Nitric Oxide Cleavage: Synthesis of Terminal Chromium(VI) Nitrido Complexes via Nitrosyl Deoxygenation

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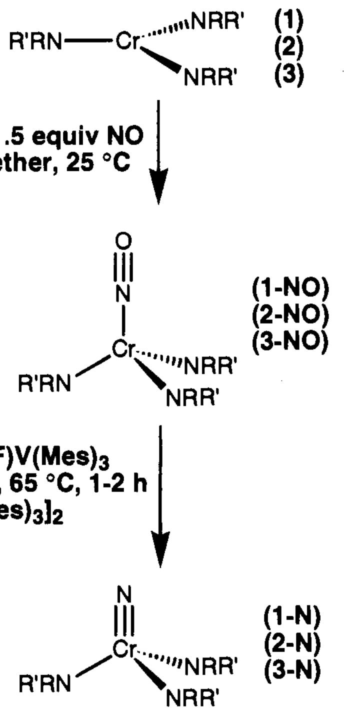
We are interested in developing nitric oxide[1] as a nitrogen atom source in transition-metal chemistry.[2] Twenty-five years ago, Bradley and co-workers showed that the pseudotetrahedral chromium(II) nitrosyl complexes $(ON)Cr(NR_2)_3$ (R = *i*-Pr, $SiMe_3$) are readily prepared[3] by addition of nitric oxide to monomeric $Cr(NR_2)_3$ precursors.[4] In this report we describe the deoxygenation of such nitrosyl complexes utilizing the known[5] vanadium(III) triaryl $(THF)V(Mes)_3$ (Mes = 2,4,6-C_6H_2-Me_3) as the oxygen atom acceptor. Access to nitrido chromium(VI) complexes is of particular interest in view of the prominent role of chromium(VI) oxo species as oxidants,[6] coupled with the current drive for new nitrogen atom[7] or group[8] transfer processes.

Monomeric $Cr(NRR')_3$ species, formally 13e, are readily prepared by treatment of anhydrous $CrCl_3$ with 3 equiv of Li-(N-*i*-Pr_2),[9] $Li(NRAr)(OEt_2)$ (R = $C(CD_3)_2CH_3$, Ar = 3,5-C_6H_3-Me_2),[10] or $Li(NRAr_F)(OEt_2)$[11] (Ar_F = 2,5-C_6H_3FMe) in ether. Representative isolated yields for Cr(N-*i*-Pr_2)$_3$ (**1**),[12] $Cr(NRAr_F)_3$ (**2**),[13] and $Cr(NRAr)_3$ (**3**)[13] are 53, 94, and 76%, respectively; we typically prepare these substances on a scale of ~25–50 mmol. Although the complexes are unstable to oxygen and water, they are thermally robust and easily manipulated in an inert atmosphere. X-ray structural investigations have been carried out for Cr(N-*i*-Pr_2)$_3$[4] and $Cr(NRAr)_3$;[14] the latter trigonal planar complex is isostructural with its recently-discovered molybdenum counterpart.[15]

Scheme 1



1: R = R' = *i*-Pr
2: R = $C(CD_3)_2CH_3$, R' = 2,5-C_6H_3FMe
3: R = $C(CD_3)_2CH_3$, R' = 3,5-$C_6H_3Me_2$

Addition of nitric oxide (~1.5 equiv) via syringe to ether solutions of **1**, **2**, or **3** resulted in a rapid color change to orange-red. The soluble, diamagnetic, crystalline $(ON)Cr(NRR')_3$ complexes **1**-NO,[3] **2**-NO,[13] and **3**-NO[13] formed in essentially quantitative yield (Scheme 1) and, for synthetic purposes, did not require purification beyond removal of volatile material. Infrared stretching frequencies (ν_{NO}) for **1**-NO, **2**-NO, and **3**-NO are respectively 1643, 1673, and 1662 cm^{-1}, suggesting the order N-*i*-Pr_2 > NRAr > $NRAr_F$ for the electron-donor properties of these amides. The labeled derivatives **1**-^{15}NO and **2**-^{15}NO were prepared similarly,[13] employing 99% ^{15}N-enriched nitric oxide. These complexes exhibited ν_{NO} bands at 1610 and 1637 cm^{-1}, respectively, as well as ^{15}N NMR signals 437 (**1**-^{15}NO) and 448 (**2**-^{15}NO) ppm downfield of liquid NH_3.[16] We attribute the diamagnetism (and low NO stretching frequencies[17]) of these linear[18] nitrosyl complexes to population (e^4) of a degenerate pair of Cr-based orbitals (d_{xz}, d_{yz}; p_x, p_y hybrids) that

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[2] The following treatise serves as a comprehensive guide to transition-metal nitrosyl chemistry: Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; see pp 279–280 for a summary of reactions occurring with NO bond cleavage. See also: Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41.

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[6] Muzart, J. *Chem. Rev.* **1992**, *92*, 113. Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer-Verlag: Berlin, 1984.

[7] See the following for examples of intermetal nitrogen atom transfer: Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125. Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478. Neely, F. L.; Bottomley, L. A. *Inorg. Chim. Acta* **1992**, *192*, 147. Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989**, *111*, 5955. Bakir, M.; White, P. S.; Dovletoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2835.

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[9] Alyea, E. C.; Basi, J. S.; Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc., Chem. Commun.* **1968**, 495.

[10] Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Organometallics* **1995**, *14*, 577.

[11] $Li(NRAr_F)(OEt_2)$ was prepared in a fashion essentially identical to $Li(NRAr)(OEt_2)$ (ref 10); details will be given in an upcoming full paper.

[12] The reported yield is ours since none was given (ref 9) in the original work by Bradley and co-workers.

[13] See supplementary material for full preparative and characterization data. All new compounds gave satisfactory CHN combustion analyses.

[14] Odom, A. L.; Davis, W. M.; Cummins, C. C., unpublished results (data to appear in an upcoming full paper).

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[16] ^{15}N NMR shifts are referenced to external neat nitromethane, whose chemical shift is +380.2 ppm with respect to liquid NH_3 (taken as 0 ppm): von Philipsborn, W.; Müller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 383.

[17] The stretching frequencies for NO^+, NO, and NO^- are respectively 2377, 1875, and 1470 cm^{-1}; ref 2 above.

[18] An X-ray determination has been carried out for (ON)Cr[N-$(SiMe_3)_2]_3$; the molecule exhibits a crystallographically-imposed Cr–N–O angle of 180°; ref 3 above.

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is suited for donation into the degenerate pair of NO π^* orbitals. This orbital picture corresponds to incipient $Cr{\equiv}N$ triple bond formation.

$(THF)V(Mes)_3$ (2 equiv) was employed to deoxygenate the $(ON)Cr(NRR')_3$ complexes (toluene, 65 °C, ~1 h, Scheme 1).[19] Separation of beet-colored, pentane-soluble $N{\equiv}Cr(N\text{-}i\text{-}Pr_2)_3$ (**1**-N) from $O[V(Mes)_3]_2$ was accomplished by extraction with ether/hexane and subsequent recrystallization (ether, −35 °C, 67% yield).[13] Since $N{\equiv}Cr(NRAr_F)_3$ (**2**-N) and $N{\equiv}Cr(NRAr)_3$ (**3**-N) proved to be stable to silica gel, these complexes were easily separated from the vanadium(IV) oxo byproduct by filtration of hydrocarbon solutions through this adsorbent. Subsequent recrystallization (ether, −35 °C) gave **2**-N in 91% yield[13] and **3**-N in 73% yield[13] as analytically pure substances. Infrared spectra of **1**-N and **2**-N exhibited intense absorptions at 1054 and 1046 cm^{-1} that are characteristic of the terminal nitrido functionality ($\nu_{Cr{\equiv}N}$).[20] The corresponding absorptions for **1**-^{15}N and **2**-^{15}N, which were prepared in a manner identical to the unlabeled derivatives, appeared at 1029 and 1020 cm^{-1}. ^{15}N NMR signals for **1**-^{15}N and **2**-^{15}N were located 979 and 1020 ppm downfield of liquid NH_3,[16] showing that the nitrido nitrogen atoms are substantially deshielded with respect to the precursor nitrosyl nitrogens.[21]

The molecular structure of $N{\equiv}Cr(N\text{-}i\text{-}Pr_2)_3$ (**1**-N) was determined by single-crystal X-ray diffraction (Figure 1).[22] Monomeric **1**-N exhibits an axially distorted tetrahedral geometry with approximate C_{3v} point symmetry.[23] The $Cr{\equiv}N$ distance of 1.544(3) Å is consistent with a triple bond,[24] while the Cr−N amido distances (1.844(2), 1.842(3), and 1.840(3) Å) are ~0.03 Å shorter than the corresponding distances reported for $Cr(N\text{-}i\text{-}Pr_2)_3$ (**1**),[4] consistent with the drastic difference in formal oxidation state.

Nitric oxide has thus proven effective as a nitrogen atom source in the synthesis of monomeric Cr(VI) nitrido complexes. These diamagnetic d^0 analogues of related Mo(VI)[25] and W(VI)[26] nitrido systems have not been accessible by other synthetic routes.[27] The work embodied here also represents a unique intermolecular nitric oxide cleavage process,[28] mechanistic aspects of which are currently under scrutiny in our laboratory.

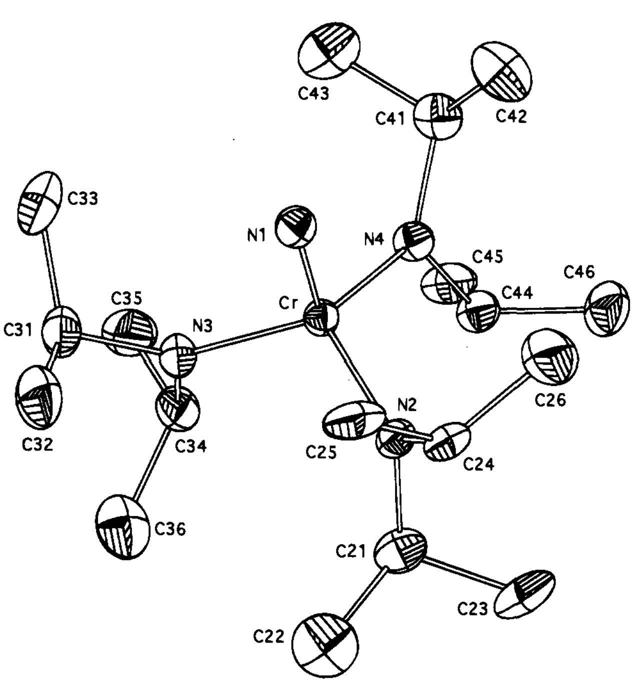

Figure 1. Structural diagram of $N{\equiv}Cr(N\text{-}i\text{-}Pr_2)_3$ (**1**-N) with thermal ellipsoids at the 30% probability level. Selected bond distances (Å): Cr−N(1), 1.544(3); Cr−N(3), 1.844(2); Cr−N(4), 1.842(3); Cr−N(2), 1.840(3). Selected bond angles (deg): N(1)−Cr−N(3), 104.98(12); N(1)−Cr−N(4), 104.72(14); N(3)−Cr−N(4), 113.43(12); N(1)−Cr−N(2), 104.83(13); N(3)−Cr−N(2), 113.94(12); N(4)−Cr−N(2), 113.66(11); C(21)−N(2)−C(24), 114.2(3); C(21)−N(2)−Cr, 117.4(2); C(24)−N(2)−Cr, 128.2(2); C(31)−N(3)−C(34), 114.7(2); C(31)−N(3)−Cr, 128.5(2); C(34)−N(3)−Cr, 116.6(2); C(44)−N(4)−C(41), 114.8(3); C(44)−N(4)−Cr, 117.0(2); C(41)−N(4)−Cr, 127.9(2).

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Supplementary Material Available: Experimental details for the X-ray structure of $N{\equiv}Cr(N\text{-}i\text{-}Pr_2)_3$ along with relevant data tables; preparative and characterization data for all new compounds (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(19) Floriani et al. have shown that $(THF)V(Mes)_3$ deoxygenates epoxides to give $V(O)(Mes)_3$, and that the latter readily combines with $(THF)V(Mes)_3$ to give the vanadium(IV) μ-oxo dimer $O[V(Mes)_3]_2$: Ruiz, J.; Vivanco, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1991**, 762. Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 1802.

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(21) The ^{15}N NMR shift for $Mo(^{15}N)(NRAr)_3$ is +840 ppm (ref 15 above). For ^{15}N NMR data on other Mo and W nitrido compounds, see: Dilworth, J. R.; Donovan-Mtunzi, S.; Kan, C. T.; Richards, R. L.; Mason, J. *Inorg. Chim. Acta* **1981**, *53*, L161. Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1984**, 469.

(22) Crystal data for **1**-N: $a = 7.8521(7)$ Å, $b = 16.4160(11)$ Å, $c = 17.484(2)$ Å, $\beta = 90.456(7)°$, $V = 2253.6(3)$ Å^3, space group $P2(1)/n$, $Z = 4$, mol wt = 366.56 for $C_{18}H_{42}CrN_4$, and $\varrho(calcd) = 1.080$ g/cm^3; $R_1 = 0.0454$ and $wR_2 = 0.0966$.

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(27) See, however: Chiu, H.-T.; Chen, Y.-P.; Lee, G.-H.; Peng, S.-M. *Abstracts of Papers*, 209th ACS National Meeting, Anaheim, CA, Spring 1995; American Chemical Society: Washington, DC, 1995. INOR 92.

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