

out to several nanoseconds; the longest delay times overlap with the data shown in Figure 1. We believe this to be the strongest spectroscopic evidence to date for establishing the 5T_2 state as the "long-lived" excited state following photoperturbation of low-spin Fe^{II} complexes.

The analogous complex $[Fe(tptn)](ClO_4)_2$, where tptn is tetrakis(2-pyridylmethyl)-1,3-propylenediamine, has its 5T_2 excited state at a somewhat higher energy than the tpen complex. For this near-to-spin-crossover complex we find a $^5T_2 \rightarrow ^1A_1$ relaxation time of 1.6 ± 0.1 ns. Careful redeterminations of the $^5T_2 \rightarrow ^1A_1$ relaxation times of $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ in aqueous solution gave values at room temperature of 676 ± 30 and 687 ± 30 ps, respectively.

Definitive evidence for the sub-picosecond formation of the 5T_2 state following excitation to the 1MLCT state was obtained. Figure 2 shows a plot of ΔOD versus time for a 1.52×10^{-3} M aqueous solution of $[Fe(tpen)](ClO_4)_2$ measured in increments of 167 fs following excitation at 314 nm with a ~ 500 -fs laser pulse.⁸ It can be seen that the kinetics are essentially time-independent on this time scale, again establishing the presence of a single kinetic species over the time interval from ≤ 700 fs to ca. 1 μ s. Deconvolution of the data in Figure 2 reveals that the rise time of the transient bleach is indistinguishable from the instrumental response. This sets a lower limit on the rate of formation of the 5T_2 state of $\geq 1.5 \times 10^{12}$ s⁻¹. Identical results were obtained from studies on aqueous solutions of $[Fe(tptn)]^{2+}$, $[Fe(bpy)_3]^{2+}$, and $[Fe(phen)_3]^{2+}$.

The implication of these results for the mechanism of intersystem crossing can be understood as follows. The Fe-N stretching mode, which has been presumed to be involved in the dynamics of spin-state interconversion,^{1,9} has a frequency of ~ 380 cm⁻¹ for low-spin Fe^{II} and Fe^{III} and ~ 230 cm⁻¹ for high-spin Fe^{II} when bound to a pyridyl-based ligand system.¹⁰ These frequencies correspond to vibrational periods of ~ 88 and ~ 145 fs, respectively. Given the fact that excitation at 314 nm instills some 8000 cm⁻¹ of excess vibrational energy into the 1MLCT state of $[Fe(tpen)]^{2+}$ ($\lambda_{max} = 414$ nm), we conclude that the conventional picture¹⁻³ of vibrational cooling followed by internal conversion and intersystem crossing cannot be accurate in view of the rapid formation of the 5T_2 state. Rather, we suggest that intersystem crossing in low-spin Fe^{II} complexes proceeds via direct $^1MLCT \rightarrow ^5T_2$ conversion at or near the configuration of the Franck-Condon state following photoexcitation.¹¹ There is simply insufficient time for the system to relax in the charge-transfer state, undergo internal conversion to lower lying singlet ligand-field states, and then repeat the process through the $S = 1$ manifold to reach the 5T_2 state in ≤ 700 fs. Furthermore, the system must rapidly relax down the 5T_2 potential surface, spending appreciable time only in the lower energy vibrational levels, in order to achieve thermalization within the observed ~ 2 ps. An experimental probe for this mechanism would require excitation with a sufficiently short laser pulse at variable wavelengths so that the rise time of the 5T_2 state could be measured. If conversion occurs from the Franck-Condon state, we would anticipate that the observed rise time will be relatively independent of λ_{pump} . In any event, it seems clear that the excited-state dynamics of these systems is quite distinct from that observed in organic systems with respect to the relative rates of vibrational cooling and internal conversion/in-

tersystem crossing. We believe this to be a very general result for these types of transition-metal systems, and further details of our work will be reported elsewhere.¹²

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Mixed-Valence Lanthanum Titanium(III/IV) Oxosilicate $La_4Ti_9Si_4O_{30}$. A Novel Perrierite-Related Compound, $La_4Ti(Si_2O_7)_2(TiO_2)_{4m}$ ($m = 2$), with a Quasi-Two-Dimensional Rutile-Based Structure

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A novel oxo compound¹ with a quasi-two-dimensional (2D) structure is reported for the first time in the reduced first row early transition metal containing systems. The structural composition, $La_4Ti_9Si_4O_{30}$, reveals that this phase is a mixed-valence lanthanum titanium(III/IV) oxosilicate. The title compound may offer an opportunity for experimental and theoretical studies of the behavior of delocalized electrons in a confined lattice because of its quasi-two-dimensionality. Compounds with quasi-low-dimensional structures, such as the bronzes, show interesting anisotropic electrical and magnetic properties.² However, the weak interchain or interlayer electron interaction, due to a small separation gap, often complicates the interpretation of the observed physical phenomena. The newly discovered reduced oxosilicate compound may rectify this situation and shed light on the possibility of designing a new series of structural models for systematic studies of electrical conduction mechanisms.

The title compound possesses an interesting quasi-2D structure that is characterized by double layers of fused titanium(III/IV) oxide octahedral slabs. Until now, the synthesis of reduced titanium oxo compounds has led to the formation of mixed frameworks that consist of either isolated TiO_6 octahedra,³ face-sharing Ti_2O_9 double-octahedra,⁴ or pseudo-one-dimensional, edge-shared TiO_6 octahedral chains.⁵ In contrast, a large col-

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(1) By the term oxo compound, we mean phases that have quasi-one-dimensional chain or two-dimensional layer transition metal oxide structures which are preserved and isolated by closed-shell, nonmagnetic groups, such as silicate and phosphate anions. Structurally, the discovery of new families of oxosilicates as well as oxophosphates is significant because the preserved metal-oxygen-metal (M-O-M) and metal-metal (M-M) linkages are common features observed in metallic transition metal oxide frameworks and are deemed important to the mechanistic studies of the transport properties which are induced by conduction electrons.

(2) (a) Greenblatt, M. *Chem. Rev.* **1988**, *88*, 31-53. (b) Schlenker, C.; Dumas, J. *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures. A Chemical and Physical Synthetic Approach*; Rouxel, J., Ed.; D. Reidel Publishing Co.: Dordrecht/Boston/Lancaster/Tokyo, 1986; pp 135-177. (c) Banks, E.; Wold, A. *Preparative Inorganic Reactions*, Jolly, W. L., Ed.; Interscience: New York, 1968; Vol. 4, pp 237-268. (d) Hagenmuller, P. *Progress in Solid State Chemistry*, Reiss, H., Ed.; Pergamon: New York, 1971; Vol. 5, pp 71-44.

(3) (a) Wang, S.; Hwu, S.-J. *Chem. Mater.* **1992**, *4*, 589-595. (b) Wang, S.; Hwu, S.-J. *J. Solid State Chem.* **1991**, *92*, 219-226. (c) Wang, S.; Hwu, S.-J. *J. Solid State Chem.* **1991**, *90*, 377-381. (d) Wang, S.; Hwu, S.-J. *J. Solid State Chem.* **1991**, *90*, 31-41. (e) Benmoussa, A.; Borel, M. M.; Grandin, A.; Leclaire, A.; Raveau, B. *J. Solid State Chem.* **1990**, *84*, 299-307. (f) Leclaire, A.; Benmoussa, A.; Borel, M. M.; Grandin, A.; Raveau, B. *J. Solid State Chem.* **1989**, *78*, 227-231. (g) Leclaire, A.; Benmoussa, A.; Borel, M. M.; Grandin, A.; Raveau, B. *J. Solid State Chem.* **1988**, *77*, 299-305.

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(8) Sub-picosecond experiments were performed using a colliding-pulse mode-locked ring dye laser amplified at 10 Hz through a four-stage amplifier using a Q-switched, frequency-doubled Nd:YAG laser as previously described (Jongeward, K. A.; Magde, D.; Taube, D. J.; Marsters, J. C.; Traylor, T. G.; Sharma, V. S. *J. Am. Chem. Soc.* **1988**, *110*, 380). The system has been modified by the introduction of two prisms to partially compensate for group velocity dispersion through the amplifier chain, and the detector is now an amplified diode array (Princeton Instruments). The duration of the frequency-doubled excitation pulse ($\lambda = 314$ nm) is ~ 500 fs FWHM.

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(11) We believe that direct conversion from the Franck-Condon state to the 5T_2 state will occur regardless of the nature (i.e., 1MLCT , 1T , or 3T) of the initial excitation. However, we have not specifically examined this issue on the ultrafast time scale.

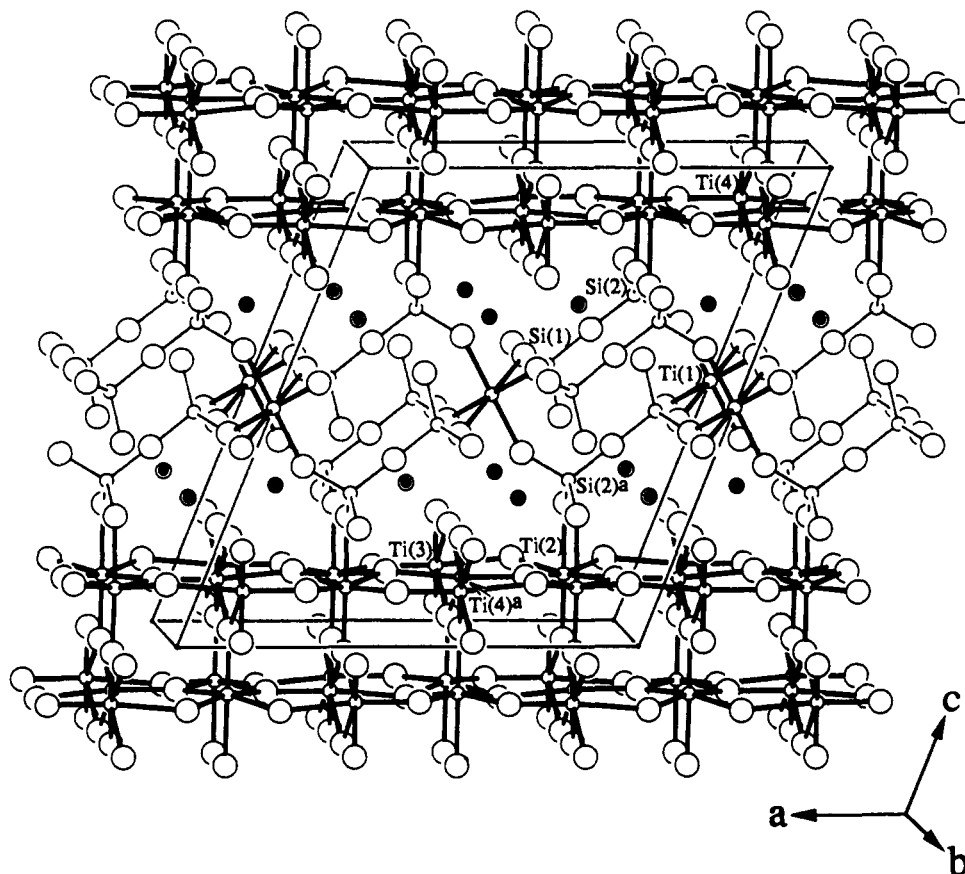


Figure 1. The structure of $\text{La}_4\text{Ti}_9\text{Si}_4\text{O}_{30}$ is viewed approximately along the b axis of the monoclinic unit cell, as outlined. All the octahedral coordinations in TiO_6 are represented by thick lines, tetrahedral coordinations in Si_2O_7 by thin lines. Small open circles represent titanium and silicon atoms and large open circles are for oxygen atoms, whereas small dotted and solid circles represent two asymmetric lanthanum atoms, La(1) and La(2), respectively. $a: \frac{1}{2} - x, \frac{1}{2} + y, 1 - z$.

lection of tungsten bronze-related,⁶ heavy transition metal phosphate compounds (mostly tungsten phosphates)⁷ have been reported with extended metal oxide frameworks. Compounds with extended lattices, such as in the title compound, have been rarely known in the first row early transition metal oxo systems. The reason is partly due to the difficulty encountered in phase nucleation when refractory oxides are incorporated, such as La_2O_3 , Ti_2O_3 , and SiO_2 in this case. Using molten halide fluxes, new materials that otherwise would only be prepared in polycrystalline form have been isolated as single crystals.⁸ In this paper we present the results of our molten salt synthesis and structural analysis of the reduced quasi-2D oxosilicate compound $\text{La}_4\text{Ti}_9\text{Si}_4\text{O}_{30}$.

Black, thin column crystals of $\text{La}_4\text{Ti}_9\text{Si}_4\text{O}_{30}$ were grown from a mixture of $\text{La}_2\text{O}_3/\text{Ti}_2\text{O}_3/\text{P}_2\text{O}_5$ (0.31:0.93:0.31 mmol). BaCl_2 salt was added to the reaction mixture as a flux in a mass ratio

of 5:1. The reaction was carried out in an evacuated, carbon-coated silica ampule and heated for 20 days at ca. 1100 °C.⁹ The crystal structure was determined by the single-crystal X-ray diffraction method.¹⁰

The $\text{La}_4\text{Ti}_9\text{Si}_4\text{O}_{30}$ structure can be viewed as alternately stacked slabs of titanium oxide and lanthanum titanium silicate. In Figure 1 the layered nature of the fused TiO_6 octahedral slabs is shown by the Ti–O bonds drawn in thick lines. The connectivity of the TiO_6 octahedra in these slabs is the same as that observed in the rutile (TiO_2) structure.¹¹ We will refer to these as rutile slabs hereafter. These rutile slabs are extended along the (001) plane by sharing common corners and opposite edges of the TiO_6 octahedra. The two parallel octahedral layers in each rutile slab are stacked along the [001] direction by sharing corner oxygens. The framework of the silicate slab is composed of one corner-shared TiO_6 octahedron per six Si_2O_7 pyrosilicate groups, ac-

(5) TiPO_4 : Kinomura, N.; Muto, F.; Koizum, M. *J. Solid State Chem.* **1982**, *45*, 252–258.

(6) Examples of tungsten bronzes: (a) Magnéli, A. *Acta Chem. Scand.* **1953**, *7*, 315–324. (b) Magnéli, A. *Ark. Kemi.* **1949**, *33*, 273–276. (c) Magnéli, A. *Ark. Kemi.* **1949**, *32*, 269–272. (d) Magnéli, A. *Ark. Kemi.* **1949**, *24*, 213–221.

(7) Examples of mono- and diphosphate tungsten bronzes and references cited therein: (a) Labbe, Ph.; Goreaud, M.; Raveau, B. *J. Solid State Chem.* **1986**, *61*, 324–331. (b) Domenges, B.; Hervieu, M.; Raveau, B. *J. Solid State Chem.* **1984**, *54*, 10–28. (c) Benmoussa, A.; Giroult, D.; Labbe, Ph.; Raveau, B. *Acta Crystallogr.* **1984**, *C40*, 573–576. (d) Labbe, Ph.; Ouachee, D.; Goreaud, M.; Raveau, B. *J. Solid State Chem.* **1983**, *50*, 163–172. (e) Giroult, J. P.; Goreaud, M.; Labbe, Ph.; Raveau, B. *Acta Crystallogr.* **1982**, *B38*, 2342–2347. (f) Giroult, J. P.; Goreaud, M.; Labbe, Ph.; Provost, J.; Raveau, B. *Mater. Res. Bull.* **1981**, *16*, 811–816. (g) Lamire, M.; Labbe, Ph.; Goreaud, M.; Raveau, B. *J. Solid State Chem.* **1987**, *71*, 342–348.

(8) (a) Levin, E. M.; Robbins, C. R.; McMurdie, H. F. *Phase Diagram for Ceramists*; The American Ceramic Society: Columbus, OH, 1969; Vol. II. (b) Other examples: (i) $\text{Ba}_2\text{Nb}_2\text{Si}_4\text{O}_{17}$, Serra, D. L.; Hwu, S.-J. *J. Solid State Chem.* **1992**, in press. (ii) CaYb_2S_4 , Carpenter, J. D.; Hwu, S.-J. *J. Solid State Chem.* **1992**, *97*, 332–339.

(9) Single crystals of the title compound (~10% yield) were isolated by washing the reaction products with deionized water, using a suction filtration method. Qualitative chemical analysis by energy dispersive spectroscopy using a Cameca SX-50 was performed on the data crystal and showed three cationic elements, La, Ti, and Si. The source of silicon is the reaction ampule.

(10) The $\text{La}_4\text{Ti}_9\text{Si}_4\text{O}_{30}$ oxosilicate crystallizes in a monoclinic unit cell ($C2/m$), $a = 13.542$ (8) Å, $b = 5.750$ (3) Å, $c = 15.186$ (3) Å, $\beta = 110.94$ (2)°, $V = 1104.5$ (9) Å³, $Z = 2$. A total of 1401 reflections ($2\theta_{\text{max}} = 55^\circ$) were collected (at room temperature) from two octants ($+h, +k, \pm l$), of which 1214 reflections with $I > 3\sigma(I)$ were used for the structural determination. An absorption correction was applied based upon three azimuthal scans ($2\theta = 14.20^\circ, 14.49^\circ, 28.62^\circ$). The structural and thermal parameters were refined by full-matrix least-squares methods to $R = 0.027$, $R_w = 0.035$, and $\text{GOF} = 1.34$ based on F with 129 variables. Total asymmetric atoms is nineteen, including two lanthanum, four titanium, two silicon, and eleven oxygen atoms.

(11) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1984; pp 247–252. As in the rutile structure, the TiO_6 octahedra are oriented as such that their pseudo-four-fold axes are alternately perpendicular and parallel to the ab plane. In turn, each oxygen anion in the rutile layer has three coplanar titanium cation near neighbors.

companied with four lanthanum atoms (in two asymmetric LaO_8 polyhedra) to give rise to the structural formula $[\text{La}_4\text{Ti}(\text{Si}_2\text{O}_7)_2] \equiv [\text{La}_4\text{Ti}(\text{Si}_2\text{O}_7)_{6/3}]$. 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, $178.9 (5)^\circ$, 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 $\text{La}_4\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{TiO}_2)_{4m}$ 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)O₆ octahedra and the Si(2)O₄ 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., $\text{La}_8\text{-Ti}(1)^{\text{IV}}_2\text{Ti}(2)^{\text{III}}_8\text{Ti}(3)^{\text{IV}}_4\text{Ti}(4)^{\text{IV}}_4\text{Si}_8\text{O}_{60} \equiv 2\text{-}(\text{La}_4\text{Ti}_9\text{Si}_4\text{O}_{30})$. 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 $\text{Ti}^{3+}\text{-Ti}^{3+}$ bonding pair) or delocalized throughout the rutile slab.¹⁴

It is intriguing to look into the possibility of developing a new series of $\text{La}_4\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{TiO}_2)_{4m}$ compounds with various sized rutile slabs. The presently studied structure is related to that of perrierite. In the mineral perrierite, $\text{La}_4\text{Mg}_2\text{Ti}_3\text{Si}_4\text{O}_{22}$,¹⁵ the structural formula can be written as $\text{La}_4\text{Mg}(\text{Si}_2\text{O}_7)_2(\text{Mg}_{0.25}\text{-Ti}_{0.75}\text{O}_2)_4$, where a single-layer rutile slab of mixed TiO₆ and MgO₆ octahedra is observed. The separation of the rutile slabs is dictated by the similar arrangement of the $\text{La}_4\text{M}(\text{Si}_2\text{O}_7)_2$ ($\text{M} = \text{Ti}$ 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.

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(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. $s = \exp[-(R - R_0)/\beta]$; $R_0(\text{Ti}^{\text{III/IV}}) = 1.823$ Å and $\beta = 0.324$.

(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 superconducting cuprate $\text{YBa}_2\text{Cu}_3\text{O}_7$.

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(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 TiO₂ structure. Note that by using this formula the calculated *c* lattice constant for the perrierite structure (with $\beta = 113.88^\circ$, ref 15a) is the same as the observed value, 11.79 Å.

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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.

A Unique $\mu\text{-}\eta^1\text{:}\eta^2\text{-NO}$ Ligand in a Bimetallic Alkylidene Nitrosyl Complex of Molybdenum¹

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In general, 16-electron $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ complexes [$\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ (Cp) or $\eta^5\text{-C}_5\text{Me}_5$ (Cp^*); $\text{M} = \text{Mo}$ or W ; $\text{R} = \text{alkyl}$ 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 $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ species, namely, $\text{CpMo}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ (**1**), which transforms to the unprecedented complex $[\text{CpMo}(\text{NO})](\mu\text{-}\eta^1\text{:}\eta^2\text{-NO})(\mu\text{-CHCMe}_3)[\text{CpMo}(\text{=CHCMe}_3)]$ (**2**) (Scheme 1).

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 $\text{CpMo}(\text{NO})(\text{CHCMe}_3)$ whose structure is unique for two significant reasons: (1) the $\text{CpMo}(\text{NO})(\text{CHCMe}_3)$ units are associated very asymmetrically through bridging nitrosyl and alkylidene groups even though there are no apparent factors prohibiting symmetric association;⁶ (2) a $\mu\text{-}\eta^1\text{:}\eta^2\text{-NO}$ 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 $\text{Mo}(\mu\text{-}\eta^1\text{:}\eta^2\text{-NO})\text{Mo}$ 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 $\mu\text{-}\eta^1\text{:}\eta^2\text{-CO}$ ligands have been documented; see: Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* 1984, 23, 219.