The First Nitrosyl Complexes of Niobium and Tantalum

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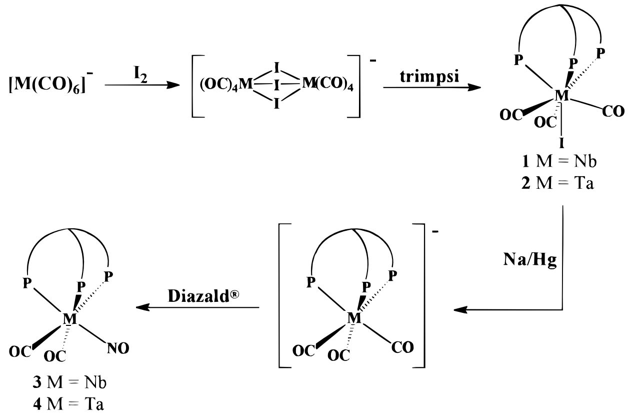
It is well-known that NO is a very strong π-acceptor ligand[1] and that the extent of M→NO back-bonding plays a significant role in determining the chemistry displayed by transition-metal nitrosyl complexes. Typically, this back-bonding is manifested both in nitrosyl ligand-based reactivity[2] and in unusual chemical behavior at the metal centers.[3] To date it has also been established that NO binds strongly to most of the d-block metals of groups 6−10 to afford series of important metallonitrosyl complexes.[4] However, early-transition-metal nitrosyls are much fewer in number despite the fact that in the lower formal oxidation states required to complex NO effectively these metals would be expected to be capable of particularly strong M→NO back-bonding.[5] For the group 5 elements, for instance, there are no well-characterized niobium or tantalum nitrosyl complexes, although some vanadium derivatives have been reported.[6] We now report the synthesis and characterization of (trimpsi)M(NO)(CO)$_2$ (trimpsi = *tert*-BuSi(CH$_2$PMe$_2$)$_3$; M = Nb, Ta), the first nitrosyls of these elements (Scheme 1).

We reasoned that the paucity of early-transition-metal nitrosyl complexes might be a manifestation of two factors. First, since most nitrosylating agents are also rather unselective oxidants, their use in the presence of the more oxophilic early transition metals might tend to result in metal−oxo complexes rather than metal nitrosyls.[7] Second, electronic enhancement of the M→NO π-interaction mentioned above might be an important prerequisite to the formation of kinetically stable early metal nitrosyl complexes. This enhancement could be achieved by establishing a coligand set that significantly augments the overall electron density at the metal center. Our successful implementation of this reasoning is reflected in the chemistry summarized in Scheme 1. Thus, treatment of the hexacarbonyl metalates [Et$_4$N][M(CO)$_6$] (M = Nb, Ta)[8] in DME (1,2-dimethoxyethane) with I$_2$ at −78 °C produces solutions of the bimetallic anions [M$_2$(μ-I)$_3$(CO)$_8$]$^-$.[9] Subsequent addition of the strongly electron-donating tripodal phosphine, trimpsi,[5] followed by warming affords the new tricarbonyl iodide complexes (trimpsi)M(CO)$_3$I (M = Nb, **1**; Ta, **2**),[10] which are isolable as free-flowing, air-stable, red microcrystalline solids in high yields.[11] Reduction of DME solutions of these materials generates solutions of the yellow metalates Na[(trimpsi)M(CO)$_3$].[12] Finally, treatment of these very air-sensitive solutions at −78 °C with Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide), a very selective and nonoxidative nitrosylating agent,[4] affords the air-sensitive complexes (trimpsi)M(NO)(CO)$_2$ (M = Nb, **3**; Ta, **4**) in high yields (>70% overall) after workup. By adhering to this general methodology (Scheme 1), multigram quantities of high purity **3** and **4** have been prepared in under 2 days starting from the appropriate hexacarbonylmetalates.[11]

Scheme 1



Complexes **3** and **4** are thermally stable, purple crystalline solids that are readily soluble in CH$_2$Cl$_2$, THF, and DME. The IR spectra of **3** and **4** as Nujol mulls exhibit strong nitrosyl-stretching absorptions at 1518 and 1515 cm^{-1}, respectively. These frequencies are significantly lower in energy than analogous absorptions displayed by related tungsten and vanadium complexes such as (HB(3,5-Me$_2$pz)$_3$W(NO)(CO)$_2$ (ν(NO) = 1662 cm^{-1}),[13a] [(tacn)W(NO)(CO)$_2$]$^+$ (ν(NO) = 1630 cm^{-1}),[13b] (η^5-C$_5$H$_5$)W(NO)(CO)$_2$ (ν(NO) = 1655 cm^{-1}),[13c] (CH$_3$C(CH$_2$PPh$_2$)$_3$)V(NO)(CO)$_2$ (ν(NO) = 1573 cm^{-1}),[6d] and (Me$_2$PCH$_2$CH$_2$PMe$_2$)V(NO)(CO)$_3$ (ν(NO) = 1601 cm^{-1})[6d] and clearly attest to the existence of strong M→NO back-bonding in these compounds. X-ray diffraction analyses of **3**[14] and **4**[15] reveal the solid-state

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(1) (a) Bursten, B. E.; Cayton, R. H. *Organometallics* **1987**, *6*, 2004. (b) Bursten, B. E.; Cayton, R. H.; Gatter, M. G. *Organometallics* **1988**, *7*, 1342 and ref 22 therein.

(2) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; pp 339−342.

(3) Selected recent examples of such chemistry include: (a) Ogasawara, M.; Huang, D.; Streib, W. E.; Huffmann, J. C.; Gallego-Planas, N.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 8642. (b) Tran, E.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 5071. (c) Burkey, D. J.; Debad, J. D.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 1139.

(4) For a recent survey of metallonitrosyl chemistry, see: Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

(5) The low effective nuclear charges of early-transition-metal atoms compared to the later metals result in d orbitals of greater radial extension. The closer energy match between the occupied metal dπ and vacant ligand π* orbitals leads to substantially improved back-bonding with π-acidic ligands. This subject has been addressed in relation to the stability and spectroscopic properties of group 4 metal carbonyl and naphthalene complexes, see: (a) Spencer, M. D.; Girolami, G. S. *J. Organomet. Chem.* **1994**, *483*, 99. (b) Gardner, T. G.; Girolami, G. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1693. (c) Gardner, T. G.; Girolami, G. S. *Organometallics* **1987**, *6*, 2551.

(6) See, for instance: (a) Bottomley, F.; Darkwa, J.; Sutin, L.; White, P. S. *Organometallics* **1986**, *5*, 2165. (b) Bottomley, F.; Darkwa, J.; White, P. S. *Organometallics* **1985**, *4*, 961. (c) Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2303. In this paper are also reported mass spectral and IR data for an inseparable mixture of otherwise poorly characterized tantalum carbonyl nitrosyl phosphine complexes. (d) Schiemann, J.; Weiss, E.; Näumann, F.; Rehder, D. *J. Organomet. Chem.* **1982**, *232*, 219. (e) Näumann, F.; Rehder, D. *J. Organomet. Chem.* **1981**, *204*, 411. (f) Herberhold, M.; Klein, R.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 220.

(7) (a) Bottomley, F. *Polyhedron* **1992**, *11*, 1707. (b) Middleton, A. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1888. (c) Daff, P. J.; Legzdins, P.; Sayers, S. F. unpublished observations. See also ref 6a,b.

(8) (a) Ellis, J. E.; Warnock, G. F.; Barybin, M. V.; Pomije, M. K. *Chem. Eur. J.* **1995**, *1*, 521. (b) Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. *Organometallics* **1983**, *2*, 388.

(9) Calderazzo, F.; Castellani, M.; Pampaloni, G.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1985**, 1989.

(10) Related carbonyl halo complexes involving other multidentate phosphines have been prepared in a similar manner, see: (a) Calderazzo, F.; Pampaloni, G.; Englert, U.; Strähle, J. *J. Organomet. Chem.* **1990**, *383*, 45. (b) Calderazzo, F.; Pampaloni, G.; Pelizzi, G.; Vitali, F. *Organometallics* **1988**, *7*, 1083. (c) Luetkens, M. L., Jr.; Santure, D. J.; Huffmann, J. C.; Sattelberger, A. P. *J. Chem. Soc., Chem. Commun.* **1985**, 522.

(11) Preparative details and full characterization data for all new compounds are provided in the Supporting Information.

(12) Lippard and co-workers have previously described the use of this methodology for the preparation of related phosphino tantalates, see: Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90 and references therein.

(13) (a) HB(3,5-Me$_2$pz)$_3$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate: Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 2675. (b) tacn = 1,4,7-triazacyclononane: Chaudhuri, P.; Wieghardt, K.; Tsai, Y.-H.; Kruger, C. *Inorg. Chem.* **1984**, *23*, 427. (c) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.

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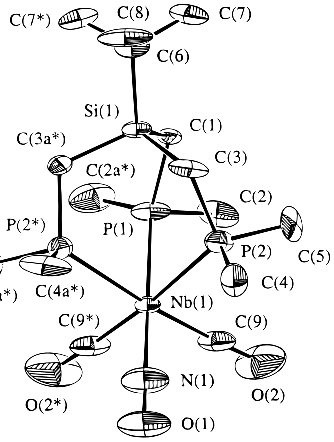

Figure 1. Solid-state molecular structure of **3**.

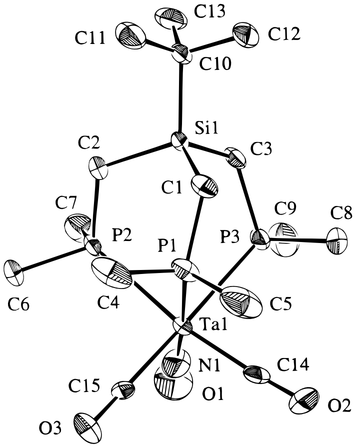

Figure 2. Solid-state molecular structure of **4**.

molecular structures shown in Figures 1 and 2, respectively. As anticipated, the geometries at the metal centers are essentially octahedral, and in both structures, the tridentate phosphine exhibits a trigonal twist distortion about the Si−M (M = Nb, Ta) vector similar to that observed in other crystallographically characterized complexes of this ligand.[5,16] The M−P and M−CO bond lengths (Nb−P = 2.5777(14) and 2.6316(11) Å, Nb−CO = 1.935(5) Å, C−O = 1.191(5) Å in **3** and Ta−P = 2.618(2), 2.610(2), and 2.584(2) Å, Ta−CO = 1.970(7) and 1.936(8) Å, C−O = 1.152(8) and 1.197(9) Å in **4**) lie within the normal ranges for low-valent (formal oxidation states −1 to +1) niobium and tantalum compounds.[9,10,17] The nitrosyl ligands are bonded via their N atoms, and in both cases, the M−N−O angles are essentially 180°. However, contrary to the trends observed in other crystallographically characterized carbonylnitrosyls,[4] the M−N and C−O bonds are longer than the M−C and N−O bonds, respectively, in **3** and **4**. Nevertheless, the Nb−N and Ta−N bond lengths of 2.094(5) and 2.144(10) Å, respectively, are shorter than typical Nb−N and Ta−N single bonds (2.3−2.5 Å) and are consistent with the existence of M−N multiple bond character resulting from M→NO back-bonding. The N−O bond length in **3** is 1.158(5) Å, whereas that in **4** is rather short at 1.066(9) Å when compared to typical N−O distances in metal nitrosyls which fall in the range of 1.15−1.25 Å.[18] The short N−O bond length measured in the structure of **4** is probably an artifact of significant thermal disorder in the MNO group, a feature common to some terminal nitrosyls that often leads to reductions in the observed N−O distance.[19]

The room-temperature NMR spectra of **3** and **4** in CD_2Cl_2 display the anticipated signals[11] and indicate that the principal features inherent to their solid-state molecular structures are retained in solution. The rapid reversal of the twist distortion in the coordinated trimpsi ligand (Figures 1 and 2) imposes apparent C_s symmetry upon **3** and **4** at ambient temperatures. Additional NMR studies are currently in progress to evaluate if this represents the only significant dynamic process which **3** and **4** undergo in solutions. Our findings in this regard will be reported in a future contribution.

Finally, we intend to utilize the synthetic methodology summarized in Scheme 1 to prepare also the triazacyclononane-containing analogues of complexes **3** and **4**. It is anticipated that this general class of $L_3M(NO)(CO)_2$ dicarbonylnitrosyl derivatives will prove to be excellent starting materials for the initiation of a comprehensive reactivity study of this area of low-valent early-transition-metal chemistry just as the related Cp′M(NO)(CO)$_2$ complexes of chromium, molybdenum, and tungsten have been valuable precursors to a vast array of group 6 organometallic nitrosyl complexes.[20] Our investigations in this regard are currently in progress.

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Supporting Information Available: Experimental procedures for the preparation of complexes **1**−**4**, complete characterization data for complexes **1**−**4**, and full details of the crystal structure analyses including associated tables for **3** and **4** (49 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(14) Crystal data for **3**: orthorhombic, space group *Pnma* (No. 62), a = 16.5158(10) Å, b = 13.6408(8) Å, c = 10.426(2) Å, V = 2348.8(6) Å^3, Z = 4, R_1 = 0.057, R_w = 0.036, and GOF(F^2) = 2.22 for 3474 reflections ($2\theta_{max}$ = 60.1°, T = −93 °C) and 155 variables.

(15) Crystal data for **4**: monoclinic, space group $P2_1/n$ (No. 14), a = 9.7532(14) Å, b = 17.5506(15) Å, c = 14.2268(5) Å, β = 101.5387(8)°, V = 2386.0(3) Å^3, Z = 4, R_1 = 0.048, R_w = 0.050, and GOF(F^2) = 2.03 for 6039 reflections ($2\theta_{max}$ = 61.3°, T = −93 °C) and 217 variables.

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