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Further Studies on the Substitutional Behavior of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$. Alkyl, Amide, Phosphide, Alkoxide, and Thiolate for Bromide Exchange and Isomerizations of 1,1- and 1,2-$Mo_2X_2(CH_2SiMe_3)_4$ Compounds[†]

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Reactions involving 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ and each of $LiNMe_2$ and $HNMe_2$ in hexane at −50 °C proceed to give 1,1′-$Mo_2(NMe_2)BrR_4$, where $R = CH_2SiMe_3$, as the first product of Br for amide exchange at the Mo_2^{6+} center. Further substitution in reactions with $LiNMe_2$ gives 1,1-$Mo_2(NMe_2)_2R_4$, but with $HNMe_2$ the 1,2-$Mo_2(NMe_2)_2R_4$ isomer is formed. These two do not interconvert thermally (>100 °C) and undergo aminolysis ($HNMe_2$-d_6) and alcoholysis (^tBuOH) with retention of regiochemistry. 1,1- to 1,2-isomerization of $Mo_2(NMe_2)_2R_4$ is catalyzed by the presence of Me_2NH_2Br. The mechanisms of these metathetic reactions are discussed in terms of plausible pathways that may promote alkyl group migration across the Mo≡Mo bond. Further studies of the bromide substitution by alkyl, aryl, alkoxide, thiolate, and phosphide ligands are described for 1,1′-$Mo_2(NMe_2)BrR_4$ and 1,2-$Mo_2Br_2R_4$. The new compounds of formula $Mo_2(NMe_2)YR_4$ ($Y = CH_2SiMe_3$, Ph, O^tBu, O^iPr, S^tBu, PPh_2, and Br) and $Mo_2(S^tBu)_2R_4$ have been characterized by variable-temperature ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry and for $Y = PPh_2$ by single-crystal X-ray crystallography.

Introduction

Insight into the formation and rupture of carbon−element bonds has allowed the rapid and remarkable developments in total synthesis of natural[1] and unnatural products[2] in organic chemistry. The reaction mechanisms of metal−ligand bond formation and rupture (or exchange) are by far less well understood. In part, this is a natural consequence of the wide variety of metal ions and ligands and the nature of the medium in which they may be present.[3] For example, despite their utility[4a] the nature of organolithium reagents is still poorly understood with respect to solvation and complexing reagents.[4b,c,d] Our best understanding of metal−ligand bond-forming and exchange reactions involves so-called "inert" complexes such as simple mononuclear 18-electron organometallic complexes, e.g., $M(CO)_5$, where M = Fe, Ru, or Os,[5] and $t_{2g}{}^6$ ML_6 octahedral complexes, which include the classical Werner complexes of Co(III).[6] Also the substitution chemistry for d^8 square-planar ML_4 complexes,[7] in particular those of Pt(II) which are relatively slow, have been extensively studied.

Few mechanistic studies have been undertaken on dinuclear complexes, and no simple trend has emerged. For example, for $M_2(CO)_{10}$ compounds (M = Mn, Re) carbonyl exchange may occur by two limiting situations which are independent of the entering ligand, namely, M−M bond homolysis or M−CO bond dissociation, and in some cases both of these processes may contribute to the overall rate.[8] There may, in addition, be a

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[†] Dedicated to Professor R. A. Walton on the occasion of his 60th birthday.

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dependence on the entering ligand. M_2X_6 compounds (M = Mo or W, and X = a uninegative ligand such as alkyl, amide, alkoxide) that contain an ethane-like $E_3M{\equiv}ME_3$ core (E = C, N, O, etc.) exhibit numerous substitution and exchange reactions, but little is known of the intimate mechanism by which metal–ligand bonds are formed and broken.[9] Some time ago, we noted that Br-for-NMe_2 substitution in 1,2-$Mo_2Br_2R_4$ could give either 1,1- or 1,2-$Mo_2(NMe_2)_2R_4$ products (R = CH_2SiMe_3) and furthermore that these isomers were persistent or inert to isomerization once formed.[10] Studies of the substitution chemistry of 1,2-$Mo_2Br_2R_4$ were impeded at that time because of the difficulties in obtaining significant quantities of its precursor complex $Mo_2(CH_2SiMe_3)_6$, a compound originally prepared by Wilkinson from the reaction between $MoCl_5$ and $LiCH_2SiMe_3$.[11] With the advent of an improved synthesis of $Mo_2(CH_2SiMe_3)_6$, from $MoCl_3$(dme), where dme is dimethoxyethane,[12] we are now able to re-examine the fundamental substitution chemistry of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ and report here on further findings.

Experimental Section

All manipulations were carried out under an inert atmosphere of oxygen-free UHP-grade argon using standard Schlenk techniques or under a dry and oxygen-free atmosphere of nitrogen in a Vacuum Atmospheres Co. Dry Lab System. Hexane was degassed and distilled from sodium benzophenone ketyl under nitrogen. Pentane was degassed and distilled from calcium hydride under nitrogen. Toluene-d_8 was degassed and stored over 4 Å sieves for 24 h prior to use. Dimethylamine was purchased from Aldrich and used as received. Dimethylamine-d_6 was purchased from CDN Isotopes and was used as received. Addition of gases to reaction mixtures was done by using a calibrated gas vacuum manifold.

1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ was prepared according to a modified literature procedure.[10] Lithium salts were prepared by dropwise addition of ^nBuLi in hexanes (Aldrich) to a hexane solution of the appropriate reagent at or below 0 °C.

NMR spectra were obtained on 300 MHz Varian Gemini 2000, 400 MHz Varian ^{UNITY}Inova, or 400 MHz Varian VXR spectrometers. All ^1H NMR chemical shifts are reported in ppm relative to the ^1H impurity in toluene-d_8 at δ 2.09. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and placed in aluminum capsules in the glovebox prior to combustion. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Solid-state spectra were taken as Nujol mulls between KBr plates. Mass spectra were taken on a Kratos MS-80 high-resolution mass spectrometer using negative ion CI with methane (CH_4) as reagent gas.

Preparation of 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$. To a suspension of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ (0.100 g, 0.143 mmol) in pentane (15 mL) was added $HNMe_2$ (ca. 10 equiv) by use of a calibrated vacuum manifold. This led to rapid precipitation of $H_2NMe_2{}^+Br^-$. The solution was further stirred 2 h. Filtration through a medium glass frit with a Celite pad, followed by stripping the solvent, gave a yellow oil, which was identified as 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ by ^1H NMR spectroscopy: the spectrum was identical to that previously reported.[10] The $^{13}C\{^1H\}$ NMR spectrum was obtained at −20 °C in touene-d_8 and is reported here: δ 2.84 (s, Si*Me*$_3$), 3.29 (s, Si*Me*$_3$), 41.42 (s, distal *Me* of NMe_2 group), 44.59 (s, *C*H_2), 52.46 (s, *C*H_2), 57.88 (s, proximal *Me* of NMe_2 group).

Preparation of 1,1′-$Mo_2(NMe_2)(Br)(CH_2SiMe_3)_4$. To a suspension of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ (0.100 g, 0.143 mmol), in a 25 mL round-bottomed flask in pentane (15 mL) at 0 °C, was added $HNMe_2$ (ca. 10 equiv) over 5 min by use of a calibrated vacuum manifold. This led to the rapid precipitation of $H_2NMe_2{}^+Br^-$. The solution was further stirred 15 min with the last 5 min at room temperature. Filtration through a medium glass frit with a Celite pad, followed by stripping the solvent, gave a yellow liquid identified as 1,1′-$Mo_2(NMe_2)$(Br)$(CH_2SiMe_3)_4$ (>95% crude yield). NMR data were obtained in toluene-d_8 at ambient temperature. ^1H: δ 0.18 (s, Si*Me*$_3$, 9H), 0.21 (s, Si*Me*$_3$, 27H), 1.86 (d, C*H*$_2$, J_{H-H} = 11.7 Hz, 3H), 2.00 (d, C*H*$_2$, J_{H-H} = 12.3 Hz, 1H), 2.08 (d, C*H*$_2$, J_{H-H} = 11.7 Hz, 3H), 2.12 (d, C*H*$_2$, J_{H-H} = 12.3 Hz, 1H), 2.62 (s, distal *Me* on NMe_2 group), 3.61 (s, proximal *Me* on NMe_2 group, 3H). $^{13}C\{^1H\}$: δ 2.56 (s, Si*Me*$_3$, 9C), 2.88 (s, Si*Me*$_3$, 3C), 42.78 (s, distal *Me* of NMe_2 group), 48.99 (s, *C*H_2), 59.67 (s, proximal Me of NMe_2 group), 65.06 (s, *C*H_2). The observed *m*/*z* distribution for the 1,1′-$Mo_2(NMe_2)(Br)(CH_2SiMe_3)_4{}^+$ ion is in good agreement with the calculated *m*/*z* distribution. In both cases the molecular ion of maximum ion current was at 667 Da.

Preparation of 1,1′-$Mo_2(NMe_2)(Ph)(CH_2SiMe_3)_4$. To 1,1′-$Mo_2(NMe_2)(Br)(CH_2SiMe_3)_4$ (0.100 g, 0.149 mmol) was added PhLi (0.0125 g, 0.149 mmol) in a 25 mL round-bottomed flask. Hexane (15 mL) was added to the mixture at 0 °C, and the solution was stirred for 2 h while warming to ambient temperature. Filtration through a medium frit with a Celite pad gave a clear dark solution. Removing the solvent in vacuo gave a dark yellow liquid identified as 1,1′-$Mo_2(NMe_2)(Ph)(CH_2SiMe_3)_4$ in >90% crude yield as determined by ^1H NMR spectroscopy. NMR data were obtained in toluene-d_8. ^1H at 45 °C: δ 0.01 (s, Si*Me*$_3$, 27H), 0.13 (s, Si*Me*$_3$, 9H), 1.03 (d, C*H*$_2$, J_{H-H} = 12.3 Hz, 1H), 1.82 (d, C*H*$_2$, J_{H-H} = 11.4 Hz, 3H), 1.98 (d, C*H*$_2$, J_{H-H} = 11.7 Hz), 2.78 (d, C*H*$_2$, J_{H-H} = 12 Hz), 3.08 (br s, N*Me*$_2$, 6H), 7.09–7.77 (m, *Ph*, 5H). $^{13}C\{^1H\}$ at −45 °C: δ 2.43 (s, 3 Si*Me*$_3$), 3.10 (S, 1 Si*Me*$_3$), 34.81 (s, *C*H_2), 40.63 (s, distal *Me* of NMe_2 group), 48.31 (s, *C*H_2), 57.65 (s, proximal *Me* of NMe_2 group) 125–136 m, *Ph*). The observed *m*/*z* distribution for the 1,1′-$Mo_2(NMe_2)(Ph)(CH_2SiMe_3)_4{}^+$ ion is in good agreement with the calculated *m*/*z* distribution. In both cases the molecular ion of maximum ion current was at 662 Da.

Preparation of 1,2-$Mo_2(S^tBu)_2(CH_2SiMe_3)_4$. A mixture of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ (0.100 g, 0.143 mmol) and LiS^tBu (0.028 g, 0.286 mmol) was placed in a 25 mL round-bottomed flask. Hexane (20 mL) was added, and the solution was stirred for 5 h. Filtration through a medium glass frit with a Celite pad gave a clear red solution. Removing the solvent in vacuo gave a red crystalline solid identified as 1,2-$Mo_2(S^tBu)_2(CH_2SiMe_3)_4$. Alternatively, it is possible to obtain the product by crystallization from hexane (ca. 5 mL) at −20 °C in 70% yield. NMR data were obtained in toluene-d_8 at ambient temperature. ^1H: δ 0.36 (s, Si*Me*$_3$, 36H), 1.40 (s, *S*^{t}*Bu*, 9H), 1.81 (d, C*H*$_2$, J_{H-H} = 10.8 Hz, 4H), 2.65 (d, C*H*$_2$, J_{H-H} = 10.5 Hz). $^{13}C\{^1H\}$: δ 2.92 (s, Si*Me*$_3$, 12C), 36.31 (s, *S*^{t}*Bu*), 67.48 (s, CH_2, 4C). IR (cm^{-1}): 1459(s), 1377(m), 1364(m), 1363(w), 1256(m), 1244(s), 1154(m), 935(w), 880(m), 846(s), 741(m), 699(w), 681(w). The observed *m*/*z* distribution for the 1,2-$Mo_2(S^tBu)_2(CH_2SiMe_3)_4{}^+$ ion with loss of one *tert*-butyl group ($C(CH_3)_3$) is in good agreement with the calculated *m*/*z* distribution. In both cases the molecular ion of maximum ion current was at 662 Da. Anal. Calcd for $Mo_2S_2C_{24}H_{62}$: C, 40.09; H, 8.69; S, 8.92. Found: C, 39.34; H, 8.00; S, 8.58.

Preparation of 1,2-$Mo_2(S^tBu)(Br)(CH_2SiMe_3)_4$. To 1,2-$Mo_2Br_2R_4$ (0.100 g, 0.143 mmol) was added LiS^tBu (0.014 g,

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0.143 mmol) in a 25 mL round-bottomed flask. Hexane (20 mL) was added, and the solution was stirred for 1 h at ambient temperature. Filtration through a medium frit with a Celite pad gave a mixture of compounds: 1,2-$\mathrm{Mo_2Br_2R_4}$, 1,2-$\mathrm{Mo_2(S^tBu)BrR_4}$, and 1,2-$\mathrm{Mo_2(S^tBu)_2R_4}$. The characterization data of 1,2-$\mathrm{Mo_2Br_2R_4}$ and 1,2-$\mathrm{Mo_2(S^tBu)_2R_4}$ have been given previously. ^{1}H NMR data for 1,2-$\mathrm{Mo_2(S^tBu)BrR_4}$ obtained at −20 °C in toluene-d_8: δ 0.31 (s, $\mathrm{Si}Me_3$, 18H), 0.36 (s, $\mathrm{Si}Me_3$, 18H), 0.90 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 10.8$ Hz, 2H), 1.39 (s, S^tBu, 9H), 2.21 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 10.8$ Hz) 2.50 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 10.2$ Hz), 4.94 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.1$ Hz).

Preparation of 1,1′-$\mathbf{Mo_2(NMe_2)(S^tBu)(CH_2SiMe_3)_4}$. To 1,1′-$\mathrm{Mo_2(NMe_2)(Br)(CH_2SiMe_3)_4}$ (0.100 g, 0.149 mmol) was added $\mathrm{LiS^tBu}$ (0.0143 g, 0.149 mmol) in a 25 mL round-bottomed flask. Hexane (20 mL) was added, and the solution was stirred for 2 h at ambient temperature. Filtration through a medium frit with a Celite pad gave a clear dark solution. Removing the solvent in vacuo gave a dark yellow oil identified as 1,1′-$\mathrm{Mo_2(NMe_2)(S^tBu)(CH_2SiMe_3)_4}$ in >95% crude yield as determined by ^{1}H NMR spectroscopy. NMR data were obtained in toluene-d_8. ^{1}H at 40 °C: δ 0.19 (s, $\mathrm{Si}Me_3$, 9H), 0.23 (s, $\mathrm{Si}Me_3$, 27H), 0.50 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.7$ Hz, 1H), 1.38 (s, S^tBu, 9H), 1,81 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.1$ Hz, 3H), 2.19 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.4$ Hz, 3H), 2.98 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.7$ Hz, 1H), 3.24 (br s, $\mathrm{N}Me_2$, 6H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ at −60 °C: δ 2.32 (s, 3 $\mathrm{Si}Me_3$), 3.15 (s, 1 $\mathrm{Si}Me_3$), 37.46 (s, S^tBu), 42.49 (s, distal *Me* of $\mathrm{NMe_2}$ group), 43.47 (s, proximal *Me* of $\mathrm{NMe_2}$ group), 46.64 (s, $C\mathrm{H_2}$), 58.02 (s, $C\mathrm{H_2}$). The observed *m*/*z* distribution for the 1,1′-$\mathrm{Mo_2(NMe_2)(S^tBu)(CH_2SiMe_3)_4^+}$ ion is in good agreement with the calculated *m*/*z* distribution. In both cases the molecular ion of maximum ion current was at 674 Da.

Preparation of 1,2-$\mathbf{Mo_2(NMe_2)(PPh_2)(CH_2SiMe_3)_4}$. To a slurry of $\mathrm{LiPPh_2}$ (0.028 g, 0.142 mmol) in hexane (20 mL), in a 25 mL round-bottomed flask at −30 °C, was added 1,1′-$\mathrm{Mo_2(NMe_2)(Br)(CH_2SiMe_3)_4}$ (0.095 g, 0.142 mmol) in hexane (20 mL). The reaction mixture was stirred for 3 h and allowed to warm slowly to 0 °C. Filtration through a medium glass frit with a Celite pad gave a clear red solution. The solution was concentrated until ca. 5 mL of hexane remained, and the solution was cooled to −20 °C. Over a 24 h period fairly large, red, X-ray quality crystals were deposited and identified as 1,2-$\mathrm{Mo_2(NMe_2)(PPh_2)(CH_2SiMe_3)_4}$. Yield: 40%. NMR data were obtained in toluene-d_8. ^{1}H at −80 °C: δ −0.41 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 14.8$ Hz, 1H), 0.05 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 14.0$ Hz, 1H), 0.25 (s, $\mathrm{Si}Me_3$, 9H), 0.31 (s, $\mathrm{Si}Me_3$, 9H), 0.36 (s, $\mathrm{Si}Me_3$, 9H), 0.42 (s, $\mathrm{Si}Me_3$, 9H), 0.77 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 15$ Hz, 1H), 1.74 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 24.4$ Hz, 1H), 2.51 (s, distal *Me* on $\mathrm{NMe_2}$ group, 3H), 2.71 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 16$ Hz, 1H), 3.41 (s, proximal *Me* on $\mathrm{NMe_2}$ group, 3H), 3.52 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 15.2$ Hz), 3.98 (s, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 15$ Hz, 1H), 4.26 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 14.0$ Hz, 1H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ at −60 °C: δ 2.39 (s, 2 $\mathrm{Si}Me_3$, 6C), 2.63 (s, $\mathrm{Si}Me_3$, 3C), 3.47 (s, $\mathrm{Si}Me_3$, 3C), 41.52 (s, distal *Me* of $\mathrm{NMe_2}$ group), 49.06 (s, $C\mathrm{H_2}$) 50.43 (s, $C\mathrm{H_2}$), 59.74 (s, proximal *Me* of $\mathrm{NMe_2}$ group), 60.44 (d, $C\mathrm{H_2}$, trans $J_{\mathrm{c-p}}$ 21.3 Hz), 66.56 (s, $C\mathrm{H_2}$), 126−136 (m, $\mathrm{P}Ph_2$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum obtained at 20 °C and referenced to an external $\mathrm{H_3PO_4}$ standard at 20 °C: δ 208.69 (s, $P\mathrm{Ph_2}$). The observed *m*/*z* distribution for 1,2-$\mathrm{Mo_2(NMe_2)(PPh_2)(CH_2SiMe_3)_4^+}$ ion is in good agreement with the calculated *m*/*z* distribution. In both cases the molecular ion of maximum ion current was at 771 Da.

Preparation of $\mathbf{Mo_2(NMe_2)(CH_2SiMe_3)_5}$. To 1,1′-$\mathrm{Mo_2(NMe_2)(Br)(CH_2SiMe_3)_4}$ (0.100 g, 0.149 mmol) was added $\mathrm{LiCH_2SiMe_3}$ (0.014 g, 0.149 mmol) in a 25 mL round-bottom flask. Hexane (15 mL) was added to the mixture, and the reaction was stirred 12 h at ambient temperature. Filtration through a medium glass frit with a Celite pad gave a clear dark solution. Removing the solvent in vacuo gave a dark liquid identified as $\mathrm{Mo_2(NMe_2)(CH_2SiMe_3)_5}$ in >95% crude yield as determined by ^{1}H NMR spectroscopy. NMR data were obtained in toluene-d_8. ^{1}H at 50 °C: δ 0.16 (s, $\mathrm{Si}Me_3$, 18H), 0.19 (s, $\mathrm{Si}Me_3$, 27H), 0.73 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.7$ Hz, 2H), 1.81 (s, $\mathrm{C}H_2$, 6H), 2.35 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 12.3$ Hz, 2H), 3.13 (br s, $\mathrm{N}Me_2$, 6H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ at −20 °C: δ 2.24 (s, $\mathrm{Si}Me_3$), 2.80 (s, $\mathrm{Si}Me_3$), 47.56 (s, $C\mathrm{H_2}$), 57.26 (s, $C\mathrm{H_2}$), 61.70 (br s, $\mathrm{N}Me_2$). The observed *m*/*z* distribution for the $\mathrm{Mo_2NMe_2(CH_2SiMe_3)_5^+}$ ion is in good agreement with the calculated *m*/*z* distribution. In both cases the molecular ion of maximum ion current was at 672 Da.

Preparation of 1,1′-$\mathbf{Mo_2(NMe_2)(O^iPr)R_4}$. To 1,1′-$\mathrm{Mo_2(NMe_2)(Br)(CH_2SiMe_3)_4}$ (0.100 g, 0.149 mmol) was added $\mathrm{LiO^iPr}$ (0.010 g, 0.149 mmol) in a 25 mL round-bottom flask. Hexane (15 mL) was added to the mixture at 0 °C, and the solution was stirred for 2 h while warming to 20 °C. Filtration through a medium frit with a Celite pad gave a clear dark solution. Removing the solvent in vacuo gave a dark liquid, most of which was identified as 1,1′-$\mathrm{Mo_2(NMe_2)(O^iPr)R_4}$ in >80% crude yield as determined by ^{1}H NMR spectroscopy. NMR data were obtained in toluene-d_8. ^{1}H at 20 °C: δ 0.18 (s, $\mathrm{Si}Me_3$, 9H), 0.20 (s, $\mathrm{Si}Me_3$, 27H), 1.33 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 12.9$ Hz, 1H), 1.39 (d, $\mathrm{C}H_3$, 3 $J_{\mathrm{H-H}} = 6$ Hz, 3H), 1.47 (d, $\mathrm{C}H_3$, 3 $J_{\mathrm{H-H}} = 6.3$ Hz, 3H), 1.60 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.7$ Hz, 3H), 1.94 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.7$ Hz, 3H), 1.99 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 12.9$ Hz, 1H), 3.12 (br s, $\mathrm{NMe_2}$), 5.42 (septet, $\mathrm{C}H\mathrm{(CH_3)_2}$, 1H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ at −45 °C: δ 3.27 (s, $\mathrm{Si}Me_3$), 3.35 (s, $\mathrm{Si}Me_3$), 26.93 (s, $\mathrm{OCH}(C\mathrm{H_3})_2$, 43.17 (s, distal *Me* on $\mathrm{NMe_2}$ group), 58.00 (s, proximal *Me* on $\mathrm{NMe_2}$ group), 61.67 (s, $C\mathrm{H_2}$), 79.06 (s, $C\mathrm{H_2}$), 80.74 (s, $\mathrm{O}C\mathrm{H(CH_3)_2}$. The observed *m*/*z* distribution for the $\mathrm{Mo_2(NMe_2)(O^iPr)(CH_2SiMe_3)_4^+}$ ion is in good agreement with the calculated *m*/*z* distribution. In both cases the molecular ion of maximum ion current was at 644 Da.

Preparation of 1,1′-$\mathbf{Mo_2(NMe_2)(O^tBu)R_4}$. To 1,1′-$\mathrm{Mo_2(NMe_2)(Br)(CH_2SiMe_3)_4}$ (0.100 g, 0.149 mmol) was added $\mathrm{LiO^tBu}$ (0.012 g, 0.149 mmol) in a 25 mL round-bottom flask. Hexane (15 mL) was added to the mixture at −50 °C, and the solution was stirred for 5 h while warming to 20 °C. Filtration through a medium frit with a Celite pad gave a clear dark solution. Removing the solvent in vacuo gave a dark liquid identified as 1,1′-$\mathrm{Mo_2(NMe_2)(O^tBu)R_4}$ in >90% crude yield as determined by ^{1}H NMR spectroscopy. NMR data were obtained in toluene-d_8. ^{1}H at 20 °C: δ 0.17 (s, $\mathrm{Si}Me_3$, 9H), 0.19 (s, $\mathrm{SiMe_3}$, 27H), 1.41(s, $\mathrm{C(C}H_3)$, 9H), 1.59 (d, $\mathrm{C}H_2$, $J_{\mathrm{H-H}}$ 11.7 Hz, 3H), 1.68 (s, $\mathrm{C}H_2$, 2H), 1.91 (s, $\mathrm{C}H_2$, $J_{\mathrm{H-H}} = 11.7$ Hz, 3H), 2.6 (br s, proximal Me on $\mathrm{NMe_2}$ group), 3.75 (br s, distal Me on $\mathrm{NMe_2}$ group). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ at −60 °C: δ 2.59 (s, $\mathrm{Si}Me_3$), 2.62 (s, $\mathrm{Si}Me_3$), 43.29 (s, distal Me of $\mathrm{NMe_2}$ group), 57.82 (s, proximal Me of $\mathrm{NMe_2}$ group), 57.97 (s, $C\mathrm{H_2}$), 78.25 (s, $C\mathrm{H_2}$). The observed *m*/*z* distribution for the $\mathrm{Mo_2(NMe_2)(O^tBu)(CH_2SiMe_3)_4^+}$ ion is in good agreement with the calculated *m*/*z* distribution. In both cases the molecular ion of maximum ion current was at 658 Da.

NMR Tube Reactions. (1) To an NMR tube containing 1,1′-$\mathrm{Mo_2(NMe_2)BrR_4}$ (100 mg, 0.149 mmol) and 1 mL of toluene-d_8 was added an excess of $\mathrm{HNMe_2}$-d_6 (>10 equiv). The reaction was monitored by ^{1}H NMR spectroscopy at −20 °C over a period of 4 h. Approximately 2 h after adding $\mathrm{HNMe_2}$-d_6, the formation of 1,2-$\mathrm{Mo_2(NMe_2)_2R_4}$ was observed. Shortly thereafter, the formation of $\mathrm{HNMe_2}$ was observed. No formation of 1,1-$\mathrm{Mo_2(NMe_2)_2R_4}$ occurred. (2) To an NMR tube containing 1,1-$\mathrm{Mo_2(NMe_2)_2R_4}$ (100 mg, 0.156 mmol) and 1 mL of toluene-d_8 was added an excess of $\mathrm{HNMe_2}$-d_6 (>10 equiv). The reaction was monitored by ^{1}H NMR spectroscopy at −20 °C. The formation of protio-$\mathrm{HNMe_2}$ was observed after 1 h, but no isomerization occurred. The reaction was further monitored at 20 °C for 5 days, and no formation of 1,2-$\mathrm{Mo_2(NMe_2)_2R_4}$ was observed, but the concentration of $\mathrm{HNMe_2}$ steadily increased as the intensity of the protio $\mathrm{NMe_2}$ signals of 1,1-$\mathrm{Mo_2(NMe_2)_2R_4}$ decreased. (3) To an NMR tube containing 1,1-$\mathrm{Mo_2(NMe_2)_2R_4}$ (100 mg, 0.156 mmol) and 1 mL of toluene-d_8 was added excess $\mathrm{^nBu_4NI}$. The NMR tube was rotated over a period of 24 h, and the reaction was monitored intermittently by ^{1}H NMR spectroscopy. No isomerization occurred. (4) To an NMR tube containing 1,1-$\mathrm{Mo_2(NMe_2)_2R_4}$ (100 mg, 0.156

mmol) and 1 mL of toluene-d_8 was added excess $^nBu_4NBr$. The NMR tube was rotated (gently shaken) over a period of 24 h, and the reaction was monitored intermittently by ^1H NMR spectroscopy. No isomerization occurred. (5) To an NMR tube containing 1,1-$Mo_2(NMe_2)_2R_4$ (100 mg, 0.156 mmol) and 1 mL of toluene-d_8 was added TMSBr (0.156 mmol, 20 μL), and the reaction was monitored intermittently by ^1H NMR spectroscopy. After 1 h the formation of 1,1′-$Mo_2(NMe_2)BrR_4$ was detected by ^1H NMR spectroscopy. After 24 h complete conversion had taken place. (6) To an NMR tube containing 1,1-$Mo_2(NMe_2)_2R_4$ (100 mg, 0.156 mmol), 2,6-di-*tert*-butyl pyridine (0.156 mmol, 38 μL), and 1 mL of toluene-d_8 was added TMSBr (1 equiv, 20 μL), and the reaction was monitored intermittently by ^1H NMR spectroscopy. After 1 h the formation of 1,1′-$Mo_2(NMe_2)BrR_4$ was detected by ^1H NMR spectroscopy. After 24 h complete conversion had taken place. (7) To an NMR tube containing 1,1-$Mo_2(NMe_2)_2R_4$ (100 mg, 0.156 mmol) in tolune-d_8, which was submerged into a dry ice acetone bath and connected to a calibrated vacuum gas manifold, was added HBr (0.312 mmol). The NMR tube was slowly allowed to warm to room temperature, and the NMR tube was rotated for several hours. ^1H NMR spectroscopy revealed that only 1,1′-$Mo_2(NMe_2)BrR_4$ was present in the NMR tube. (8) To 1,2-$Mo_2(NMe_2)_2R_4$ (100 mg, 0.156 mmol) in tolune-d_8, which was submerged into a dry ice/acetone bath and connected to a calibrated vacuum gas manifold, was added HBr (0.312 mmol). The NMR tube was slowly allowed to warm to room temperature, and the NMR tube was rotated for several hours. ^1H NMR spectroscopy revealed the presence of 1,1′-$Mo_2(NMe_2)BrR_4$.

Attempted Preparation of $Mo_2Y_2(CH_2SiMe_3)_4$ Compounds. To a hexane solution of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ was added 2 equiv of LiY at −50 °C. In each case (Y = Ph, C≡CSiMe$_3$, CH=CH$_2$, and PPh$_2$) a rapid reaction occurred, but no single isolable organometallic compound was obtained. Rather, in each reaction, the solution darkened rapidly and only insoluble salts were obtained.

Crystal and Molecular Structure of 1,2-$Mo_2(NMe_2)(PPh_2)(CH_2SiMe_3)_4$. The Bruker-AXS SMART6000 system was used for data collection. The data were collected using 5 s frames with an omega scan of 0.30°. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged using the Bruker SAINT software as well as utility programs from the XTEL library.

The structure was readily solved using SHELXTL and Fourier techniques. It was discovered that two independent molecules were present in the asymmetric unit. Although the conformation of the two molecules is nearly identical, there was no evidence of a space group ambiguity (see below however). The BMFIT program was used to examine the differences between the two independent molecules, which are very slight. Near the end of the refinement, it was noticed that the largest peaks remaining in the difference Fourier corresponded to “ghosts” of the metal positions. When these were included as low-occupancy metal atoms, the residual dropped dramatically and several atoms that were previously behaving erratically converged properly. It appears that a slight disorder (or twinning) may be responsible. The occupancies of the eight partial molybdenum atoms varied from 2.1 to 3.4%.

A final difference Fourier still had several peaks of intensity up to 2 e/Å^3, mostly in the vicinity of the various metal atoms. A summary of crystal data is shown in Table 1.

Table 1. Summary of Crystallographic Data for 1,2-$Mo_2(NMe_2)(PPh_2)(CH_2SiMe_3)_4$

empirical formula	$C_{30}H_{60}Mo_2NPSi_4$
fw	770.01
space group	$P\bar{1}$
a (Å)	11.179(1)
b (Å)	17.565(2)
c (Å)	21.060(2)
α (deg)	81.23(1)
β (deg)	75.85(1)
δ (deg)	84.58(1)
temp (K)	108.15
Z	4
V (Å^3)	3976.27
d_{calc} (g cm^{-1})	1.286
λ (Å)	0.71073
μ (cm^{-1})	8.089
$R(F)$	0.0769
$R_w(F)$	0.0659
GoF	1.801

Results and Discussion

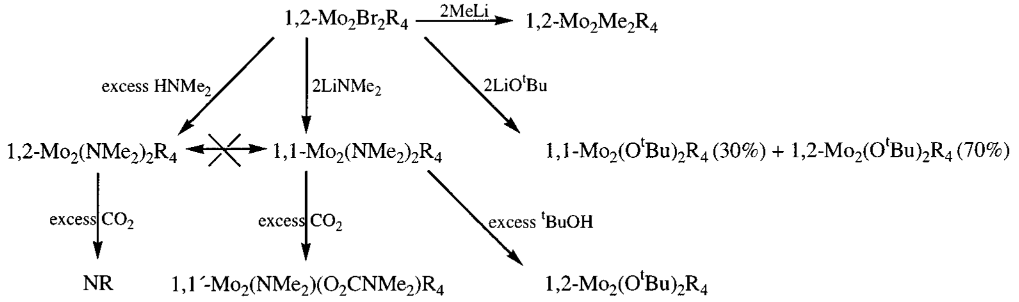
It is pertinent to present first the results and then speculate on reaction mechanisms. Moreover, we must acknowledge the key pioneering contributions made by Rothwell,[10] which are summarized in Scheme 1. Formation of 1,1-$Mo_2(NMe_2)_2R_4$ (R = CH_2SiMe_3) in the reaction with $LiNMe_2$ requires an alkyl group transfer across the M−M triple bond. The most simple question to be addressed is the following. At what stage in the NMe_2-for-Br substitution does this occur? Similarly, in the reaction between 1,2-$Mo_2Br_2R_4$ and $HNMe_2$ in hexane one may ask whether the regiochemistry about the M_2 template is retained in each NMe_2-for-Br substitution. To address these questions, we have studied the stepwise substitution chemistry of 1,2-$Mo_2Br_2R_4$ by low-temperature reactions in hexane and by NMR studies in toluene-d_8.

The reaction between 1,2-$Mo_2Br_2R_4$ and $LiNMe_2$, 1 equiv, is complicated by the fact that the second NMe_2-for-Br exchange occurs at a rate not much slower than the first even at −50 °C. This is evident from the fact that one obtains a mixture of unreacted 1,2-$Mo_2Br_2R_4$ and 1,1-$Mo_2(NMe_2)_2R_4$ along with the desired product $Mo_2(NMe_2)BrR_4$, which is present as ca. 70% of the mixture. Note, this is a kinetic distribution of products, as 1,1-$Mo_2(NMe_2)_2R_4$ can be prepared as described below and is not labile to ligand scrambling. However, the NMR data for the latter compound clearly identify it as the 1,1′-$Mo_2(NMe_2)BrR_4$ isomer. Thus, the first NMe_2-for-Br substitution proceeds with alkyl group transfer across the Mo≡Mo bond. The second proceeds with retention of regiochemistry.

Studies of the reaction between 1,2-$Mo_2Br_2R_4$ and $HNMe_2$ (ca. 10 equiv) in hexane reveal that there is a significant difference in the rate of the first NMe_2-for-Br substitution, and at short reaction times, namely 15 min, essentially complete conversion to $Mo_2(NMe_2)BrR_4$ is attained along with Me_2NH_2Br, which precipitates from hexane. This reaction also produces the 1,1′-isomer. So we now know that in the reactions between 1,2-$Mo_2Br_2R_4$ and both $LiNMe_2$ and $HNMe_2$ there is a common intermediate, $Mo_2(NMe_2)BrR_4$, with the same regiochemistry. The reaction between $Mo_2Br_2R_4$ and $HNMe_2$ which yields $Mo_2(NMe_2)BrR_4$ has proved useful in allowing us to interrogate the subsequent substitution chemistry. A number of substitution reactions involving lithium reagents are shown in Scheme 2. Here it is seen that in all cases, except that of $LiPPh_2$, the regiochemistry is retained. In the latter reaction 1,2-$Mo_2(NMe_2)(PPh_2)R_4$ is formed.

With the now more accessible availability of 1,2-$Mo_2Br_2R_4$, we have also examined some of its substitution reactions with regard to 1 equiv and 2 equiv of lithium

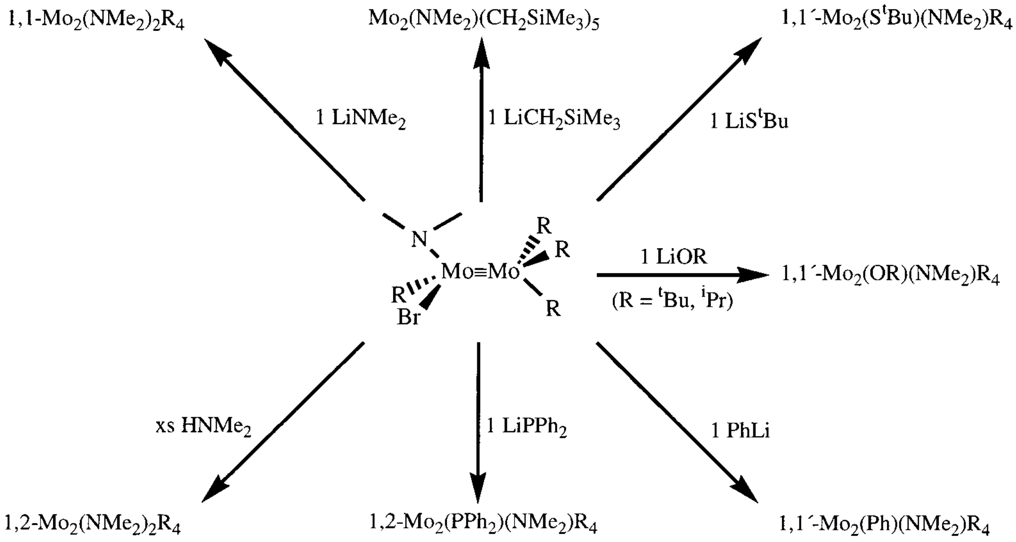
Scheme 1. Substitution Reactions Involving 1,2-$Mo_2Br_2R_4$, where R = CH_2SiMe_3[a]



1,1-$Mo_2X_2R_4$ = $RX_2Mo{\equiv}MoR_3$; 1,2-$Mo_2X_2R_4$ = $XR_2Mo{\equiv}MoXR_2$

[a] Taken from Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 251.

Scheme 2. Bromide Substitution Reactions Involving 1,1′- $Mo_2(NMe_2)Br(CH_2SiMe_3)_4$



reagents. The dinuclear template is far from inert, and from reactions involving alkynyllithium reagents ($LiC{\equiv}CBu^t$, $LiC{\equiv}CPh$, $LiC{\equiv}CSiMe_3$), LiPh, and $LiPPh_2$ no simple organometallic compound was isolable. However, some interesting and noteworthy results were obtained from related studies. For example, reactions employing LiO^tBu proceed first to give 1,2-$Mo_2(O^tBu)BrR_4$ and then a 30:70 mixture of 1,1- and 1,2-$Mo_2(O^tBu)_2R_4$ (as noted by Rothwell[10]). In this instance the second substitution of Br by O^tBu is accompanied by some alkyl group transfer. In contrast, reactions employing LiS^tBu lead in a stepwise manner to 1,2-$Mo_2(S^tBu)_2R_4$ with retention of regiochemistry. These results are of particular interest in that reactions employing 1,1-$Mo_2(NMe_2)_2R_4$ and alcohols or thiols lead to 1,1-$M_2X_2R_4$ compounds (X = OR or SR).

Interconversion of 1,1- and 1,2-$Mo_2(NMe_2)_2R_4$ Isomers. That the formation of these isomers in reactions employing $LiNMe_2$ and $HNMe_2$ should proceed via a common intermediate, namely, 1,1′-$Mo_2(NMe_2)BrR_4$ was extremely puzzling to us. We first supposed that the excess Me_2NH employed in the simple amine substitution was the catalyst in the transformation of the kinetic isomer to the thermodynamic isomer, eq 1.

$$\text{1,1-}Mo_2(NMe_2)_2R_4 \xrightarrow[\text{hexane}]{\text{catalyst}} \text{1,2-}Mo_2(NMe_2)_2R_4 \quad (1)$$

Initial studies of reaction **1** employing added $HNMe_2$ gave erratic results, and it soon became apparent that $HNMe_2$ could not be the catalyst. Only in the case of adventitious Me_2NH_2Br or trace quantities of $Mo_2Br_2R_4$ did we observe the "amine-catalyzed" transformation shown in eq 1. (In the presence of $Mo_2Br_2R_4$, the addition of $HNMe_2$ generates Me_2NH_2Br.) Labeling studies involving $HNMe_2$-d_6 revealed that 1,1-$Mo_2(NMe_2)_2R_4$ merely undergoes aminolysis without any 1,1- to 1,2-isomerization. Finally, we were able to show that the isomerization of 1,1- to 1,2-$Mo_2(NMe_2)_2R_4$ could be brought about by the presence of catalytic, i.e., trace amounts, of Me_2NH_2Br. At this point, we questioned whether the role of Me_2NH_2Br might merely be as a source of Br^- which could associate to the Mo_2^{6+} center and facilitate alkyl group transfer by favoring bridge formation. There are two precedents in the chemistry of Mo_2^{6+}–ethane-like "dimers" that foster such a suspicion. (1) It was shown that addition of OR^- leads to $Mo_2(OR)_7^-$, which has a single OR bridging group in the solid state (R = $CH_2{}^tBu$) and is fluxional on the NMR time scale.[13] (2) The addition of PMe_3 to 1,2-$Mo_2(CH_2Ph)_2(O^iPr)_4$ in hydrocarbon solutions has been shown to reversibly give $(PMe_3)(PhCH_2)_2(Pr^iO)Mo{\equiv}Mo(OPr^i)_3$, wherein one four-coordinate Mo atom and one three-

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[13] Budzichowski, T. A.; Chisholm, M. H.; Martin, J. D.; Huffman, J. C.; Moodley, K. G.; Streib, W. E. *Polyhedron* **1993**, *12*, 343.

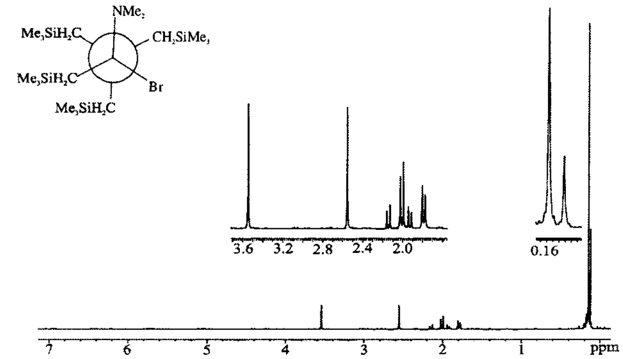

Figure 1. ^{1}H NMR spectrum of 1,1′-$Mo_2(NMe_2)BrR_4$ recorded at 20 °C, 300 MHz in toluene-d_8.

coordinate Mo atom are united by the Mo═Mo bond.[14] The reversible formation of the latter compound involves both benzyl and isopropoxy group transfer reactions, which we have previously shown to be dependent on PMe_3 association to the Mo_2^{6+} center.

To investigate the potential catalysis by halide anion, we examined the reactivity of 1,1-$Mo_2(NMe_2)_2R_4$ in hydrocarbon solvents toward $^nBu_4N^+X^-$, where X = Br and I. In neither instance is any isomerization of the 1,1- to the 1,2-$Mo_2(NMe_2)_2R_4$ isomer observed. We, therefore, conclude that the isomerization reaction shown in eq 1 is catalyzed by the presence of Me_2NH_2Br, which is present during the reaction between $Mo_2Br_2R_4$, and an excess of $HNMe_2$ (ca. 10 equiv). We shall return to speculate on the more detailed reaction pathways that are involved in reactions between $Mo_2Br_2R_4$ and each of $LiNMe_2$ and $HNMe_2$. We first present the evidence for assignment of regiochemistry and our formulation of the compounds as presented.

Characterization Data. Many of the new compounds are yellow or dark yellow viscous oils, which does not endear them to purification or characterization by single-crystal X-ray crystallography. However, some of the new compounds were solids, and at least one, namely, 1,2-$Mo_2(NMe_2)(PPh_2)R_4$, proved suitable for a single-crystal X-ray study (vida infra). All compounds were examined by mass spectrometry and by variable-temperature NMR spectroscopy, and the latter provided information pertaining not only to molecular formula but also to molecular structure. The NMR spectra are in all cases temperature dependent, as rotations about the central Mo≡Mo bond and the Mo−NC_2 bond occur at rates that are comparable to the NMR time scale. Full NMR data are given in the Experimental Section, but it is worth examining the variable-temperature NMR behavior of two representative compounds.

The room-temperature ^{1}H NMR spectrum of 1,1′-$Mo_2(NMe_2)BrR_4$ is shown in Figure 1. Because of rapid rotation about the Mo≡Mo bond, the $SiMe_3$ groups appear as two singlets in the integral ratio 3:1, while the methylene protons which are all diastereotopic appear as two sets of AB quartets again in the ratio 3:1. The NMe_2 signals appear as two singlets, indicating that proximal and distal NMe_2 group exchange is slow in this compound. Indeed, only upon heating to +60 °C does exchange occur with a significant rate to cause the appearance of a single broad resonance. In contrast, for 1,1-$Mo_2(NMe_2)_2R_4$ the proximal−distal site exchange is still not frozen out at −60 °C. For a series of 1,1′-$Mo_2(NMe_2)XR_4$ compounds the rates of NMe proximal ⇌ distal exchange follow the order X = Me_2N > ^{t}BuO > ^{t}BuS > Ph ≈ CH_2SiMe_3 > Br, which roughly correlates with the ability of the X ligand to σ- and π-donate to the Mo_2^{6+} center. For X = Br, which is both a poor π-donor and electronegative, the sole NMe_2 ligand π-donates to the Mo $d_{x^2-y^2}/d_{xy}$ orbital most strongly, which favors alignment of the NC_2 plane and the Mo−Mo axis and imposes a higher rotational barrier.

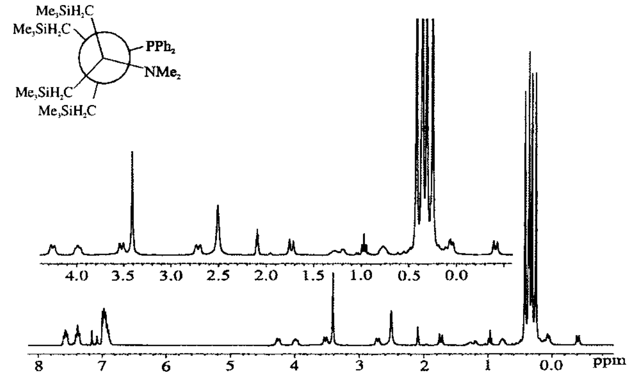

Figure 2. ^{1}H NMR spectrum of 1,2-$Mo_2(NMe_2)(PPh_2)R_4$ recorded at −80 °C, 300 MHz in toluene-d_8.

The ^{1}H NMR spectrum for 1,2-$Mo_2(NMe_2)(PPh_2)R_4$ at room temperature shows only two $SiMe_3$ groups in the ratio 2:2. The CH_2 protons are not visible at this temperature and the NMe_2 signal is broadened. However, this is sufficient to establish the regiochemistry of substitution as 1,2-$Mo_2(NMe_2)(PPh_2)R_4$, and at −80 °C a very informative ^{1}H NMR spectrum is obtained, as shown in Figure 2. There are now, in addition to the phenyl proton resonances (δ 6.8 to 7.8), four singlets of equal intensity for the $SiMe_3$ groups and eight methylene proton signals, the connectivity of which is easily established by a COSY spectrum, together with proximal and distal NMe singlets. At −80 °C in toluene-d_8 rotation about the Mo≡Mo bond is frozen out and we observe just the gauche rotamer. An inspection of the methylene proton signals and, indeed, the distal NMe signal reveals some small coupling to ^{31}P which is not fully resolved. The only other point worthy of mention is that for a compound of formula 1,2-$Mo_2X_2R_4$ the appearance of one $SiMe_3$ signal and a single AX or AB spectrum for the methylene protons cannot distinguish between the presence of only the anti rotamer or a situation wherein rotation about the Mo≡Mo bond is rapid. That this is seen for X = Br and S^{t}Bu even at −80 °C leads us to propose that the anti rotamer is present since for other compounds rotation about the M≡M is slow on the NMR time scale at this temperature.

Molecular Structure of 1,2-$Mo_2(NMe_2)(PPh_2)R_4$. An ORTEP drawing of the molecule is given in Figure 3, and selected bond distances and bond angles are given in Table 2. The gauche rotamer is present in the solid-state structure, and this was seen in the low-temperature NMR spectra. The metrical parameters for the Mo_2C_4NP skeleton are readily reconciled with what has been seen before for mixed amido alkyl and amido phosphido compounds.[15]

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[14] Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 5385.

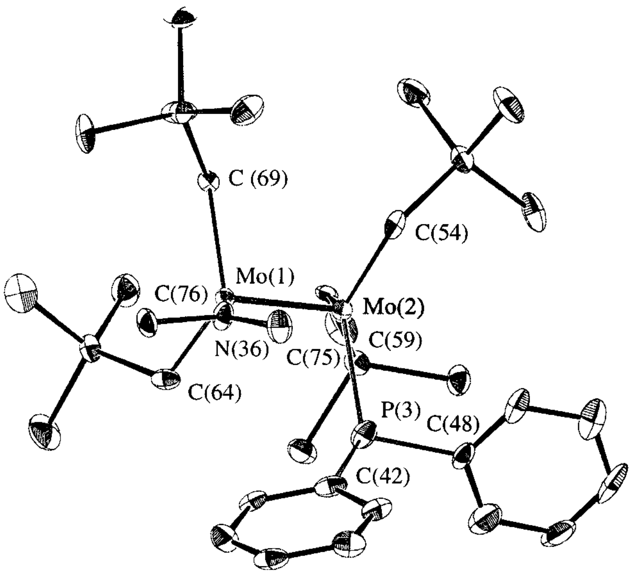
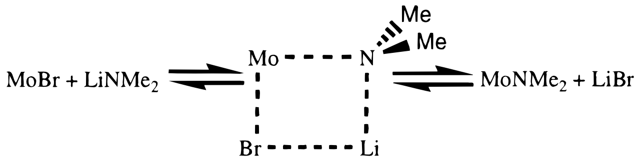


Figure 3. Molecular structure of 1,2-$Mo_2(NMe_2)(PPh_2)(CH_2SiMe_3)_4$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1,2-$Mo_2(NMe_2)(PPh_2)(CH_2SiMe_3)_4$

Mo(1)−Mo(2)	2.1911(9)	Mo(2)−C(54)	2.111(7)
Mo(1)−C(64)	2.133(7)	Mo(2)−C(59)	2.127(7)
Mo(1)−N(36)	1.917(6)	Mo(2)−P(3)	2.357(2)
Mo(1)−C(69)	2.172(6)		
Mo(2)−Mo(2)−N(36)	105.9(2)	Mo(1)−Mo(2)−C(54)	97.2(2)
Mo(1)− N(36)−C(75)	135.1(5)	Mo(1)−Mo(2)−C(59)	102.3(2)
Mo(1)−N(36)−C(76)	113.3(4)	P(3)−Mo(2)−C(54)	111.8(2)
Mo(2)−Mo(1)−C(69)	106.0(2)	P(3)−Mo(2)−C(59)	120.6(2)
Mo(2)−Mo(1)−C(64)	98.7(2)	Mo(1)−Mo(2)−P(3)	101.0(1)
N(36)−Mo(1)−C(64)	113.5(2)	Mo(2)−P(3)−C(48)	110.3(2)
N(36)−Mo(1)−C(69)	111.5(2)	Mo(2)−P(3)−C(42)	129.6(2)
C(75)−N(36)−C(76)	111.4(6)	C(42)−P(3)−C(48)	104.1(3)

Scheme 3. Simplified σ-Bond Metathesis at a Mononuclear Metal Center



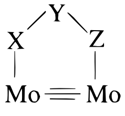
(a) Speculation about the Intimate Mechanism of Substitution and Further Reactions by Lithium Reagents. The seemingly simple metathetic reaction shown in eq 2 below is still well beyond our detailed understanding.

$$1,2\text{-}Mo_2Br_2R_4 + LiNMe_2 \xrightarrow[\text{hexane}]{-50\ °C} 1,1'\text{-}Mo_2(NMe_2)BrR_4 + LiBr \quad (2)$$

A simplified picture for a σ-bond metathesis reaction of the S_F2 type (substitution, front-side, bimolecular) depicted by Scheme 3 fails to address the order in which N-to-Mo and Li-to-Br bonding occurs, fails to recognize the unknown oligomeric nature of $LiNMe_2$, and does not in any way account for the fact that LiBr is ultimately formed as a crystalline species. It is, however, the most useful starting point in that it stresses the importance of the fact that in the metathetic exchange Li···Br bond formation is probably equally important to Me_2N-to-Mo bond formation. The coordination of Br to Li will weaken the Mo−Br bond and at the same time weaken the Li−N bond. As the Me_2N-to-Mo bond is formed, the Mo−Br bond and Li−NMe_2 bonds are weakened and ultimately broken. Since it is known that Mo−halogen bonds are stronger than Mo−NMe_2 bonds, the ultimate thermodynamic driving force is derived from the greater difference in the thermodynamic stability of LiBr over $LiNMe_2$ in their respective crystalline and oligomeric states.

Recognizing the limitations of the simplified σ-bond metathesis shown in Scheme 3, we propose a hypothetical reaction sequence shown in Scheme 4. This reaction pathway recognizes that Li···Br bond formation and Mo···NMe_2 bond formation may occur at different metal centers. Furthermore, as LiBr is formed and, to be more precise, as the bromide ligand is removed from the metal center, then an alkyl group transfer occurs to generate a MoR_3 center and the 1,1′-$Mo_2(NMe_2)BrR_4$ isomer.

There are many structural precedents of NH- - -halogen bonding across dinuclear M−M bonded centers,[17] and Cotton and co-workers have shown just how often the type of structural motif shown in A occurs with bridging ligands such as acetates, formaminidates, and triazines, where X, Y, Z represent various combinations of the elements C, O, N, S, and P.[18]



A

Why do reagents such as LiO^tBu and LiS^tBu react with 1,2-$Mo_2Br_2R_4$ to give 1,2-$Mo_2(Y)BrR_4$, where Y = O^tBu or S^tBu? This is a difficult point upon which to speculate. Perhaps the different oligomeric structures of the alkoxide and thiolate lithium salts cause a σ-bond metathesis to occur at a single Mo center. However, we cannot rule out that the initial LiY interaction is again across the Mo−Mo bond as shown in Scheme 3, but in the act of removing the bromide ligand with the lithium ion it is Br that migrates instead of CH_2SiMe_3.

In the reactions involving organolithium reagents and 1,1′-$Mo_2(NMe_2)BrR_4$ the products 1,1′-$Mo_2(Y)BrR_4$ are formed when Y = CH_2SiMe_3, Ph, NMe_2, O^tBu, O^iPr, and S^tBu. Again two possible explanations can be offered. One is that the initial interaction of the Li−Y reagent occurs across the Mo−Mo bond, and as LiBr is eliminated, a concurrent or consecutive alkyl and amide group are transferred such that the NMe_2 group that

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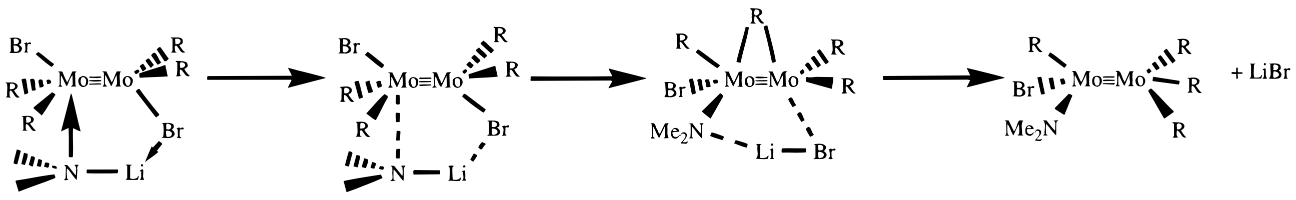
(15) For 1,2-$M_2(R_2)(NMe_2)_4$ see: Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C.; Janos, J. *J. Am. Chem. Soc.* **1983**, *105*, 1163. Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046. (b) For 1,2-$M_2(PR_2)_2(NMe_2)_4$ see: Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Martin, J. D.; Streib, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 557.

(16) Alaimao, P. J.; Bergman, R. G. *Organometallics* **1999**, *18*, 2707.

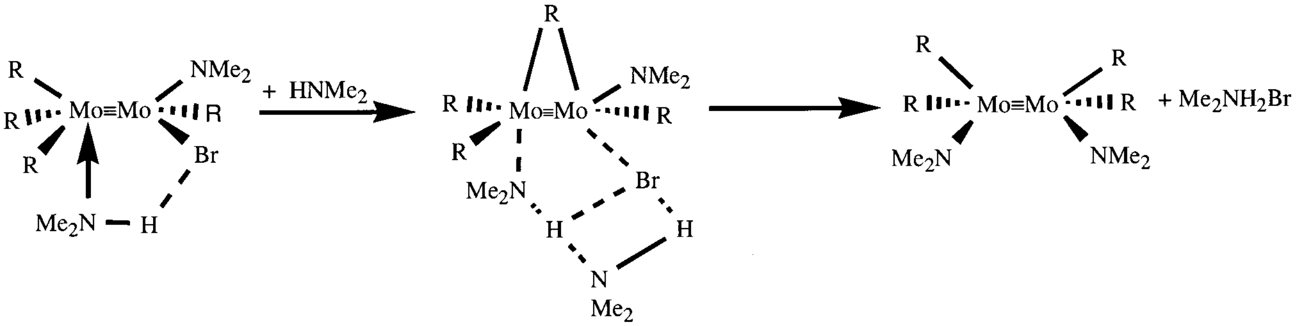
(17) Bradley, D. C.; Errington, R. J.; Hursthouse, M. B.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1986**, 1305. (b) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 3268.

(18) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, U.K., 1993.

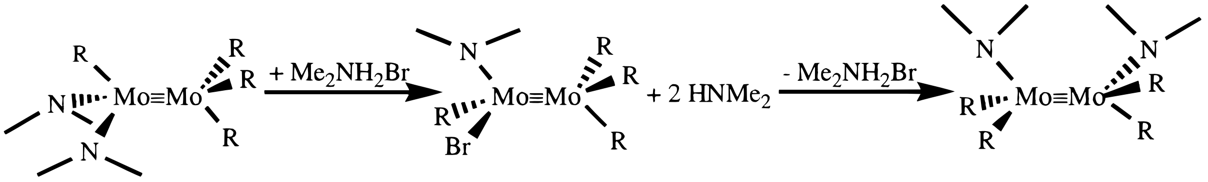
Scheme 4. Simplified σ-Bond Metathesis at the Mo_2^{6+} Center Leading to Alkyl Group Transfer



Scheme 5. Aminolysis at the Mo_2^{6+} Center Leading to Alkyl Group Transfer



Scheme 6. Me_2HN_2Br-Catalyzed Isomerization of 1,1-$Mo_2(NMe_2)_2R_4$ to 1,2-$Mo_2(NMe_2)_2R_4$



was originally at the $Mo(NMe_2)BrR$ center is transferredto the previous MoR_3 center. This seems unlikely to us, although we cannot rule it out. We prefer the second alternative, which we think is simpler. The presence of both the Br and NMe_2 groups at one metal affords a chelate to the entering lithium atom of the LiY reagent, and exchange/metathesis occurs just at one metal center. That 1,1-$Mo_2(NMe_2)_2R_4$ reacts with R′OH to give 1,1-$Mo_2(OR')_2R_4$ (R′ = ^{t}Bu and ^{i}Pr) and with $HNMe_2$-d_6 to give 1,1-$Mo_2(NMe_2\text{-}d_6)_2R_4$ can also most easily be explained by a S_F2 reaction (σ-bond metathesis) at a single metal center. Certainly such reactions are well documented for mononuclear $M(NMe_2)_n$ complexes. The reaction between $LiPPh_2$ and 1,1′-$Mo_2(NMe_2)BrR_4$, which generates 1,2-$Mo_2(NMe_2)(PPh_2)R_4$, may do so because this is the thermodynamically favored product and the PPh_2 ligand at the Mo_2^{6+} center may facilitate bridge formation leading to mutual exchange of PPh_2 and R groups. If the $LiPPh_2$ interaction occurred across the Mo−Mo bond, then it is not clear why R rather than amide group transfer would occur.

(b) By Aminolysis. A similar pictorial representation of the aminolysis reaction, can be envisaged and is shown in Scheme 5. Once again it is recognized that $HNMe_2$ in a nonpolar solvent will exist as hydrogen-bonded oligomers and H-to-Br hydrogen bonding may well occur in an initial "outer-sphere" hydrogen-bonding process prior to Me_2N-to-Mo bond formation.[16] Also, in Scheme 5, it is recognized that HBr does not leave but rather $Me_2NH_2^+Br^-$ is formed, which is likely to be hydrogen bonded with $HNMe_2$ prior to crystallization. One thing we can attest to is the chemical persistence of 1,1-$Mo_2(NMe_2)_2R_4$ in solution in the absence of trace quantities of Me_2NH_2Br, which yield a slow isomerization. Also the reaction between 1,1′-$Mo_2(NMe_2)BrR_4$ and $HNMe_2$ in toluene-d_8 proceeds to give 1,2-$Mo_2(NMe_2)_2R_4$ without any apparent formation of 1,1-$Mo_2(NMe_2)_2R_4$. This aminolysis occurs more slowly than that which produced 1,1′-$Mo_2(NMe_2)BrR_4$ from $Mo_2Br_2R_4$.

(c) By HBr and TMSBr. We speculate that the role of Me_2NH_2Br is one of delivering an equivalent of HBr to 1,1-$Mo_2(NMe_2)_2R_4$ to form 1,1′-$Mo_2(NMe_2)BrR_4$, which in the presence of $HNMe_2$ (2 equiv) then reacts as shown in Scheme 6. This proposed pathway involves the formation of a Mo_2BrHN five-membered ring, and as in Schemes 4 and 5, the departure of the bromide ligand promotes an alkyl group transfer. The reaction is a slower process because the nitrogen lone pair must coordinate to the $Mo(CH_2SiMe_2)_3$ center, which is sterically crowded and does not contain any electron-withdrawing (electronegative) groups. It is, however, coordinatively unsaturated and certainly capable of Lewis base association. Further evidence that the role of Me_2NH_2Br is one of delivering an equivalent of HBr comes from the reaction between 1,1-$Mo_2(NMe_2)_2R_4$ and 2 equiv of HBr, which yields 1,1′-$Mo_2(NMe_2)BrR_4$. The latter two reactions prompted us to speculate that TMSBr may also react with 1,1-$Mo_2(NMe)_2R_4$ via a similar mechanism, namely, that HBr would be generated in situ and react with 1,1-$Mo_2(NMe)_2R_4$. Our speculation was based on the amine-catalyzed chloro-for-dimethylamide exchange reactions known to be operative in the reaction between $W_2(NMe_2)_6$ and TMSCl.[19] The reaction

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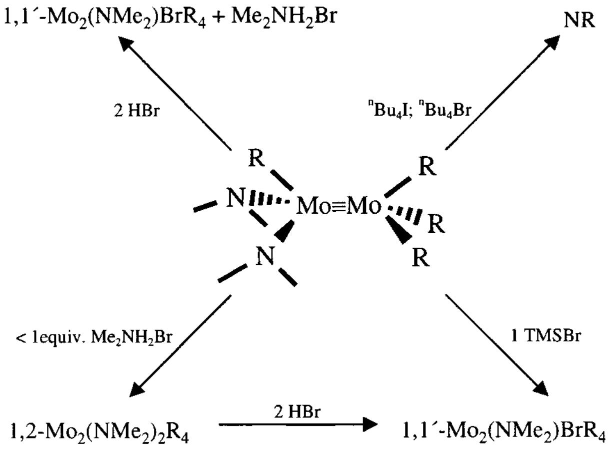
(19) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

Scheme 7. Reaction Scheme for 1,1-Mo$_2$(NMe$_2$)$_2$(CH$_2$SiMe$_3$)$_4$



sequence we envisage is shown in eq 3.

$$\mathrm{Me_3SiBr + HNMe_2 \rightleftharpoons Me_3SiNMe_2 + HBr} \qquad (3)$$

$$\mathrm{L}_n\mathrm{MoNMe_2 + HBr \rightleftharpoons L}_n\mathrm{MoBr + HNMe_2}$$

However, we must concede that the reaction involving TMSBr and 1,1-Mo$_2$(NMe$_2$)$_2$R$_4$ may proceed by a direct S$_F$2 σ-bond metathesis reaction since when the reaction is done in the presence of a proton sponge (2,6-di-*tert*-butylpyridine), 1,1′-Mo$_2$(NMe$_2$)BrR$_4$ is still obtained and without any apparent change in the rate of formation. These reactions involving 1,1-Mo$_2$(NMe$_2$)$_2$R$_4$ are summarized in Scheme 7.

One last reaction to note is that between 1,2-Mo$_2$(NMe$_2$)$_2$R$_4$ and 2 equiv of HBr, which yields 1,1′-Mo$_2$(NMe$_2$)BrR$_4$. Though the outcome of this reaction does not seem intuitively obvious, one must recognize that it is simply the reverse of the reaction by which 1,2-Mo$_2$(NMe$_2$)$_2$R$_4$ is formed (see Scheme 2).

Concluding Remarks

The present findings bear testimony to our lack of understanding of seemingly some of the simplest of σ-bond metathesis reactions at dinuclear centers. Hopefully these results and our speculation will inspire others to ponder on this subject and to devise experiments that could elucidate further on these matters. We note for example that a compound of formula 1,1′-Mo$_2$(NMe$_2$)BrR$_4$ contains a chiral Mo center. Thus the introduction of a chiral amide or other ligand Y* could yield a pair of diastereomers 1,1-Mo$_2$Br(Y*)R$_4$ which could be readily distinguished by NMR spectroscopy and separated by their different physical properties. In this way a pure enantiomer 1,1′-Mo$_2$Br(Y*)R$_4$ could be employed to interrogate the nature of the second substitution step. Further studies along these lines could prove fruitful just as studies of (1,3-C$_3$R$_2$H$_3$-η^5)M(CO)(L)X piano-stool complexes did in the past.[20]

Acknowledgment. We thank the National Science Foundation for support of this work.

Supporting Information Available: CIF data for 1,2-Mo$_2$(NMe$_2$)(PPh$_2$)(CH$_2$SiMe$_3$)$_4$ along with representative mass spectra for the latter and 1,1′-Mo$_2$(NMe$_2$)(Br)(CH$_2$SiMe$_3$)$_4$ are available. ^{1}H NMR spectra for 1,2-Mo$_2$(S^{t}Bu)$_2$(CH$_2$SiMe$_3$)$_4$, 1,1′-Mo$_2$(S^{t}Bu)(NMe$_2$)(CH$_2$SiMe$_3$)$_4$, Mo$_2$(NMe$_2$)(CH$_2$SiMe$_3$)$_5$, 1,1′-Mo$_2$(NMe$_2$)(Ph)(CH$_2$SiMe$_3$)$_4$, and 1,1′-Mo$_2$(O^{t}Bu)(NMe$_2$)(CH$_2$SiMe$_3$)$_4$ are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0003584

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[20] Reich-Rohrwig, P.; Wojiciki, A. *Inorg. Chem.* **1974**, *13*, 2457.