Further Studies on the Substitutional Behavior of 1,2-Mo₂Br₂(CH₂SiMe₃)₄. Alkyl, Amide, Phosphide, Alkoxide, and Thiolate for Bromide Exchange and Isomerizations of 1,1- and 1,2-Mo₂X₂(CH₂SiMe₃)₄ Compounds[†]

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Reactions involving 1,2-Mo₂Br₂(CH₂SiMe₃)₄ and each of LiNMe₂ and HNMe₂ in hexane at -50 °C proceed to give 1,1'-Mo₂(NMe₂)BrR₄, where R = CH₂SiMe₃, as the first product of Br for amide exchange at the Mo₂⁶⁺ center. Further substitution in reactions with LiNMe₂ gives 1,1-Mo₂(NMe₂)₂R₄, but with HNMe₂ the 1,2-Mo₂(NMe₂)₂R₄ isomer is formed. These two do not interconvert thermally (>100 °C) and undergo aminolysis (HNMe₂-*d*₆) and alcoholysis ('BuOH) with retention of regiochemistry. 1,1- to 1,2-isomerization of Mo₂(NMe₂)₂R₄ is catalyzed by the presence of Me₂NH₂Br. 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'-Mo₂(NMe₂)BrR₄ and 1,2-Mo₂Br₂R₄. The new compounds of formula Mo₂(NMe₂)YR₄ (Y = CH₂SiMe₃, Ph, O'Bu, O'Pr, S'Bu, PPh₂, and Br) and Mo₂(S'Bu)₂R₄ have been characterized by variable-temperature ¹H and¹³C{¹H} NMR spectroscopy and mass spectrometry and for Y = PPh₂ 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 natural¹ and unnatural products² 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 d⁸ square-planar ML₄ 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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dependence on the entering ligand. M₂X₆ 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 Brfor-NMe₂ substitution in 1,2-Mo₂Br₂R₄ could give either 1,1- or 1,2-Mo₂(NMe₂)₂ R_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-Mo₂Br₂R₄ 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 MoCl₅ and LiCH₂SiMe₃.¹¹ With the advent of an improved synthesis of Mo₂(CH₂SiMe₃)₆, from MoCl₃(dme), where dme is dimethoxyethane,¹² we are now able to re-examine the fundamental substitution chemistry of 1,2-Mo₂Br₂(CH₂SiMe₃)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 "BuLi 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 (CH₄) as reagent gas.

Preparation of 1,2-Mo₂(NMe₂)₂(CH₂SiMe₃)₄. To a suspension of 1,2-Mo₂Br₂(CH₂SiMe₃)₄ (0.100 g, 0.143 mmol) in pentane (15 mL) was added HNMe₂ (ca. 10 equiv) by use of a calibrated vacuum manifold. This led to rapid precipitation of H₂NMe₂⁺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-Mo₂(NMe₂)₂(CH₂SiMe₃)₄ by ¹H NMR spectroscopy: the spectrum was identical to that previously reported.¹⁰ The ¹³C-{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 NMe₂ group), 44.59 (s, CH_2), 52.46 (s, CH_2), 57.88 (s, proximal Me of NMe₂ group).

Preparation of 1,1'-Mo2(NMe2)(Br)(CH2SiMe3)4. To a suspension of 1,2-Mo₂Br₂(CH₂SiMe₃)₄ (0.100 g, 0.143 mmol), in a 25 mL round-bottomed flask in pentane (15 mL) at 0 °C, was added HNMe₂ (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'-Mo₂(NMe₂)-(Br)(CH₂SiMe₃)₄ (>95% crude yield). NMR data were obtained in toluene- d_8 at ambient temperature. ¹H: δ 0.18 (s, SiMe₃, 9H), 0.21 (s, SiMe₃, 27H), 1.86 (d, CH_2 , $J_{H-H} = 11.7$ Hz, 3H), 2.00 (d, CH_2 , $J_{H-H} = 12.3$ Hz, 1H), 2.08 (d, CH_2 , $J_{H-H} = 11.7$ Hz, 3H), 2.12 (d, CH_2 , $J_{H-H} = 12.3$ Hz, 1H), 2.62 (s, distal Me on NMe₂ group), 3.61 (s, proximal Me on NMe₂ group, 3H). ¹³C{¹H}: δ 2.56 (s, SiMe₃, 9C), 2.88 (s, SiMe₃, 3C), 42.78 (s, distal Me of NMe₂ group), 48.99 (s, CH₂), 59.67 (s, proximal Me of NMe₂ group), 65.06 (s, CH_2). The observed m/z distribution for the 1,1'-Mo₂(NMe₂)(Br)(CH₂SiMe₃)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'-Mo₂(NMe₂)(Ph)(CH₂SiMe₃)₄. To 1,1'-Mo₂(NMe₂)(Br)(CH₂SiMe₃)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'-Mo₂(NMe₂)(Ph)(CH₂-SiMe₃)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, SiMe₃, 27H), 0.13 (s, SiMe₃, 9H), 1.03 (d, CH₂, $J_{\rm H-H} = 12.3$ Hz, 1H), 1.82 (d, C H_2 , $J_{\rm H-H} = 11.4$ Hz, 3H), 1.98 (d, CH₂, $J_{H-H} = 11.7$ Hz), 2.78 (d, CH₂, $J_{H-H} = 12$ Hz), 3.08 (br s, NMe2, 6H), 7.09-7.77 (m, Ph, 5H). ¹³C{¹H} at -45 °C: δ 2.43 (s, 3 SiMe₃), 3.10 (S, 1 SiMe₃), 34.81 (s, CH₂), 40.63 (s, distal Me of NMe2 group), 48.31 (s, CH2), 57.65 (s, proximal Me of NMe₂ group) 125-136 m, Ph). The observed m/zdistribution for the 1,1'-Mo₂(NMe₂)(Ph)(CH₂SiMe₃)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-Mo₂(S^tBu)₂(CH₂SiMe₃)₄. A mixture of 1,2-Mo₂Br₂(CH₂SiMe₃)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-Mo₂(S^tBu)₂(CH₂-SiMe₃)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, SiMe₃, 36H), 1.40 (s, S^tBu, 9H), 1.81 (d, CH_{2} , $J_{H-H} = 10.8$ Hz, 4H), 2.65 (d, CH_{2} , $J_{H-H} = 10.5$ Hz). ¹³C-{¹H}: δ 2.92 (s, SiMe₃, 12C), 36.31 (s, S^tBu), 67.48 (s, CH₂, 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-Mo₂(S^tBu)₂(CH₂-SiMe₃)₄⁺ ion with loss of one *tert*-butyl group (C(CH₃)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 Mo₂S₂C₂₄H₆₂: C, 40.09; H, 8.69; S, 8.92. Found: C, 39.34; H, 8.00; S, 8.58.

Preparation of 1,2-Mo₂(S'Bu)(Br)(CH₂SiMe₃)₄. To 1,2-Mo₂Br₂R₄ (0.100 g, 0.143 mmol) was added LiS'Bu (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-Mo₂Br₂R₄, 1,2-Mo₂(S^t-Bu)BrR₄, and 1,2-Mo₂(S^tBu)₂R₄. The characterization data of 1,2-Mo₂Br₂R₄ and 1,2-Mo₂(S^tBu)₂R₄ have been given previously. ¹H NMR data for 1,2-Mo₂(S^tBu)BrR₄ obtained at -20 °C in toluene-*d*₈: δ 0.31 (s, Si*Me*₃, 18H), 0.36 (s, Si*Me*₃, 18H), 0.90 (d, C*H*₂, *J*_{H-H} = 10.8 Hz, 2H), 1.39 (s, S^tBu, 9H), 2.21 (d, C*H*₂, *J*_{H-H} = 10.8 Hz) 2.50 (d, C*H*₂, *J*_{H-H} = 10.2 Hz), 4.94 (d, C*H*₂, *J*_{H-H} = 11.1 Hz).

Preparation of 1,1'-Mo2(NMe2)(StBu)(CH2SiMe3)4. To 1,1'-Mo₂(NMe₂)(Br)(CH₂SiMe₃)₄ (0.100 g, 0.149 mmol) was added LiStBu (0.0143 g, 0.149 mmol) in a 25 mL roundbottomed 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'-Mo₂(NMe₂)(S^tBu)(CH₂SiMe₃)₄ in >95% crude yield as determined by ¹H NMR spectroscopy. NMR data were obtained in toluene-*d*₈. ¹H at 40 °C: δ 0.19 (s, Si*Me*₃, 9H), 0.23 (s, Si*Me*₃, 27H), 0.50 (d, CH_2 , $J_{H-H} = 11.7$ Hz, 1H), 1.38 (s, S^tBu , 9H), 1,81 (d, CH_2 , $J_{H-H} = 11.1$ Hz, 3H), 2.19 (d, CH_2 , $J_{H-H} = 11.4$ Hz, 3H), 2.98 (d, CH_2 , $J_{H-H} = 11.7$ Hz, 1H), 3.24 (br s, NMe_2 , 6H). ¹³C{¹H} at -60 °C: δ 2.32 (s, 3 SiMe₃), 3.15 (s, 1 SiMe₃), 37.46 (s, StBu), 42.49 (s, distal Me of NMe2 group), 43.47 (s, proximal Me of NMe₂ group), 46.64 (s, CH₂), 58.02 (s, CH₂). The observed m/z distribution for the 1,1'-Mo₂(NMe₂)(S^tBu)- $(CH_2SiMe_3)_4^+$ ion is in good agreement with the calculated m/zdistribution. In both cases the molecular ion of maximum ion current was at 674 Da.

Preparation of 1,2-Mo2(NMe2)(PPh2)(CH2SiMe3)4. To a slurry of LiPPh2 (0.028 g, 0.142 mmol) in hexane (20 mL), in a 25 mL round-bottomed flask at -30 °C, was added 1,1'-Mo₂(NMe₂)(Br)(CH₂SiMe₃)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-Mo₂(NMe₂)(PPh₂)(CH₂SiMe₃)₄. Yield: 40%. NMR data were obtained in toluene- d_8 . ¹H at -80 °C: δ -0.41 (d, CH₂, J_{H-H} = 14.8 Hz, 1H), 0.05 (d, CH_2 , J_{H-H} = 14.0 Hz, 1H), 0.25 (s, SiMe3, 9H), 0.31 (s, SiMe3, 9H), 0.36 (s, SiMe3, 9H), 0.42 (s, SiMe₃, 9H), 0.77 (d, CH₂, J_{H-H} = 15 Hz, 1H), 1.74 (d, CH₂, $J_{\rm H-H} = 24.4$ Hz, 1H), 2.51 (s, distal *Me* on NMe₂ group, 3H), 2.71 (d, CH_2 , $J_{H-H} = 16$ Hz, 1H), 3.41 (s, proximal Me on NMe₂ group, 3H), 3.52 (d, CH_2 , $J_{H-H} = 15.2$ Hz), 3.98 (s, CH_2 , J_{H-H} = 15 Hz, 1H), 4.26 (d, CH_2 , J_{H-H} = 14.0 Hz, 1H). ¹³C{¹H} at -60 °C: δ 2.39 (s, 2 SiMe₃, 6C), 2.63 (s, SiMe₃, 3C), 3.47 (s, SiMe₃, 3C), 41.52 (s, distal Me of NMe₂ group), 49.06 (s, CH₂) 50.43 (s, CH₂), 59.74 (s, proximal Me of NMe₂ group), 60.44 (d, CH₂, trans J_{c-p} 21.3 Hz), 66.56 (s, CH₂), 126-136 (m, PPh₂). ³¹P{¹H} NMR spectrum obtained at 20 °C and referenced to an external H₃PO₄ standard at 20 °C: δ 208.69 (s, *P*Ph₂). The observed m/z distribution for 1,2-Mo₂(NMe₂)(PPh₂)(CH₂SiMe₃)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 Mo₂(NMe₂)(CH₂SiMe₃)₅. To 1,1'-Mo₂(NMe₂)(Br)(CH₂SiMe₃)₄ (0.100 g, 0.149 mmol) was added LiCH₂SiMe₃ (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 Mo₂(NMe₂)(CH₂SiMe₃)₅ in >95% crude yield as determined by ¹H NMR spectroscopy. NMR data were obtained in toluene-*d*₈. ¹H at 50 °C: δ 0.16 (s, Si*Me*₃, 18H), 0.19 (s, Si*Me*₃, 27H), 0.73 (d, C*H*₂, *J*_{H-H} = 11.7 Hz, 2H), 1.81 (s, C*H*₂, 6H), 2.35 (d, C*H*₂, *J*_{H-H} = 12.3 Hz, 2H), 3.13 (br s, N*Me*₂, 6H). ¹³C{¹H} at -20 °C: δ 2.24 (s, Si*Me*₃), 2.80 (s, Si*Me*₃), 47.56 (s, *C*H₂), 57.26 (s, *C*H₂), 61.70 (br s, N*Me*₂). The observed *m*/*z* distribution for the Mo₂NMe₂(CH₂SiMe₃)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'-Mo₂(NMe₂)(OⁱPr)R₄. To 1,1'-Mo₂(NMe₂)(Br)(CH₂SiMe₃)₄ (0.100 g, 0.149 mmol) was added LiOⁱPr (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'-Mo₂(NMe₂)(OⁱPr)R₄ in ${>}80\%$ crude yield as determined by ${^1}H$ NMR spectroscopy. NMR data were obtained in toluene- d_8 . ¹H at 20 °C: δ 0.18 (s, SiMe₃, 9H), 0.20 (s, SiMe₃, 27H), 1.33 (d, CH₂, J_{H-H} = 12.9 Hz, 1H), 1.39 (d, CH_3 , 3 $J_{H-H} = 6$ Hz, 3H), 1.47 (d, CH_3 , 3 $J_{\text{H-H}} = 6.3$ Hz, 3H), 1.60 (d, CH_2 , $J_{\text{H-H}} = 11.7$ Hz, 3H), 1.94 (d, CH_{2} , $J_{H-H} = 11.7$ Hz, 3H), 1.99 (d, CH_{2} , $J_{H-H} = 12.9$ Hz, 1H), 3.12 (br s, NMe_2), 5.42 (septet, CH(CH_3)_2, 1H). $^{13}C\{^1H\}$ at -45 °C: & 3.27 (s, SiMe3), 3.35 (s, SiMe3), 26.93 (s, OCH-(*C*H₃)₂, 43.17 (s, distal *Me* on NMe₂ group), 58.00 (s, proximal Me on NMe2 group), 61.67 (s, CH2), 79.06 (s, CH2), 80.74 (s, OCH(CH₃)₂. The observed *m*/*z* distribution for the Mo₂(NMe₂)(Oⁱ- $Pr)(CH_2SiMe_3)_4^+$ 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'-Mo₂(NMe₂)(O^tBu)R₄. To 1,1'-Mo₂(NMe₂)(Br)(CH₂SiMe₃)₄ (0.100 g, 0.149 mmol) was added 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'-Mo₂(NMe₂)(O^tBu)R₄ in >90% crude yield as determined by ¹H NMR spectroscopy. NMR data were obtained in toluene-*d*₈. ¹H at 20 °C: δ 0.17 (s, Si*Me*₃, 9H), 0.19 (s, Si*M*e₃, 27H), 1.41(s, C(CH₃), 9H), 1.59 (d, CH₂, J_{H-H} 11.7 Hz, 3H), 1.68 (s, CH_2 , 2H), 1.91 (s, CH_2 , $J_{H-H} = 11.7$ Hz, 3H), 2.6 (br s, proximal Me on NMe2 group), 3.75 (br s, distal Me on NMe2 group). ${}^{13}C{}^{1}H$ at -60 °C: δ 2.59 (s, SiMe₃), 2.62 (s, SiMe₃), 43.29 (s, distal Me of NMe₂ group), 57.82 (s, proximal Me of NMe₂ group), 57.97 (s, CH₂), 78.25 (s, CH₂). The observed *m*/*z* distribution for the Mo₂(NMe₂)(O^tBu)(CH₂SiMe₃)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'-Mo₂(NMe₂)BrR₄ (100 mg, 0.149 mmol) and 1 mL of toluene- d_8 was added an excess of HNMe₂- d_6 (>10 equiv). The reaction was monitored by ¹H NMR spectroscopy at -20 °C over a period of 4 h. Approximately 2 h after adding HNMe₂ d_6 , the formation of 1,2-Mo₂(NMe₂)₂R₄ was observed. Shortly thereafter, the formation of HNMe2 was observed. No formation of $1,1-Mo_2(NMe_2)_2R_4$ occurred. (2) To an NMR tube containing 1,1-Mo₂(NMe₂)₂R₄ (100 mg, 0.156 mmol) and 1 mL of toluene- d_8 was added an excess of HNMe₂- d_6 (>10 equiv). The reaction was monitored by ¹H NMR spectroscopy at -20 °C. The formation of protio-HNMe2 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-Mo₂- $(NMe_2)_2R_4$ was observed, but the concentration of HNMe₂ steadily increased as the intensity of the protio NMe₂ signals of 1,1-Mo₂(NMe₂)₂R₄ decreased. (3) To an NMR tube containing 1,1-Mo₂(NMe₂)₂R₄ (100 mg, 0.156 mmol) and 1 mL of toluene*d*₈ was added excess ⁿBu₄NI. The NMR tube was rotated over a period of 24 h, and the reaction was monitored intermittently by ¹H NMR spectroscopy. No isomerization occurred. (4) To an NMR tube containing 1,1-Mo₂(NMe₂)₂R₄ (100 mg, 0.156

mmol) and 1 mL of toluene-d₈ was added excess ⁿBu₄NBr. 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-Mo₂(NMe₂)₂R₄ (100 mg, 0.156 mmol) and 1 mL of toluene- d_8 was added TMSBr (0.156 mmol, 20 μ L), and the reaction was monitored intermittently by ¹H NMR spectroscopy. After 1 h the formation of 1,1'-Mo₂(NMe₂)BrR₄ was detected by ¹H NMR spectroscopy. After 24 h complete conversion had taken place. (6) To an NMR tube containing 1,1-Mo₂(NMe₂)₂R₄ (100 mg, 0.156 mmol), 2,6-di-*tert*-butyl pyridine (0.156 mmol, 38 μ L), and 1 mL of toluene- d_8 was added TMSBr (1 equiv, 20 μ L), and the reaction was monitored intermittently by ¹H NMR spectroscopy. After 1 h the formation of 1,1'-Mo₂(NMe₂)BrR₄ was detected by ¹H NMR spectroscopy. After 24 h complete conversion had taken place. (7) To an NMR tube containing 1,1-Mo₂(NMe₂)₂R₄ (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'-Mo₂(NMe₂)BrR₄ was present in the NMR tube. (8) To 1,2-Mo₂(NMe₂)₂R₄ (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'-Mo2(NMe2)BrR4.

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-Mo₂(NMe₂)-(PPh₂)(CH₂SiMe₃)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.

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 = CH₂SiMe₃) in the reaction

Table 1.	Summary	of Crystal	lographic	Data for
1	.2-Mo ₂ (NM	e2)(PPh2)(CH ₂ SiMe ₃)	4

empi	rical formula	C ₃₀ H ₆₀ Mo ₂ NPSi ₄	
fw		770.01	
space	group	$P\overline{1}$	
<i>a</i> (Å)		11.179(1)	
<i>b</i> (Å)		17.565(2)	
c (Å)		21.060(2)	
α (de	g)	81.23(1)	
β (de	g)	75.85(1)	
δ (de	g)	84.58(1)	
temp	(K)	108.15	
Z		4	
V(Å ³)	3976.27	
$d_{\rm calc}$ ($g \text{ cm}^{-1}$	1.286	
λ (Å)	0 /	0.71073	
u (cm	l ⁻¹)	8.089	
R(F)	,	0.0769	
$R_{\rm w}(F)$)	0.0659	
GoF	•	1.801	

with LiNMe₂ 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 NMe₂-for-Br substitution does this occur? Similarly, in the reaction between 1,2-Mo₂Br₂R₄ and HNMe₂ in hexane one may ask whether the regiochemistry about the M₂ template is retained in each NMe₂-for-Br substitution. To address these questions, we have studied the stepwise substitution chemistry of 1,2-Mo₂Br₂R₄ by low-temperature reactions in hexane and by NMR studies in toluene- d_8 .

The reaction between $1,2-Mo_2Br_2R_4$ and LiNMe₂, 1 equiv, is complicated by the fact that the second NMe₂for-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 NMe₂-for-Br substitution proceeds with alkyl group transfer across the $Mo\equiv Mo$ bond. The second proceeds with retention of regiochemistry.

Studies of the reaction between 1,2-Mo₂Br₂R₄ and HNMe₂ (ca. 10 equiv) in hexane reveal that there is a significant difference in the rate of the first NMe₂-for-Br substitution, and at short reaction times, namely 15 min, essentially complete conversion to Mo₂(NMe₂)BrR₄ is attained along with Me₂NH₂Br, which precipitates from hexane. This reaction also produces the 1,1'isomer. So we now know that in the reactions between 1,2-Mo₂Br₂R₄ and both LiNMe₂ and HNMe₂ there is a common intermediate, Mo₂(NMe₂)BrR₄, with the same regiochemistry. The reaction between Mo₂Br₂R₄ and HNMe₂ which yields Mo₂(NMe₂)BrR₄ 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 LiPPh₂, the regiochemistry is retained. In the latter reaction 1,2-Mo₂(NMe₂)(PPh₂)R₄ is formed.

With the now more accessible availability of $1,2-Mo_2-Br_2R_4$, we have also examined some of its substitution reactions with regard to 1 equiv and 2 equiv of lithium







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

Scheme 2. Bromide Substitution Reactions Involving 1,1'- Mo₂(NMe₂)Br(CH₂SiMe₃)₄



reagents. The dinuclear template is far from inert, and from reactions involving alkynyllithium reagents (LiC≡ CBu^t, LiC≡CPh, LiC≡CSiMe₃), LiPh, and LiPPh₂ 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-Mo₂(O^tBu)BrR₄ and then a 30:70 mixture of 1.1- and 1.2-Mo₂(O^tBu)₂R₄ (as noted by Rothwell¹⁰). In this instance the second substitution of Br by O^tBu is accompanied by some alkyl group transfer. In contrast, reactions employing LiSt-Bu 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-Mo₂- $(NMe_2)_2R_4$ 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 LiNMe₂ and HNMe₂ 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 Me₂NH employed in the simple amine substitution was the catalyst in the transformation of the kinetic isomer to the thermodynamic isomer, eq 1.

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

Initial studies of reaction 1 employing added HNMe₂ gave erratic results, and it soon became apparent that HNMe₂ could not be the catalyst. Only in the case of adventitious Me₂NH₂Br or trace quantities of Mo₂Br₂R₄ did we observe the "amine-catalyzed" transformation shown in eq 1. (In the presence of $Mo_2Br_2R_4$, the addition of HNMe₂ generates Me₂NH₂Br.) Labeling studies involving HNMe₂- d_6 revealed that 1.1-Mo₂- $(NMe_2)_2R_4$ 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-Mo₂(NMe₂)₂R₄ could be brought about by the presence of catalytic, i.e., trace amounts, of Me₂NH₂Br. At this point, we questioned whether the role of Me₂NH₂Br 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 Mo₂(OR)₇⁻, which has a single OR bridging group in the solid state ($R = CH_2^{t}Bu$) and is fluxional on the NMR time scale.¹³ (2) The addition of PMe₃ to 1.2-Mo₂(CH₂-Ph)₂(OⁱPr)₄ in hydrocarbon solutions has been shown to reversibly give (PMe₃)(PhCH₂)₂(PrⁱO)Mo=Mo(OPrⁱ)₃, wherein one four-coordinate Mo atom and one three-

⁽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. ¹H NMR spectrum of 1,1'-Mo₂(NMe₂)BrR₄ 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 ${}^{n}Bu_4N^+X^-$, where X = Brand 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_2 -Br, which is present during the reaction between Mo_2 -Br₂R₄, and an excess of HNMe₂ (ca. 10 equiv). We shall return to speculate on the more detailed reaction pathways that are involved in reactions between Mo_2 -Br₂R₄ and each of LiNMe₂ and HNMe₂. 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-Mo₂(NMe₂)(PPh₂)R₄, proved suitable for a single-crystal X-ray study (vida infra). All compounds were examined by mass spectrometry and by variabletemperature 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-NC₂ 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 ¹H NMR spectrum of 1,1'-Mo₂-(NMe₂)BrR₄ is shown in Figure 1. Because of rapid rotation about the Mo \equiv Mo bond, the SiMe₃ 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 NMe₂ signals appear as two singlets, indicating that proximal and distal NMe₂ 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



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

1,1-Mo₂(NMe₂)₂R₄ the proximal-distal site exchange is still not frozen out at -60 °C. For a series of 1,1'-Mo₂-(NMe₂)XR₄ compounds the rates of NMe proximal \Rightarrow distal exchange follow the order X = Me₂N > 'BuO > 'BuS > Ph \approx CH₂SiMe₃ > Br, which roughly correlates with the ability of the X ligand to σ - and π -donate to the Mo₂⁶⁺ center. For X = Br, which is both a poor π -donor and electronegative, the sole NMe₂ ligand π -donates to the Mo d_{x²-y²}/d_{xy} orbital most strongly, which favors alignment of the NC₂ plane and the Mo-Mo axis and imposes a higher rotational barrier.

The ¹H NMR spectrum for 1,2-Mo₂(NMe₂)(PPh₂)R₄ at room temperature shows only two SiMe₃ groups in the ratio 2:2. The CH₂ protons are not visible at this temperature and the NMe₂ signal is broadened. However, this is sufficient to establish the regiochemistry of substitution as 1,2-Mo₂(NMe₂)(PPh₂)R₄, and at -80 °C a very informative ¹H 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 SiMe₃ 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 ³¹P 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 SiMe₃ 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^tBu 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-Mo₂(NMe₂)(PPh₂)R₄. 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

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



Figure 3. Molecular structure of 1,2-Mo₂(NMe₂)(PPh₂)(CH₂-SiMe₃)₄.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1,2-Mo₂(NMe₂)(PPh₂)(CH₂SiMe₃)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**

$$MoBr + LiNMe_{2} \longrightarrow Mo - N \longrightarrow Me Me MoNMe_{2} + LiBr MoNMe_{3} + LiBr MoNMe_{4} + LiBr MoNM$$

(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.

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

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 LiNMe2, 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 Me₂N-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 Me₂N-to-Mo bond is formed, the Mo-Br bond and Li–NMe₂ bonds are weakened and ultimately broken. Since it is known that Mo-halogen bonds are stronger than Mo-NMe₂ bonds, the ultimate thermodynamic driving force is derived from the greater difference in the thermodynamic stability of LiBr over LiNMe2 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····NMe₂ 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 MoR₃ center and the 1,1'-Mo₂(NMe₂)BrR₄ 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



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'Bu or S'Bu? 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 CH₂SiMe₃.

In the reactions involving organolithium reagents and 1,1'-Mo₂(NMe₂)BrR₄ the products 1,1'-Mo₂(Y)BrR₄ are formed when $Y = CH_2SiMe_3$, Ph, NMe₂, O^tBu, OⁱPr, 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 NMe₂ group that

⁽¹⁵⁾ For 1,2-M₂(R₂)(NMe₂)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.

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Scheme 4. Simplified *o*-Bond Metathesis at the Mo₂⁶⁺ Center Leading to Alkyl Group Transfer



Scheme 5. Aminolysis at the Mo₂⁶⁺ Center Leading to Alkyl Group Transfer



Scheme 6. Me₂HN₂Br-Catalyzed Isomerization of 1,1-Mo₂(NMe₂)₂R₄ to 1,2-Mo₂(NMe₂)₂R₄



was originally at the Mo(NMe₂)BrR center is transferredto the previous MoR₃ 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 NMe₂ 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-Mo₂(NMe₂)₂R₄ reacts with R'OH to give $1,1-Mo_2(OR')_2R_4$ (R' = ^tBu and ⁱPr) and with $HNMe_2 - d_6$ to give $1, 1-Mo_2(NMe_2 - d_6)_2R_4$ 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 LiPPh₂ and 1,1'-Mo₂-(NMe₂)BrR₄, which generates 1,2-Mo₂(NMe₂)(PPh₂)R₄, may do so because this is the thermodynamically favored product and the PPh₂ ligand at the Mo₂⁶⁺ center may facilitate bridge formation leading to mutual exchange of PPh₂ and R groups. If the LiPPh₂ 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 HNMe₂ in a nonpolar solvent will exist as hydrogenbonded oligomers and H-to-Br hydrogen bonding may well occur in an initial "outer-sphere" hydrogen-bonding process prior to Me₂N-to-Mo bond formation.¹⁶ Also, in Scheme 5, it is recognized that HBr does not leave but rather Me₂NH₂⁺Br⁻ is formed, which is likely to be hydrogen bonded with HNMe₂ prior to crystallization. One thing we can attest to is the chemical persistence of 1,1-Mo₂(NMe₂)₂R₄ 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 Me₂NH₂Br is one of delivering an equivalent of HBr to 1,1-Mo₂(NMe₂)₂R₄ to form 1,1'-Mo₂(NMe₂)BrR₄, which in the presence of HNMe₂ (2 equiv) then reacts as shown in Scheme 6. This proposed pathway involves the formation of a Mo₂BrHN 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(CH₂SiMe₂)₃ center, which is sterically crowded and does not contain any electronwithdrawing (electronegative) groups. It is, however, coordinatively unsaturated and certainly capable of Lewis base association. Further evidence that the role of Me₂NH₂Br is one of delivering an equivalent of HBr comes from the reaction between 1,1-Mo₂(NMe₂)₂R₄ and 2 equiv of HBr, which yields 1,1'-Mo₂(NMe₂)BrR₄. The latter two reactions prompted us to speculate that TMSBr may also react with 1,1-Mo₂(NMe)₂R₄ via a similar mechanism, namely, that HBr would be generated in situ and react with 1,1-Mo₂(NMe)₂R₄. Our speculation was based on the amine-catalyzed chloro-for-dimethylamide exchange reactions known to be operative in the reaction between W₂(NMe₂)₆ and TMSCl.¹⁹ The reaction

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





sequence we envisage is shown in eq 3.

 $Me_3SiBr + HNMe_2 \Rightarrow Me_3SiNMe_2 + HBr$ (3)

$$L_nMoNMe_2 + HBr = L_nMoBr + HNMe_2$$

However, we must concede that the reaction involving TMSBr and 1,1-Mo₂(NMe₂)₂R₄ may proceed by a direct S_F2 σ -bond metathesis reaction since when the reaction is done in the presence of a proton sponge (2,6-di-*tert*-butylpyridine), 1,1'-Mo₂(NMe₂)BrR₄ is still obtained and without any apparent change in the rate of formation. These reactions involving 1,1-Mo₂(NMe₂)₂R₄ are summarized in Scheme 7.

One last reaction to note is that between $1,2-Mo_2-(NMe_2)_2R_4$ 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 $1,2-Mo_2(NMe_2)_2R_4$ 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'-Mo₂-(NMe₂)BrR₄ contains a chiral Mo center. Thus the introduction of a chiral amide or other ligand Y* could yield a pair of diastereomers 1,1-Mo₂Br(Y*)R₄ which could be readily distinguished by NMR spectroscopy and separated by their different physical properties. In this way a pure enantiomer $1,1'-Mo_2Br(Y^*)R_4$ could be employed to interrogate the nature of the second substitution step. Further studies along these lines could prove fruitful just as studies of $(1,3-C_3R_2H_3-\eta^5)M_-$ (CO)(L)X piano-stool complexes did in the past.²⁰

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Supporting Information Available: CIF data for 1,2-Mo₂(NMe₂)(PPh₂)(CH₂SiMe₃)₄ along with representative mass spectra for the latter and 1,1'-Mo₂(NMe₂)(Br)(CH₂SiMe₃)₄ are available. ¹H NMR spectra for 1,2-Mo₂(S'Bu)₂(CH₂SiMe₃)₄, 1,1'-Mo₂(S'Bu)(NMe₂)(CH₂SiMe₃)₄, Mo₂(NMe₂)(CH₂SiMe₃)₅, 1,1'-Mo₂(NMe₂)(Ph)(CH₂SiMe₃)₄, and 1,1'-Mo₂(O'Bu)(NMe₂)(CH₂-SiMe₃)₄ are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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⁽²⁰⁾ Reich-Rohrwig, P.; Wojiciki, A. Inorg. Chem. 1974, 13, 2457.