv of benzoic acid simply generates mixtures of the tris(amido) starting material and the bis(benzoate) complex, **1**.[7]

Organometallic Cr(II) complexes are readily obtained via salt metathesis reactions of the benzoate ligands of **1**, as illustrated in Scheme 1. Reaction of Na(DME)Cp[8] with **1** affords $CpCr(NO)(N^iPr_2)(OC(O)Ph)$ (**2**),

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⊗ Abstract published in *Advance ACS Abstracts*, July 15, 1997.

(1) π-Bonding and Reactivity in Transition Metal Nitrosyl Complexes, Part 3. For Part 2 see ref 13.

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(3) (a) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861. (b) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591. (c) Laplaza, C. E.; Johnson, M. L. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623. (d) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9. (e) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.

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(5) (a) Bradley, D. C.; Newing, C. W. *J. Chem. Soc., Chem. Commun.* **1970**, 219. (b) Bradley, D. C.; Newing, C. W.; Chisholm, M. H.; Kelly, R. L.; Haitko, D. A.; Little, D.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1980**, *19*, 3010. (c) Odom, A. L.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6613.

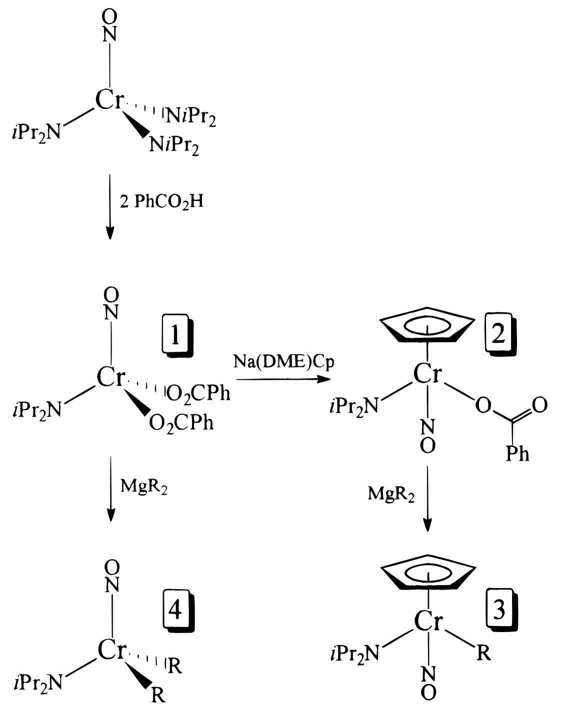
(6) Linear mononitrosyl compounds of Cr(II) are more accurately described as having a $\{Cr(NO)\}^4$ electronic configuration using Enemark−Feltham notation, see: Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

(7) $Cr(NO)(N^iPr_2)(O_2CPh)_2$ reacts slowly with $PhCO_2H$ to produce a green, paramagnetic solid whose IR spectrum (CH_2Cl_2) is devoid of infrared bands in the nitrosyl-stretching region.

(8) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788.

S0276-7333(97)00488-3 CCC: $14.00

Scheme 1[a]



[a] R = CH_2SiMe_3, MgR_2 = $Mg(CH_2SiMe_3)_2 \cdot x$(dioxane)

which subsequently yields $CpCr(NO)(N^iPr_2)(CH_2SiMe_3)$ (**3**) when treated with $Mg(CH_2SiMe_3)_2 \cdot x$(dioxane).[9] Both **2** and **3** are air-stable as solids, and they display four distinct doublets for the four inequivalent amido methyl groups in their room-temperature ^1H NMR spectra (C_6D_6). The large separation between the antisymmetric $\nu(CO_2)$ and symmetric $\nu(CO_2)$ bands at 1629 and 1375 cm^{-1} in the Nujol-mull IR spectrum of **2** is diagnostic of an η^1-benzoate ligand. The solid-state molecular structures of **2** and **3** (Figures 1 and 2) have been established by X-ray crystallographic analyses[10] and provide evidence for strong chromium–amide π-bonding interactions. For both structures, the sum of the bond angles at the amide nitrogen is 360°, the Cr–N(amide) bond lengths are short[11] (1.840(2) and 1.833(2) Å for **2** and **3**, respectively) and the N(nitrosyl)–Cr–N(amide)–C torsion angles are within 4° of 0° and 180°. These features are fully consistent with the alignment of the filled N(amide) p orbital with the empty Cr d orbital orthogonal to the Cr–NO axis.[12]

We have recently reported that $CpCr(NO)Cl_2$ is unstable with respect to loss of the nitrosyl ligand as NO, presumably due to the accessibility of a high-spin, $S = 1$ configuration.[13] The stability of the benzoate (**2**) and alkyl (**3**) complexes, as well as the previously reported $CpCr(NO)(NPh_2)I$[11b] and $Cp^*Cr(NO)(O^iPr)_2$,[12b] may be attributed to their low-spin, $S = 0$ configuration resulting from the increased HOMO–LUMO gap induced by the combination of the strong π-donor amide (or alkoxide) and the strong π-acceptor nitrosyl ligands in chromium's coordination spheres.[14] In marked contrast to these π-stabilized species, the paramagnetic, $S = 1$ spin state adopted by $CpCr(N(SiMe_2CH_2PPh_2)_2)$ demonstrates that amide π-donation to attain a closed-shell configuration is *not* a general phenomenon for $CpCr(NR_2)L_2$ species.[11d]

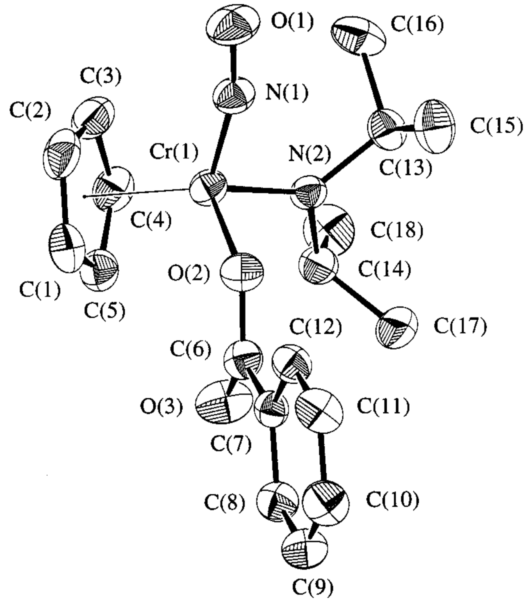


Figure 1. Solid-state molecular structure of **2**; 50% probability thermal ellipsoids are shown.

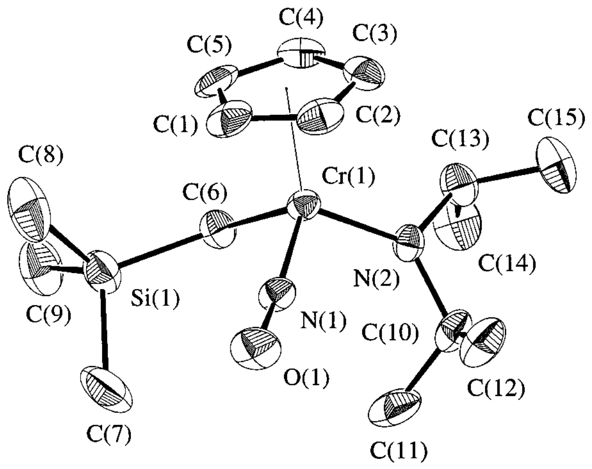


Figure 2. Solid-state molecular structure of **3**; 50% probability thermal ellipsoids are shown.

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(9) (a) Andersen, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 809. (b) Dryden, N. H.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 2857.

(10) (a) Crystal data for **2**: $a = 9.6028(7)$ Å, $b = 11.292(1)$ Å, $c = 8.954(1)$ Å, $\alpha = 95.786(10)°$, $\beta = 96.597(8)°$, $\gamma = 105.207(7)°$, $V = 922.0(2)$ Å^3, space group $P\bar{1}$; $Z = 2$, mol wt = 368.40 for $C_{18}H_{24}CrN_2O_3$, and ρ(calcd) = 1.327 g/cm^3; $R(F) = 0.035$ and $R_w(F) = 0.032$. (b) Crystal data for **3**: $a = 10.568(2)$ Å, $b = 13.584(3)$ Å, $c = 14.158(3)$ Å, $\alpha = 89.945(6)°$, $\beta = 85.289(3)°$, $\gamma = 71.2344(12)°$, $V = 1917.3(6)$ Å^3, space group $P1$; $Z = 4$, mol wt = 334.50 for $C_{15}H_{30}CrN_2OSi$, and ρ(calcd) = 1.159 g/cm^3; $R(F^2) = 0.096$ and $R_w(F^2) = 0.073$.

(11) Cr–N bond lengths range from 1.77 to 2.12 Å for nonbridging Cr(II) amides, see: (a) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 567. (b) Sim, G. A.; Woodhouse, D. I.; Knox, G. R. *J. Chem. Soc., Dalton Trans.* **1979**, 83. (c) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Spek, A. L.; Smeets, W. J. J.; Chiang, M. Y. *J. Chem. Soc., Dalton Trans.* **1993**, 789. (d) Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. R. *Organometallics* **1995**, *14*, 5193.

(12) The alignment of π-donors along the metal–nitrosyl axis has been previously noted for $CpMo(NO)(SPh)_2$,[12a] $Cp^*Cr(NO)(O^iPr)_2$,[12b] and $Cp^*W(NO)(NH^tBu)_2$.[12c] See also ref 13 and references contained therein. (a) Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730. (b) Hubbard, J. L.; McVicar, W. K. *Inorg. Chem.* **1992**, *31*, 910. (c) Legzdins, P.; Ross, K. J.; Sayers, S. F.; Rettig, S. J. *Organometallics* **1997**, *16*, 190.

(13) Legzdins, P.; McNeil, W. S.; Rettig, S. J.; Smith, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 3513.

(14) (a) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25. (b) Poli, R. *Chem. Rev.* **1996**, *96*, 2135.

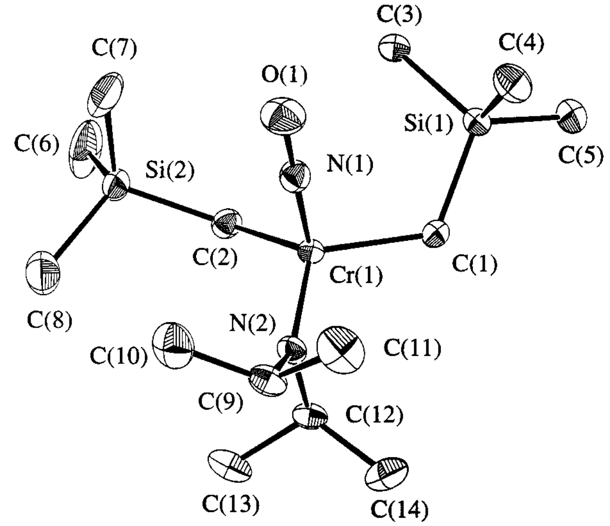

Figure 3. Solid-state molecular structure of **4**; 50% probability thermal ellipsoids are shown.

Previous attempts to rationally synthesize amide-stabilized Cr(II) nitrosyl species from available d^5 CpCr(NO)(halide) starting materials via (a) amide-for-halide metathesis and (b) one-electron oxidation (in either order) have been unsuccessful.[15] Our successful synthesis of CpCr(NO)(N^iPr_2)(OC(O)Ph) and CpCr(NO)(N^iPr_2)(CH_2SiMe_3) relies on the preformation of the Cr(II) amido nitrosyl core in the inorganic Cr(NO)$(N^iPr_2)_3$ precursor prior to the introduction of the organometallic ligands.

Finally, reaction of the bis(benzoate) complex **1** with $Mg(CH_2SiMe_3)_2{\cdot}x$(dioxane) produces Cr(NO)(N^iPr_2)$(CH_2SiMe_3)_2$ (**4**). The solid-state molecular structure of **4** (Figure 3) confirms its formulation as a pseudotetrahedral, monomeric bis(alkyl) complex. The sum of the amide bond angles is 359.8°, the Cr−N(amide) bond length is 1.767 Å, and the N(nitrosyl)−Cr−N(amide)−C torsion angles are within 4° of 0° and 180°, indicative of a strong Cr−N(amide) π-bond.[16] The physical and spectroscopic properties of **4** suggest that the monomeric, tetrahedral geometry determined by X-ray crystallography is maintained in solution. The IR spectrum of **4** has a single, strong ν(NO) band at 1670 cm^{-1} (Nujol), and its mass spectrum displays no signals at m/z values higher than 356 (P^+). The Me_3SiCH_2 groups exhibit sharp, equivalent signals in the ^1H and ^{13}C NMR spectra of **4** in C_6D_6, and the observed coupling constant for the methylene carbons ($^1J_{CH} = 116$ Hz) indicates that no agostic interactions are present.[17] The apparent fluxionality of the amide ligand about the Cr−N^iPr_2 linkage[18] suggests the presence of more than one empty π-symmetry Cr d orbital in the bis(alkyl) complex. The monomeric geometry of **4** is evidently enforced by the steric bulk of its large amide and alkyl ligands.[5b] The thermal stability of **4** contrasts with the proposed adduct generated by treatment of $Cr(CH(SiMe_3)_2)_3$ with NO gas. Despite containing ligands of comparable or greater steric bulk than **4**, "$Cr(NO)(CH(SiMe_3)_2)_3$" was reported to decompose in solution and was characterized solely by IR (1672 cm^{-1}).[19]

While unsaturated, diamagnetic $CpM(NO)(alkyl)_2$ complexes are readily obtained from low-spin bis(halide) precursors for M = Mo or W,[20] the instability of CpCr(NO)Cl_2 prevents the synthesis of congeneric chromium alkyl complexes by analogous reactions. Selective substitution of two N^iPr_2 groups in Cr(NO)$(N^iPr_2)_3$ through amine elimination and salt metathesis reactions provides synthetic access to Cr(II) alkyl complexes containing the "strong-field" amide and nitrosyl ligands. The strong metal−ligand π-bonds in the $[Cr(NO)(N^iPr_2)]^{2+}$ fragment are presumably responsible for the spin pairing of all electrons in both the saturated (**3**) and unsaturated (**4**) alkyl complexes. Previous studies of Cr−C σ-bonds (inspired in part by the commercial application of Cr-based polymerization catalysts) have been hampered by the paramagnetism of monomeric, midvalent Cr alkyl complexes.[11d,21] The characteristic reactivity of the new diamagnetic alkyl compounds containing the Cr(II) amido nitrosyl core is currently under investigation.

Note Added In Proof: Since the submission of this paper, the nitrido analogue of **4**, Cr(N)(N^iPr_2)$(CH_2SiMe_3)_2$, has been reported from the reaction of Cr(N)(N^iPr_2)$(OPh)_2$ with $LiCH_2SiMe_3$; see: Odom, A. L.; Cummins, C. C. *Polyhedron*, in press. We thank Prof. Cummins for providing us with a copy of this manuscript prior to publication.

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.

Supporting Information Available: Text giving experimental procedures and complete characterization data for complexes **1**−**4** and full details of the crystal structure analyses tables of crystallographic data, atomic coordinates, bond lengths, bond angles, hydrogen atom coordinates, anisotropic displacement parameters, torsion angles, and selected nonbonded contacts for **2**−**4** (39 pages). Ordering information is given on any current masthead page.

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(15) McNeil, W. S. Ph.D. Dissertation, The University of British Columbia, Vancouver, British Columbia, 1995.

(16) Bond lengths and angles are the average values of the two crystallographically independent molecules of **4** in the asymmetric unit. Crystal data for **4**: $a = 11.2004(12)$ Å, $b = 12.8210(9)$ Å, $c = 16.979(2)$ Å, $\alpha = 91.035(\underline{7})°$, $\beta = 91.743(3)°$, $\gamma = 113.6640(8)°$, $V = 2231.0(3)$ $Å^3$, space group $P1$; $Z = 4$, mol wt = 356.62 for $C_{14}H_{36}CrN_2OSi_2$, and ρ(calcd) = 1.062 g/cm^3; $R(F^2) = 0.101$ and $R_w(F^2) = 0.100$.

(17) Meijboom, N.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1990**, *9*, 774.

(18) The amide ^1H NMR signals, which are very broad at room temperature, become more defined below 10 °C.

(19) (a) Barker, G. K.; Lappert, M. F. *J. Organomet. Chem.* **1974**, *76*, C45. (b) Barker, G. K.; Lappert, M. F.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1978**, 734.

(20) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41.

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