needles upon standing 24 h at room temperature (Scheme II). Very fast reaction was observed in boiling THF. A similar fate was observed for the pyridine complex **4**, whose royal blue solutions turned brown at room temperature within 24 h, forming olive green needles of $TiCl_3(py)_3$ upon cooling. Complex **3** decomposes only slowly in boiling toluene. Conversely, complex **5** and the mixed-valence species **1** are thermally robust and can be refluxed in THF for several days without observing any appreciable decomposition. That **1** is a Ti(II)/Ti(III) mixed-valence species has been indicated by its quantitative formation from $TiCl_3(THF)_3$ with $TiCl_2(TMEDA)_2$ (1:1 ratio). In accordance, chemical degradation of **1** with pyridine gave a mixture of olive green $TiCl_3(py)_3$ and royal blue $TiCl_2(py)_4$, which have been identified after fractional crystallization. While the 1:1 ratio has been confirmed by analytical data,[16] the dimeric structure has been tentatively assigned on the basis of the close similarities with the results obtained in the chemistry of analogous vanadium derivatives.[12b] Satisfactory elemental analyses have been obtained for all the complexes.[16]

The low value of the magnetic moment of **1**[16] is consistent with the presence of one unpaired electron per demeric unit. The ESR spectrum at X-band frequency at 295 K showed an isotropic spectrum characteristic of an octahedral species $S = {}^1/_2$ (g = 1.9384), and the g anisotropy observed at 77 K ($g_\perp$ = 1.9485, $g_\parallel$ = 1.9264) confirmed that the complex has an axial symmetry.[17] These observations suggests also that a strong Ti···Ti interaction (probably bonding) may be present in complex **1**. With the only exception of **5**, which is diamagnetic, the other complexes are paramagnetic, with values of μ_{eff}[16] as expected for a high-spin d^2 electronic configuration.

The general tendency of **2** to take part in aggregation reactions with MX_n species (M = Al, Zn, Mg, Ln; X = Cl, Me, Et, OR, H) is at present under investigation in view of its relevance to Ziegler–Natta modeling studies.

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Supplementary Material Available: Text giving experimental details for the preparation of all the complexes and listings of crystallographic details, atomic positional and thermal parameters, anisotropic thermal parameters, and complete bond distances and angles (6 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(16) Analytical data are as follows. **1**: brown, 95%, μ_{eff} = 0.75 μ_B per Ti atom. Anal. Calcd (found) for $C_{12}H_{32}N_4Cl_5Ti_2$: C, 28.48 (28.87); H, 6.33 (6.28); N, 11.07 (10.52); Cl, 35.11 (34.97); Ti, 18.99 (18.45). **2**: light violet, 68%, μ_{eff} = 2.64 μ_B. Anal. Calcd (found) for $C_{12}H_{32}N_4Cl_2Ti$: C, 40.99 (40.77); H, 9.11 (9.06); N, 15.94 (15.87); Cl, 20.21 (20.21); Ti, 13.66 (13.48). **3**: pink, 75%, μ_{eff} = 2.57 μ_B. Anal. Calcd (found) for $C_{10}H_{28}N_4Cl_2Ti$: C, 37.15 (37.01); H, 8.67 (8.55); N, 17.33 (17.27); Cl, 21.98 (21.89); Ti, 14.86 (14.83). **4**: royal blue, 80%, μ_{eff} = 2.67 μ_B. Anal. Calcd (found) for $C_{20}H_{20}N_4Cl_2Ti$: C, 55.17 (55.14); H, 4.59 (4.49); N, 12.87 (12.84); Cl, 16.32 (16.24); Ti, 11.03 (10.90). **5**: deep blue, 84%, diamagnetic. Anal. Calcd (found) for $C_{20}H_{18}N_4Cl_2Ti$: C, 55.42 (55.31); H, 4.16 (4.09); N, 12.93 (12.88); Cl, 16.39 (16.27); Ti, 11.08 (11.01).

(17) ESR spectra of **1** were recorded in the solid state by using the following instrument settings: ν = 9.34 GHz; microwave power 2 mW; field modulation amplitude 0.1 G.

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Activated Molybdenum–Molybdenum Quadruple Bonds. 2. First Example of Alkyne Additions to Metal–Metal Quadruple Bonds

Quadruply-bonded dimetal complexes have been known for more than 26 years;[1] however, their use in activation of alkynes and other small molecules has received little attention.[2–6] Previously, we reported that ethylenediamine (en) solutions of $Mo_2(O_2CMe)_4$ (**1**) produced an "activated" quadruply-bonded dimolybdenum dication, $[Mo_2(en)_4(O_2CMe)_2]^{2+}[(O_2CMe)_2]^{2-}\cdot en$, that showed unusual reactivity toward a variety of inorganic and organic substrates.[7,8] As a continuation of these studies, we describe here the first alkyne derivatives of a metal–metal quadruply-bonded complex.[9] The alkyne ligands in these compounds are thermally hydrogenated and extruded as alkenes via an unusual amine-to-alkyne hydrogen-transfer reaction.

Addition of the terminal aryl alkynes 4-$RC_6H_4C{\equiv}CH$ (R = H, Me, *i*-Pr) to en solutions of $Mo_2(O_2CMe)_4$ at room temperature affords the alkyne adducts **2** (R = H), **3** (R = Me), and **4** (R = *i*-Pr) of empirical formula $[Mo_2(\mu\text{-}4\text{-}RC_6H_4CCH)(\mu\text{-}O_2CMe)(en)_4{}^{3+}][O_2CMe^-)_3]\cdot 2en$. The three compounds are formed in two isomeric configurations, **a** and **b**, in approximately a 1:1 ratio (eq 1), as determined by ^1H and ^{13}C NMR spectroscopy.[10] Newman projections of the two isomers viewed down the Mo–Mo bonds are shown as follows:

$$Mo_2(O_2CMe)_4 + 4\text{-}RC_6H_4C{\equiv}CH \xrightarrow{en} \mathbf{a} + \mathbf{b} \qquad (1)$$

R = H, **2a** and **2b**
R = Me, **3a** and **3b**
R = *i*-Pr, **4a** and **4b**

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(10) To an orange-red solution of **1** (90 mg, 0.21 mmol) in en (anhydrous, 2 mL) was added 4-$MeC_6H_4C{\equiv}CH$ (29 mg, 0.25 mmol), producing an immediate color change to dark red. After several days, red-purple crystals of **3a** and **3b** coprecipitated and were dried in vacuo (74 mg; 44%, based on **1**). The same procedure is used for the synthesis of **2a**, **2b**, **3a**, and **3b**. Selected NMR data for an appropriate equimolar mixture of **2a** and **2b** are as follows. ^1H NMR (DMSO-d_6, 25 °C): δ 8.44 (s, 1 H), 7.13 (s, 1 H) ($C_6H_5CC\mathit{H}$); δ 7.34 (t, J = 7.5 Hz, 2 H, meta); δ 7.22 (d, J = 7.7 Hz, 2 H, ortho); δ 7.13 (t, J = 7.0 Hz, 1 H, para); δ 7.26 (t, J = 7.6 Hz, 2 H, meta); δ 7.02 (t, J = 7.1 Hz, 1 H, para); δ 6.99 (d, J = 8.0 Hz, 2 H, ortho) ($C_6\mathit{H}_5CCH$). ^{13}C NMR (DMSO-d_6, 25 °C): δ 141.5, 127.2 ($C_6H_5C\mathit{C}H$). Selected spectroscopic data for an approximate equimolar mixture of **3a** and **3b** are as follows. ^1H NMR (DMSO-d_6, 25 °C): δ 8.40 (s, 1 H), 7.10 (s, 1 H) (4-$MeC_6H_4CC\mathit{H}$); δ 7.16 (d, J = 8 Hz, 2 H), 7.12 (d, J = 8 Hz, 2 H), 7.09 (d, J = 8 Hz, 2 H), 6.90 (d, J = 8 Hz, 2 H) (4-$MeC_6\mathit{H}_4CCH$); δ 2.39 (s, 3 H), 2.34 (s, 3 H) (4-$\mathit{Me}C_6H_4CCH$). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 141.6, 127.3 (4-$MeC_6H_4C\mathit{C}H$). Molar conductivity (DMSO, 25 °C): 32 Ω^{-1} cm^2 M^{-1}. Anal. Calcd for $C_{29}H_{68}N_{12}O_8Mo_2$: C, 38.50; H, 7.57; N, 18.58. Found: C, 38.64; H, 7.85; N, 19.68. Selected NMR data for an approximate equimolar mixture of **4a** and **4b** are as follows. ^1H NMR (DMSO-d_6, 25 °C): δ 8.48 (s, 1 H) (4-*i*-$PrC_6H_4CC\mathit{H}$); δ 7.2 (m, 7 H) (4-*i*-$PrC_6\mathit{H}_4CCH$ and [4-*i*-$PrC_6H_4CC\mathit{H}$]; δ 6.93 (d, J = 8 Hz, 2 H) (4-*i*-$PrC_6\mathit{H}_4CCH$); δ 1.22 (d, J = 9 Hz, 6 H), 1.20 (d, J = 9 Hz, 6 H) (4-*i*-$\mathit{Pr}C_6H_4CCH$). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 25.4, 23.9 (4-*i*-$\mathit{Pr}C_6H_4CCH$).

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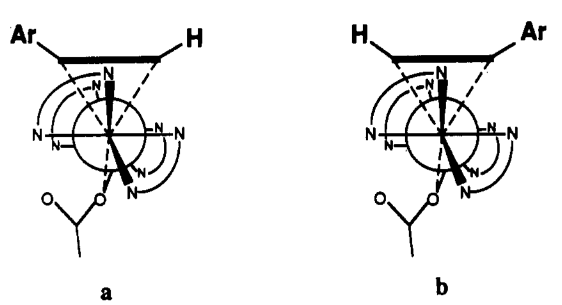

Ar = C_6H_5, 4-MeC_6H_4, 4-i-PrC_6H_4

The molecular structure of the $Mo_2(\mu$-4-$MeC_6H_4CCH)(\mu$-$O_2CMe)(en)_4{}^{3+}$ ion of **3b** is shown in Figure 1. The isomers cocrystallize from solution, also in a ca. 1:1 ratio, as determined by ^{13}C labeling studies, solid-state ^{13}C CP/MAS NMR spectroscopy, and single-crystal X-ray diffraction studies (vide infra). Thus far, it has not been possible to separate **a** from **b** in bulk by fractional crystallization for any set of alkyne adducts, although a single crystal picked from a crystalline mixture identified **3b**. Because of the small size of the individual single crystals, we have been unable to establish which set of NMR resonances corresponds to the structurally characterized isomer **3b** at this time. The air-sensitive, dark maroon compounds are insoluble in nonpolar solvents but are soluble in H_2O, methanol, ethanol, and DMSO.

Isomers **a** and **b** are formed competitively in a kinetically controlled reaction and do not interconvert in DMSO-d_6 at an observable rate at 25 °C. These conclusions are based on the observation that one isomer completely decomposes at 60 °C in DMSO-d_6 after 5 min whereas the other isomer persists for several hours under these conditions. If the solution that is depleted in the more reactive isomer is cooled to 25 °C, reappearance of the thermalized isomer is not observed after 2 days (i.e. no equilibration). To verify that **a** and **b** cocrystallize and are not generated in solution from a common crystalline isomer, the solid-state ^{13}C CP/MAS NMR spectrum was recorded for a polycrystalline sample of **2a** and **2b** containing ^{13}C-enriched $C_6H_5C{\equiv}{}^*CH$. The spectrum shows two broad, equal-intensity resonances at 142.0 and 129.4 ppm, corresponding to the two C_6H_5CCH ^{13}C absorptions observed in solution at δ = 141.5 and 127.2 ppm, thus confirming the presence of the two isomers in the solid state.

The NMR spectra of 1:1 mixtures of **2a** and **2b** in DMSO-d_6 exhibit two equal-intensity sets of resonances. Two $C_6H_5CC\mathit{H}$ ^1H NMR resonances are observed at δ = 8.44 and 7.13 ppm (J_{C-H} = 199 and 192 Hz, respectively) as well as two $C_6H_5C\mathit{C}H$ ^{13}C NMR resonances at δ = 141.5 and 127.2 ppm (see Figure 2, supplementary material). These data are within the ranges observed for d^1–d^1 dinuclear complexes of tungsten and molybdenum with perpendicular alkyne bridging ligands;[11] thus, anisotropies associated with the partial Mo–Mo double-bond character in the present compounds do not appear to significantly alter the spectroscopic properties of the alkyne ligands. The ^{13}C NMR and ^1H NMR spectra for compounds **3a**, **3b**, **4a**, and **4b** are quite similar to those of **2a** and **2b**, respectively, suggesting that the isomers are mutually isostructural.[10] Moreover, the similarities between the solid-state and solution spectra suggest the core structure of the $[Mo_2(\mu$-$C_6H_5CCH)(\mu$-$O_2CMe)(en)_4]^{3+}$ ion is maintained in DMSO-d_6.

The structure[12] of the $[Mo_2(\mu$-4-$MeC_6H_4CCH)(\mu$-$O_2CMe)(en)_4]^{3+}$ ion of **3b** (Figure 1) contains an edge-shared bioctahedral M_2L_{10} core in which the μ-alkyne ligand occupies a single coordination site at each metal. The ion has no rigorous symmetry but contains a virtual mirror plane defined by C(1), C(2), and O(1). The η^1-acetate ligand symmetrically bridges the two metals with Mo–O distances of 2.15 (1) Å (average). The carbonyl oxygen O(2) is hydrogen bonded to N(4), as evidenced by the 2.87 (4)-Å N···O contact. Six of the eight Mo–N distances are similar at 2.24 (2) Å (average), whereas the two Mo–N contacts involving N(2) and N(6) (trans to the μ-alkyne ligand) appear to be somewhat longer at 2.30 (2) Å (average).

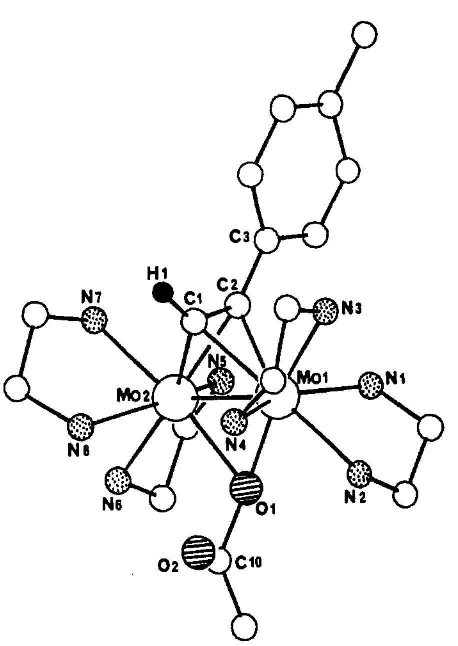

Figure 1. Chem-X[18] view of the trication $[Mo_2(\mu$-4-$MeC_6H_4CCH)(\mu$-$O_2CMe)(en)_4]^{3+}$. For clarity, the carbon atoms of the ethylene backbone on the en ligands are not labeled. Selected bond distances (Å): Mo(1)–Mo(2), 2.486 (3); Mo(1)–C(1), 2.07 (2); Mo(1)–C(2), 2.15 (2); Mo(2)–C(1), 2.09 (2); Mo(2)–C(2), 2.11 (2); C(1)–C(2), 1.39 (2); Mo(1)–N(1), 2.25 (1); Mo(1)–N(2), 2.32 (1); Mo(1)–N(3), 2.24 (2); Mo(1)–N(4), 2.23 (1); Mo(2)–N(5), 2.23 (1); Mo(2)–N(6), 2.28 (2); Mo(2)–N(7), 2.23 (1); Mo(2)–N(8), 2.23 (1); Mo(1)–O(1), 2.15 (1); Mo(2)–O(1), 2.15 (1); O(1)–C(10), 1.43 (3); O(2)–C(10), 1.29 (3). Selected bond angles (deg): N(2)–Mo(1)–N(4), 76.8 (5); N(3)–Mo(1)–N(4), 76.7 (5); N(1)–Mo(1)–N(4), 146.5 (5); O(1)–Mo(1)–N(3), 170.6 (5); O(1)–Mo(2)–N(7), 168.7 (5); N(5)–Mo(2)–N(8), 147.2 (5); N(6)–Mo(2)–N(8), 77.1 (5); N(5)–Mo(2)–N(6), 75.1 (5); O(1)–C(10)–O(2), 112 (2); C(1)–C(2)–C(3), 134 (2).

The Mo–Mo distance in **3b** of 2.486 (3) Å is indicative of a Mo–Mo double bond [cf. $Mo_2(O$-i-$Pr)_8$; Mo–Mo = 2.523 (a) Å].[2,13] In addition, the C(1)–C(2) distance of 1.39 (2) Å is consistent with a highly reduced alkyne fragment similar to that observed in $Mo_2(\mu$-$C_2H_2)(O$-i-$Pr)_6(py)$ [C–C = 1.37 (1) Å].[14,15] Thus, the complex can be viewed as a composite of a d^2–d^2 $Mo_2{}^{8+}$ fragment with a "four-minus" alkyne ligand. The edge-shared bioctahedral geometry observed in **3b** apparently reflects the optimization of metal–alkyne and metal–metal bonding in a Mo_2 d^2–d^2 system.[19]

All of the acetate counterions in the crystal lattice are hydrogen bonded to either the amine hydrogens of the chelating en ligands or the en solvate molecules. Extensive hydrogen bonding was also observed in $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]$·en (**5**).[8] Conductivity studies on 1:1 mixtures of **3a** and **3b** in DMSO (32 Ω^{-1} cm^2 mol^{-1}) are indicative of a 1:1 electrolyte, suggesting that tight ion pairing of the acetate counterions persists in solution.[16] Clearly, solvation effects and hydrogen bonding play an important role in the formation of **2–5** and greatly influence their molecular structures.[8,17]

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(12) The crystal used in the X-ray study was arbitrarily selected from a bulk crystalline sample containing mixtures of **3a** and **3b**. Crystal data for **3b** at −120 °C: a = 14.870 (9) Å, b = 17.48 (1) Å, c = 16.42 (1) Å, β = 104.82 (5)°, Z = 4, d_{calcd} = 1.456 g cm^{-3}, and space group $P2_1/n$. Of the 5606 unique reflections (Mo Kα, 6° ≤ 2θ ≤ 45°), 1927 reflections with $I > 3\sigma(I)$ were used in the full-matrix least-squares refinement. Final residuals are $R(F)$ = 0.066 and $R_w(F)$ = 0.070.

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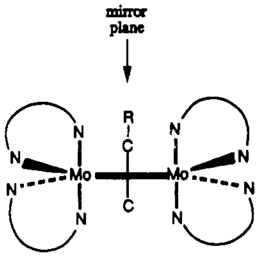
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the 4-*i*-Pr derivatives **4a** and **4b** clearly show that the alkyne ligands of both isomers reside on a mirror plane of symmetry that renders the *i*-Pr methyl groups equivalent (i.e. they are nondiasteroscopic).[10] This observation, coupled with the similarities in thermal reactivities and spectroscopic properties of the two isomers, suggests that the structure of **a** differs from that of **b** by a 180° twist of the alkyne ligand about the $Mo_2(en)_4$ core. The proposed relationship between **a** and **b** is shown by I and II, respectively, (μ-O_2CMe omitted). The alternative structure III can be discounted due to the absence of a mirror plane, which is inconsistent with data just described. Attempts to structurally characterize isomer **a** are currently in progress.



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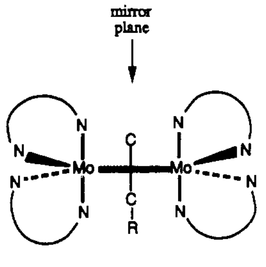

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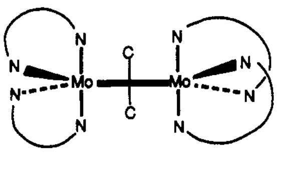

III

Preliminary thermolysis studies (anhydrous DMSO-d_6, 100 °C) have shown that the coordinated alkynes of both isomers of **2**–**4** are hydrogenated exclusively to alkenes ($4\text{-}RC_6H_4CH{=}CH_2$, where R = H, Me, and *i*-Pr) via a net amine-to-alkyne hydrogen-transfer reaction. Free alkenes are the only phenyl-containing products observed in solution after thermolysis. The fate of the inorganic components of this reaction are not known at present, but spectroscopic studies are strongly suggestive of a d^3–d^3 $Mo_2(NHCH_2CH_2NH_2)_2$ bis(amido) complex.

The formation of the $[Mo_2(\mu\text{-}4\text{-}RC_6H_4CCH)(\mu\text{-}O_2CMe)(en)_4]^{3+}$ ion from en solutions of $Mo_2(O_2CMe)_4$ represents the first example of an alkyne addition to a metal–metal quadruple bond. In addition to the steric and electronic factors that govern the alkyne chemistry at the alkoxide-supported $M{\equiv}M^{6+}$ centers,[11,14] solvation effects and hydrogen bonding play an important role in the structures and reactivities of the present compounds. Mechanistic investigations of this unusual hydrogen-transfer process are currently in progress.

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Supplementary Material Available: Complete tables of crystallographic data, fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles and figures showing an ORTEP drawing and an NMR spectrum (Figure 2) (26 pages); a listing of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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