companied with four lanthanum atoms (in two asymmetric LaO_8 polyhedra) to give rise to the structural formula $[La_4Ti(Si_2O_7)_2] \equiv [La_4Ti(Si_2O_7)_{6/3}]$. As the formula indicates, each pyrosilicate group is shared by three isolated titanium atoms, Ti(1). The Si_2O_7 groups are arranged in a parallel fashion with respect to their nearly linear, 178.9 (5)°, Si–O–Si vectors to form channels where the lanthanum atoms are located. Thus, the alternate slab stacking can be illustrated by the structural formula $La_4Ti(Si_2O_7)_2(TiO_2)_{4m}$, where the value m (= 2) represents the thickness of the rutile slab.

One of the important features of this quasi-2D compound is the structure and bonding found in the double-rutile titanium(III/IV) oxide slab. In the slab, there are two relatively short Ti–Ti distances across shared octahedron edges, i.e., 2.75 Å (for Ti(2)–Ti(2)) and 2.90 Å (for Ti(3)–Ti(4)). These distances are shorter than the 2.96 Å distance observed in the rutile structure as well as the 3.02 Å critical distance for Ti–Ti interaction,[12] indicating some significant titanium metal-to-metal interactions through the in-plane titanium d orbital overlap. An alternating short (2.75 Å) and long (3.00 Å) Ti(2)–Ti(2) distance is observed along the *b* axis, which can be attributed to the interslab connectivity between the $Ti(2)O_6$ octahedra and the $Si(2)O_4$ tetrahedra. The inhomogeneous Ti(2)–Ti(2) distances suggest the occurrence of electron localization between the two closely spaced titanium cations. This phenomena, which is not observed between the Ti(3) and Ti(4) cations, indicates that the Ti(2) cations may be reduced. This belief is further supported by the fact that the formal oxidation states will be balanced, with respect to charge neutrality and the multiplicities of the titanium cations, if Ti(2) is formally assigned a trivalent oxidation state (d^1), i.e., $La_8Ti(1)^{IV}{}_2Ti(2)^{III}{}_8Ti(3)^{IV}{}_4Ti(4)^{IV}{}_4Si_8O_{60} \equiv 2\text{-}(La_4Ti_9Si_4O_{30})$. Alternative oxidation state assignments, based upon the valence sum calculations,[13] are equally consistent in terms of charge neutrality in that Ti(1) is 2.86 v.u., while Ti(2), Ti(3), and Ti(4) are about 3.60 v.u. The total charge of all the titanium atoms is about the same for both models. This would suggest that the oxidation state assignment may not be at all obvious. Therefore, we are presently attempting to grow sizable single crystals of the title compound for magnetic and conductivity measurements in order to determine the behavior of the valence electrons, e.g., whether the d electrons are largely localized (such as trapped in the Ti^{3+}–Ti^{3+} bonding pair) or delocalized throughout the rutile slab.[14]

It is intriguing to look into the possibility of developing a new series of $La_4Ti(Si_2O_7)_2(TiO_2)_{4m}$ compounds with various sized rutile slabs. The presently studied structure is related to that of perrierite. In the mineral perrierite, $La_4Mg_2Ti_3Si_4O_{22}$,[15] the structural formula can be written as $La_4Mg(Si_2O_7)_2(Mg_{0.25}Ti_{0.75}O_2)_4$, where a single-layer rutile slab of mixed TiO_6 and MgO_6 octahedra is observed. The separation of the rutile slabs is dictated by the similar arrangement of the $La_4M(Si_2O_7)_2$ (M = Ti and Mg) slab. In the title compound, the thickness of the silicate slab is as large as 7.38 Å.[16] In light of this structural comparison and the success of our molten salt synthesis, the discovery of the title compound should lead us into a new era of the synthesis of quasi-2D, rutile-based compounds for systematic structure/property studies.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support from the National Science Foundation (SGER, Grant DMR-9012983) and the Robert A. Welch Foundation is gratefully acknowledged. Financial support for the single-crystal X-ray diffractometer by the National Science Foundation is also acknowledged.

Supplementary Material Available: Tables of detailed crystallographic data, atomic positional and thermal parameters, and selected bond distances and angles (5 pages); table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

---

(12) (a) Goodenough, J. B. *Progress in Solid State Chemistry*; Reiss, H., Ed.; Pergamon: New York, 1971; Vol. 5, pp 145–399. (b) Goodenough, J. B. *Bull. Soc. Chim. Fr.* **1965**, 1200–1206.

(13) Brown, I. D. *Structure and Bonding in Crystals*; O'Keefe, M., Navrotsky, A. Eds.; Academic Press: New York/London/Toronto/Sydney/San Francisco, 1981; Vol. II, pp 1–30. $s = \exp[-(R - R_o)/B]$; R_o ($Ti^{III/IV}$) = 1.823 Å and $B = 0.324$.

(14) A two-probe conductivity measurement was performed on a small single crystal at room temperature. The conductivity of the title compound is one order of magnitude smaller than that of the high T_c superconducing cuprate $YBa_2Cu_3O_7$.

(15) (a) Ito, J.; Arem, J. E. *Amer. Mineral.* **1971**, *56*, 307–319. (b) Ito, J. *Amer. Mineral.* **1967**, *52*, 1094–1104. (c) Gottardi, G. *Amer. Mineral.* **1960**, *45*, 1–14.

(16) Based upon their structural similarity, the *c* lattice constant for the compound series can be derived as $c \sin \beta = 3.40m + 7.38$ (Å). The 3.40 Å distance represents the thickness of the rutile layer in the title compound, comparable with the 3.25 Å distance in the TiO_2 structure. Note that by using this formula the calculated *c* lattice constant for the perrierite structure (with $\beta = 113.88°$, ref 15a) is the same as the observed value, 11.79 Å.

A Unique μ-η^1:η^2-NO Ligand in a Bimetallic Alkylidene Nitrosyl Complex of Molybdenum[1]

Peter Legzdins,* Steven J. Rettig, and John E. Veltheer

Department of Chemistry
The University of British Columbia
Vancouver, British Columbia, Canada V6T 1Z1

Received October 29, 1991
Revised Manuscript Received June 22, 1992

In general, 16-electron $Cp'M(NO)R_2$ complexes [$Cp' = \eta^5$-C_5H_5 (Cp) or η^5-C_5Me_5 (Cp*); M = Mo or W; R = alkyl or aryl] are thermally stable at 20 °C.[2] This stability reflects both the nonbonding nature of the metal-centered LUMO of these complexes and their kinetic inertness toward decomposition.[3] We now report the first example of a thermally unstable $Cp'M(NO)R_2$ species, namely, $CpMo(NO)(CH_2CMe_3)_2$ (**1**), which transforms to the unprecedented complex $[CpMo(NO)](\mu\text{-}\eta^1\text{:}\eta^2\text{-NO})(\mu\text{-}CHCMe_3)[CpMo(=CHCMe_3)]$ (**2**) (Scheme I).

In a typical experiment, a deep red CH_2Cl_2 solution of **1** (ν_{NO} 1609 cm^{-1}) was stirred at room temperature for 2 h, during which time it faded to the pale orange color of **2** (ν_{NO} 1594 and 1328 cm^{-1}). Chromatographic workup on alumina and crystallization from Et_2O yielded pale orange crystals of **2** (47% yield).[4] An X-ray analysis of **2**[5] established that the molecular unit is a dimer of $CpMo(NO)(CHCMe_3)$ whose structure is unique for two significant reasons: (1) the $CpMo(NO)(CHCMe_3)$ units are associated very asymmetrically through bridging nitrosyl and alkylidene groups even though there are no apparent factors prohibiting symmetric association;[6] (2) a μ-η^1:η^2-NO group, being a 3-electron donor to one metal and a 2-electron donor to another, has never been observed.[7,8]

The intramolecular dimensions of the $Mo(\mu\text{-}\eta^1\text{:}\eta^2\text{-NO})Mo$ entity in **2** involve an elongated N–O linkage [1.296 (3) Å][9] which is

---

(1) Organometallic Nitrosyl Chemistry. 52. Part 51: Chin, T. T.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1992**, *11*, 913.

(2) (a) Legzdins, P.; Phillips, E. C.; Sánchez, L. *Organometallics* **1989**, *8*, 940 and references therein. (b) Dryden, N. H.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics*, in press.

(3) (a) For Mo, see: Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411. (b) For W, see: Bursten, B. E.; Cayton, R. H. *Organometallics* **1987**, *6*, 2004.

(4) Complete characterization of all complexes is provided as supplementary material.

(5) Crystals of **2** are orthorhombic of space group *Pcab*; $a = 17.836$ (2) Å, $b = 18.265$ (2) Å, $c = 13.198$ (2) Å; $Z = 8$. Crystals of **3a** are monoclinic of space group $P2_1/n$; $a = 9.328$ (2) Å, $b = 15.516$ (3) Å, $c = 15.188$ (2) Å, $\beta = 93.72$ (1)°; $Z = 4$. Both structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to $R = 0.027$, $R_w = 0.026$ for **2** and $R = 0.042$, $R_w = 0.037$ for **3a**. Full details of these analyses are provided as supplementary material.

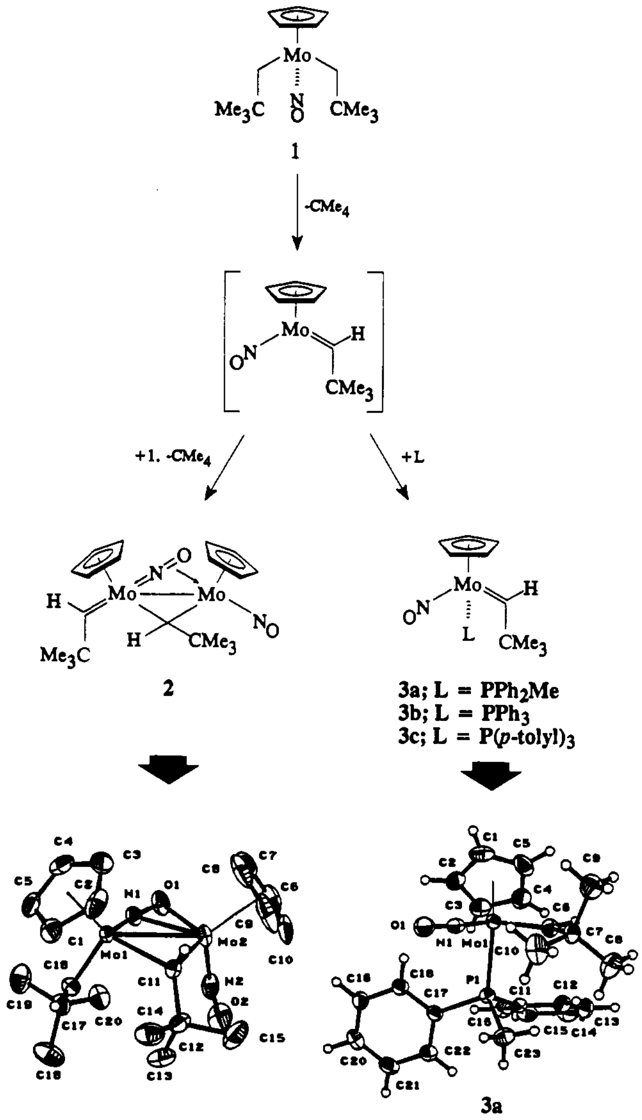
(6) Examples of complexes being associated symmetrically via two bridging alkylidene ligands,[6a] two conventionally bridging nitrosyl ligands,[6b] or multiple metal–metal bonds[6c] are well-known. For instance, see: (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135. (b) Calderón, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. W.; Iske, S. D. *J. Organomet. Chem.* **1974**, *64*, C10 and C16. (c) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610 and references therein.

(7) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; Chapter 2.

(8) Examples of μ-η^1:η^2-CO ligands have been documented; see: Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

0002-7863/92/1514-6922$03.00/0

Scheme I



essentially linear [Mo(1)–N(1)–O(1) = 165.5 (2)°] and is symmetrically disposed with respect to Mo(2) [Mo(2)–N(1) = 2.187 (3) Å and Mo(2)–O(1) = 2.149 (2) Å]. The spectroscopic properties of **2** confirm that the solid-state molecular structure persists in solution. Thus, its IR spectrum in CH_2Cl_2 exhibits terminal (1594 cm^{-1}) and bridging (1328 cm^{-1}) nitrosyl bands, and its ^1H and ^{13}C NMR spectra exhibit two sets of equal intensity Cp, CH, and CMe_3 resonances.[4]

The transformation of **1** into **2** is remarkable, but it also appears to be quite complex. Consistent with the transient formation of $CpMo(NO)({=}CHCMe_3)$ from **1**, thermolysis of **1** in the presence of phosphines, L, produces the adducts $CpMo(NO)({=}CHCMe_3)(L)$ [**3a**, L = PPh_2Me; **3b**, L = PPh_3; **3c**, L = P(*p*-tolyl)$_3$].[4,10] The intramolecular dimensions of **3a**,[5] as established by X-ray diffraction, resemble those exhibited by the related $[CpRe(NO)({=}CHPh)(PPh_3)]^+$ cation.[11]

The rate-determining formation of $CpMo(NO)({=}CHCMe_3)$ from **1** is supported by kinetic data. Thermolysis of $CpMo(NO)(CD_2CMe_3)_2$, **1**-d_4,[12] in the presence of trapping ligands, L, is cleanly first-order in **1** and zero-order in L. The decomposition of **1**-d_4 in CH_2Cl_2 at 40 °C in the presence of 3.56, 5.24, 10.17, or 13.64 equiv of PPh_2Me, 6.49 equiv of PPh_3, or 9.00 equiv of P(*p*-tolyl)$_3$ affords k_{obsd} values of $2.81 \pm 0.3 \times 10^{-4}$ s^{-1}. Additionally, an Eyring plot (15–45 °C) for the **1**-d_4 to **3a**-d_1 transformation yields values of $\Delta H^{\ddagger} = +79.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -14.4$ eu. These parameters imply the existence of a highly ordered transition state.[13]

Since the formation of $CpMo(NO)({=}CHCMe_3)$ is rate-determining, simple coupling of two molecules of $CpMo(NO)({=}CHCMe_3)$ is not a mechanistic path to **2**. Instead, the transient alkylidene monomer in all likelihood forms an adduct with a second molecule of **1**, which then eliminates neopentane and rearranges to produce **2**. Just why the dimer adopts such an asymmetric structure remains to be ascertained. The characteristic reactivity of the transient $CpMo(NO)({=}CHCMe_3)$ fragment with unsaturated organic entities capable of coupling with the alkylidene ligand is also currently being investigated.[14]

Acknowledgment. We are grateful to NSERC for support of this work and Prof. Malcolm Chisholm for providing us with a procedure for the preparation of Me_3CCD_2Br.

Supplementary Material Available: Experimental procedures and characterization of complexes **1–3** and full details of the crystal structure analyses including associated tables for **2** and **3a** (46 pages); tables of measured and calculated structure factor amplitudes for **2** and **3a** (52 pages). Ordering information is given on any current masthead page.

---

(9) For comparison, other long N–O bonds are as follows: (a) 1.247 (5) Å for the μ_3-NO of $Cp_3Mn_3(NO)_4$ (Elder, R. C. *Inorg. Chem.* **1974**, *13*, 1037); (b) 1.271 (7) Å for the μ_4-η^2-NO of a mixed Co/Mo cluster (Kyba, E. P.; Kerby, M. C.; Kashyap, R. P.; Mountzouris, J. A.; Davis, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 905); and (c) 1.47 (1) Å for $CpRe(PPh_3)(SiMe_2Cl)(NO{-}BCl_3)$ (Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 2885).

(10) To the best of our knowledge, complexes **3** are the first monomeric group 6 mononitrosyl Schrock-type alkylidene complexes to have been isolated. A few Fischer-type complexes are known, e.g.: (a) $CpCr(NO)(CO)({=}CPh_2)$. Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978. (b) $CpM(NO)(CO)({=}C(OMe)(Ph))$ (M = Cr, Mo, W). Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407.

(11) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

(12) Kinetic analyses were effected with **1**-d_4 since it is more thermally stable than **1** and hence more amenable to study. Its markedly increased thermal stability is also consistent with the view that its primary pathway for thermal decomposition involves α-H(D) elimination as the rate-determining step.

(13) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210 and references therein.

(14) For a recent example of this type of chemistry, see: Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383 and references therein.

Measurement of Long-Range ^{13}C–^{13}C J Couplings in a 20-kDa Protein–Peptide Complex†

Ad Bax,*,‡ David Max,§ and David Zax‖

Laboratory of Chemical Physics, National Institute
of Diabetes and Digestive and Kidney Diseases
National Institutes of Health
Bethesda, Maryland 20892
Magnex Scientific Ltd., 13–19 Blacklands Way
Abingdon, OX14 1DY, United Kingdom
Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853

Received April 1, 1992

^{13}C–^{13}C three-bond bond J couplings are important carriers of structural information and depend on dihedral angles in a manner similar to J_{HH} couplings.[1,2] At natural ^{13}C abundance, the long-range J_{CC} couplings are difficult to measure because the weak ^{13}C–^{13}C doublets of molecules with coupled ^{13}C nuclei are dwarfed by the nearly 200 times stronger signal from singlets of

---

† This paper is dedicated to Professor Ray Freeman, Cambridge University, on the occasion of his 60th birthday.

‡ National Institute of Diabetes and Digestive and Kidney Diseases.

§ Magnex Scientific Ltd.

‖ Cornell University.

(1) Karplus, M. *J. Phys. Chem.* **1959**, *30*, 11–15.

(2) Bystrov, V. F. *Prog. NMR Spectrosc.* **1976**, *10*, 41–81.

0002-7863/92/1514-6923$03.00/0