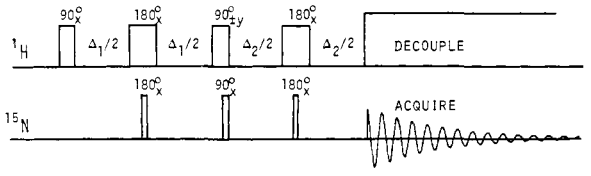


Figure 1. Pulse scheme of the INEPT experiment. The phase of the second 90° ^{1}H pulse is alternated along the $\pm y$ axis in successive experiments, and data are accordingly added and subtracted.[1,2] In the selective INEPT experiment the proton pulses are soft pulses ($\gamma H_2/2\pi \approx 50$ Hz), applied to a preselected proton. In both versions of the experiment, broad-band proton decoupling is used during acquisition. The delays $\Delta_1/2$ and $\Delta_2/2$ are, for a NH pair, of the order of $1/(4J)$, where J is the magnitude of the scalar coupling used in the transfer process.

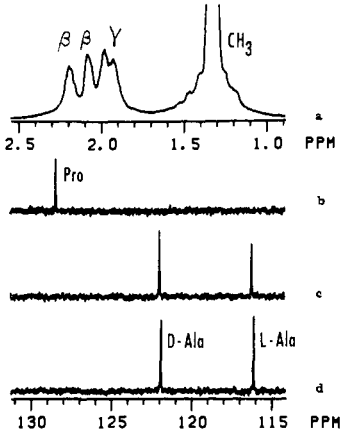


Figure 2. (a) Proton spectrum of *cyclo*-(D-Ala-L-Pro-L-Ala)$_2$ in $CDCl_3$, recorded at 500 MHz, using the decoupler coil of the 10-mm ^{15}N probe. (b) Selective INEPT spectrum of the proline ^{15}N resonance, obtained in 18 min. (c) Regular INEPT spectrum, showing only the alanine ^{15}N resonances, obtained in 2 min. (d) Conventional "one-pulse, FT" spectrum, obtained in 1 h, using continuous broad-band proton decoupling. ^{15}N spectra are referenced indirectly to NH_3, using Me_4Si as an intermediate.[16]

^{15}N magnetization vectors during the delay time Δ_2 is not affected by coupling to protons other than the one to which a selective 180° pulse is applied,[11,12] and therefore, after this time, Δ_2 ($\approx 1/(2^{lr}J_{NH})$), the ^{15}N doublet components will be parallel and broad-band proton decoupling can be started. In principle, this selective INEPT experiment can give the full factor of 10 in signal enhancement. Because the longitudinal relaxation time will generally be much shorter for the proton than for the nonprotonated ^{15}N nucleus, the experiment can be repeated much faster than a conventional "one pulse, FT" experiment, and the gain in sensitivity will even be larger.

The experiment is demonstrated for the detection of the proline ^{15}N resonance in a 0.3 M solution of the cyclic hexapeptide (D-Ala-L-Pro-L-Ala)$_2$[13] in $CDCl_3$, in a 10-mm sample tube. Experiments were performed on a NT-500 spectrometer. Figure 2a shows the proton spectrum obtained by using the decoupler coil of the ^{15}N probe, showing the rather poor ^{1}H resolution. The proline β proton at 2.08 ppm was used for the selective polarization transfer. The proton rf field strength was calibrated[14,15] to give a 90° pulse duration of 5 ms, using a sample of formamide and pulsing the α proton resonance. Figure 2b shows the proline ^{15}N resonance, obtained after 500 accumulations (18 min) with the selective INEPT experiment. Three-bond ^{1}H–^{15}N couplings are often of the order of 2–3 Hz, and on this basis, the delays $\Delta_1/2$ and $\Delta_2/2$ would have to be set to 50 ms. To minimize effects of relaxation during those delays, both delays were set to a compromise value of 30 ms. As a reference, Figure 1c shows the two ^{15}N resonances of D-Ala and L-Ala in the peptide, obtained with the regular INEPT experiment in 50 accumulations (2 min). Figure 1d shows the normal FID spectrum obtained from 1000 accumulations with broad-band decoupling throughout and a ^{15}N flip angle of 60° (1 h). Probably due to the small NOE and the long T_1, the ^{15}N proline is not observed.

From comparing Figure 2 parts b and c, it can be seen that the selective INEPT sequence is a factor of 4 less effective in enhancing the proline ^{15}N resonance than the conventional INEPT sequence is for the alanine resonances. Hence, the effective enhancement of the proline resonance is probably only a factor of 2, instead of the obtainable 10. Main reasons for this lower enhancement are the relaxation during the delays Δ_1 and Δ_2 and the fact that the selective pulses are not selective enough and also affect the nearby resonances of the γ protons and the other β proton. This also means that, in this case, a high magnetic field strength is needed in order to separate those resonances sufficiently. In principle other polarization sequences[7,8] could also be used for polarization transfer via long-range couplings, but because the total duration of those sequences is longer, relaxation effects will be stronger, and efficiency is expected to be worse.

To summarize, we have demonstrated that signal enhancement of nonprotonated ^{15}N nuclei in peptides is feasible by means of selective INEPT. The experiment is easy to set up and gives a large signal enhancement compared with conventional observation. It allows the natural abundance ^{15}N study of the structure-sensitive proline ^{15}N resonances in polypeptides.

Acknowledgment. We are indebted to R. Tschudin for technical assistance and to Drs. E. D. Becker, J. S. Cohen, D. Torchia, and H. Ziffer for many useful discussions.

Registry No. (D-Ala-L-Pro-L-Ala)$_2$, 66254-41-9; ^{15}N, 14390-96-6; L-Pro, 147-85-3.

(11) Bax, A.; Freeman, R. *J. Am. Chem. Soc.* **1982**, *104*, 1099–1100.
(12) Davis, D. G.; Agosta, W. C.; Cowburn, D. *J. Am. Chem. Soc.* **1983**, *105*, 6180–6190.
(13) Niu, C. H.; Pease, L. G.; Blout, E. R. *Biopolymers* **1978**, *17*, 115–123.
(14) Thomas, D. M.; Bendall, M. R.; Pegg, D. T.; Doddrell, D. M.; Field, J. *J. Magn. Reson.* **1981**, *42*, 298–306.
(15) Bax, A. *J. Magn. Reson.* **1983**, *52*, 76–80.
(16) Live, D.; Davis, D. G.; Agosta, W. C.; Cowburn, D. *J. Am. Chem. Soc.*, submitted for publication.

Molecular Structure and Dynamic Solution Behavior of the Bridging 1,3-Dimetallaallyl Ligand in $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3R_2SiMe_3)$ Compounds (R = H, Me, Ph) Formed by Insertion of Alkynes into a Bridging Alkylidyne Ligand

Malcolm H. Chisholm,* Joseph A. Heppert, and John C. Huffman

Department of Chemistry and Molecular Structure Center Indiana University, Bloomington, Indiana 47405

Received October 11, 1983

The considerable current interest in the reactivity of $M_2(\mu\text{-}X)$ species, particularly with respect to C–C bond-forming reactions,[1] prompts us to report some preliminary findings concerning the reactivity of the $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)_2(M\text{-}M)$ molecule[2] toward alkynes, RC≡CR, where R = H, Me, and Ph, which proceed in hydrocarbon solvents according to eq 1.

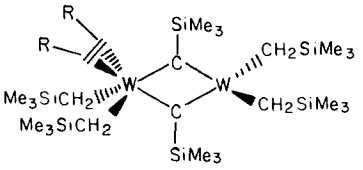
(1) For example: (i) μ-CH_2 and μ-CR_2, their utility in olefin metathesis and as models for Fischer-Tropsch processes, see: (a) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37–51. (b) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464–475. (ii) μ-CH^+, its role in "hydrocarbation" reactions, see: (c) Casey, C. P.; Fagan, P. J. *Ibid.* **1982**, *104*, 4950–4951. (iii) μ-C_2H_2 and μ-C_2R_2, their role in alkyne polymerizations, see: (d) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221–223. (e) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389–4399. (iv) μ-CR, a possible model for alkyne metathesis, see: (f) Jeffery, J. C.; Mead, K. A.; Razay, H.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 867–868.
(2) Chisholm, M. H.; Cotton, F. A.; Extine, M.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 696–698.

0002-7863/84/1506-1151$01.50/0

$$(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)_2 + RC{\equiv}CR \longrightarrow (Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)_2(C_2R_2) \longrightarrow (Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3R_2SiMe_3) \quad (1)$$

The rate of reaction is very dependent on the size of R. When R = H, the reaction proceeds rapidly to give IIa below 0 °C, and evidence for Ia is found only by ^{1}H NMR spectroscopy at or below −50 °C.[3] When R = Me, the formation of Ib occurs rapidly at room temperature and is followed by a relatively slow conversion to IIb at room temperature, the reaction being essentially complete within 10 days. For R = Ph, there is little evidence of formation of Ic at room temperature, but formation of IIc occurs within 2 weeks. At 60 °C, formation of IIc (R = Ph) is essentially complete within 4–5 days.

A plausible structure for I, shown below, is based on ^{1}H and



I

^{13}C NMR data for the compound R = Me[3], which can be isolated as a waxy brown-orange solid. There are two different μ-$CSiMe_3$ ligands and two types of CH_2SiMe_3 ligands, each having diastereotopic methylene protons. The appearance of only one acetylenic carbon and acetylenic methyl group implies either a rapidly rotating alkyne ligand or one aligned with its C–C axis perpendicular to the W–W axis.[3] Note that the extremely low chemical shift value for the acetylenic carbons is consistent with the alkyne ligand being a four-electron donor.[3] This would be expected since the tungsten atom to which it is bonded does not have an 18 valence electron shell.

The molecular structure of IIc, R = Ph,[4] shown in Figure 1, reveals the formation of the μ-C(R)C(R)$CSiMe_3$ ligand.[5] The low-temperature ^{1}H and ^{13}C NMR spectra for the two compounds R = Me and Ph[3] are entirely consistent with a structure akin to that seen for R = Ph but having a time-averaged mirror plane

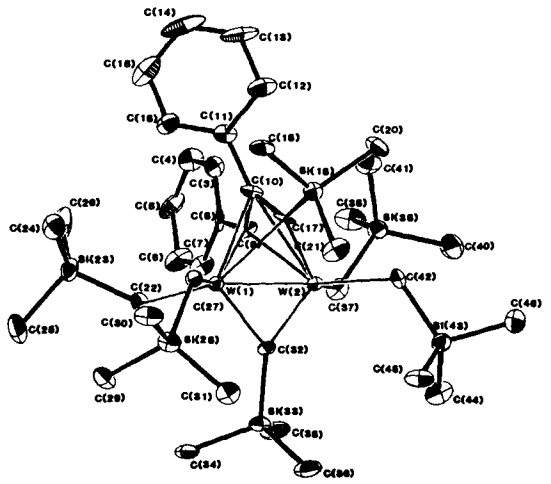


Figure 1. An ORTEP view of the $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}CPhCPhCSiMe_3)$ molecule. Some pertinent bond distances (Å) and angles (deg): W–W = 2.548 (1), W(1)–C(9) = 2.24 (1), W(1)–C(10) = 2.45 (1), W(1)–C(17) = 2.29 (1), W(2)–C(9) = 2.20 (1), W(2)–C(10) = 2.68 (1), W(2)–C(17) = 2.17 (1), W(1)–C(32) = 1.96 (1), W(2)–C(32) = 2.00 (1), C(9)–C(10) = 1.41 (2), C(10)–C(17) = 1.41 (2), W–C(alkyl) = 2.13 (2) (av), C(9)–C(10)–C(17) = 106 (1), W(1)–C(32)–W(2) = 79.9 (4), W(1)–C(9)–W(2) = 69.9 (3), W(1)–C(10)–W(2) = 59.3 (3), W(1)–C(17)–W(2) = 69.8 (3), C(22)–W(1)–C(27) = 104.7 (5), C(37)–W(2)–C(42) = 98.7 (6).

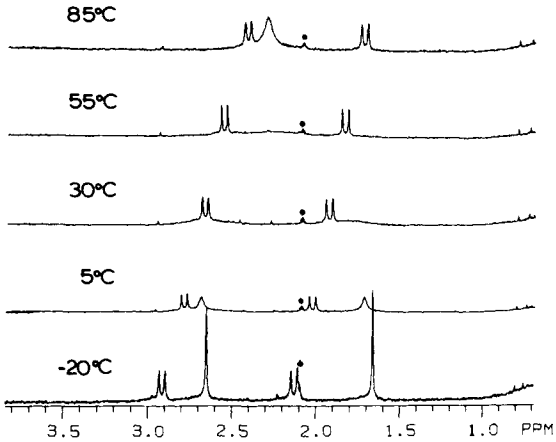
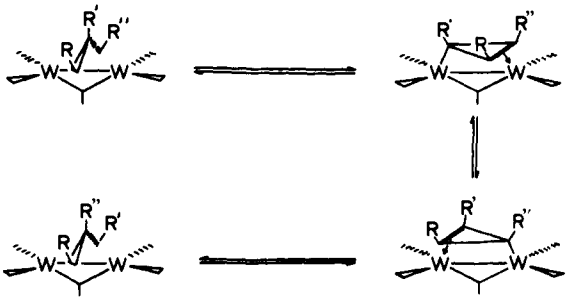


Figure 2. ^{1}H NMR spectrum of IIb in toluene-d_8 at 360 MHz showing the temperature dependence of the methyl proton resonances in the μ-C(Me)C(Me)$CSiMe_3$ ligand. * denotes the methyl protio impurity of toluene-d_8.

Scheme I



containing the μ-C_3 moiety and bisecting the W–W bond. However, for R = H a more symmetrical structure, one having real or apparent C_2 symmetry, is required.[3] This is satisfied if the $CSiMe_3$ group occupies the 2-position of the dimetallaallyl moiety. The lack of any significant (measurable) ^{183}W–^{13}C coupling for the Me_3SiC carbon of the μ-$C_3H_2SiMe_3$ ligand in Ib is also consistent with its presence at the 2-position.[3]

The ^{1}H and ^{13}C NMR spectra for IIb, R = Me, at room temperature and above, however, indicate that CMe group site

(3) NMR spectroscopic data: Ia $[(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)_2\text{-}C_2H_2]$ ^{1}H NMR δ 13.1 (2 H, s, C_2H_2), 0.62 and 0.55 (9 H, s, $CSiMe_3$), 0.13 and −0.26 (18 H, s, $CH_2Si\mathit{Me}_2$). IIa $[(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3(H)_2SiMe_3)]$ ^{1}H NMR δ 5.90 (2 H, s, $J_{^{183}W-^1H}$ = 5.6 Hz, μ-$C_3(\mathit{H})_2SiMe_3$), 0.57 and 0.28 (9 H, s, μ-$CSi\mathit{Me}_3$ and μ-$C_3(H)_2Si\mathit{Me}_3$), 0.23 (36 H, s, $CH_2Si\mathit{Me}_3$), 0.28 and −0.43 (H, d, $J_{Ha-Ha'}$ = 11 Hz, $C\mathit{H}_2SiMe_3$); partial ^{13}C[^{1}H] NMR δ 330.5 ($J_{^{183}W-^{13}C}$ = 111 Hz; μ-$CSiMe_3$), 155.8, 152.7 ($J_{^{183}W-^{13}C}$ ca. 0 and 32 Hz, respectively, μ-$C_3(H)_2SiMe_3$). Ib $[(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)_2\text{-}C_2Me_2]$ ^{1}H NMR (−40 °C) δ 3.06 (6 H, s, $C_2\mathit{Me}_2$), 1.55 and 1.27 (2 H, d, $J_{Ha-Ha'}$ = 10 Hz, $C\mathit{H}_2SiMe_3$), 1.13 and 0.85 (2 H, d, $J_{Hb-Hb'}$ = 11 Hz, $C\mathit{H}_2SiMe_3$), 0.61 and 0.43 (9 H, s, μ-$CSi\mathit{Me}_3$), 0.26 and −0.15 (18 H, s, $CH_2Si\mathit{Me}_3$); partial ^{13}C[^{1}H] NMR (−40 °C) δ 359 and 339 ($J_{^{183}W-^{13}C}$ = 121 and 79.8 Hz, respectively, μ-$CSiMe_3$), 221 (C_2Me_2), 22.5 ($C_2\mathit{Me}_2$). IIb $[(Me_3SiCH_2)_4W_2\text{-}(\mu\text{-}CSiMe_3)(\mu\text{-}C_3(Me)_2SiMe_3)]$ ^{1}H NMR (−40 °C) δ 2.58 and 1.58 (3 H, s, (μ-$C_3(\mathit{Me})_2SiMe_3$), 3.03 and −0.06 (2 H, d, $J_{Ha-Ha'}$ = 12 Hz, $C\mathit{H}_2SiMe_3$), 2.22 and −0.36 (2 H, d, $J_{Hb-Hb'}$ = 14 Hz, $C\mathit{H}_2SiMe_3$), 0.44 and 0.30 (9 H, s, μ-$CSi\mathit{Me}_3$ and μ-$C_3(Me)_2Si\mathit{Me}_3$), 0.37 and 0.13 (18 H, s, $CH_2Si\mathit{Me}_3$); partial ^{13}C[^{1}H] NMR (−60 °C) δ 334.6 ($J_{^{183}W-^{13}C}$ = 119 Hz, μ-$CSiMe_3$), 161.3 and 156.3 and 143.7 ($J_{^{183}W-^{13}C}$ = 24, ca. 0, and 30 Hz, respectively, μ-C_3-$(Me)_2SiMe_3$), 24.5 and 22.8 (μ-$C_3(\mathit{Me})_2SiMe_3$). Ic $[(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3(Ph)_2SiMe_3)]$ partial ^{1}H NMR δ 2.91 and −0.13 (2 H, d, $J_{Ha-Ha'}$ = 12 Hz, $C\mathit{H}_2SiMe_3$), 1.84 and −0.28 (2 H, d, $J_{Ha-Ha'}$ = 14 Hz, $C\mathit{H}_2SiMe_3$), 0.58 and 0.11 (9 H, s, μ-$CSi\mathit{Me}_3$ and μ-$C_3(Ph)_2Si\mathit{Me}_3$), 0.36 and 0.00 (18 H, s, $CH_2Si\mathit{Me}_3$); partial ^{13}C[^{1}H] NMR δ 340.0 ($J_{^{183}W-^{13}C}$ = 114 Hz, μ-$CSiMe_3$), 158.8, and 158.4, and 149.9 (μ-$C_3(Ph)_2SiMe_3$). For comparison with other four-electron donor alkyne complexes, see: Templeton, J. L.; Ward, B. W. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

(4) Crystal data for $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3Ph_2SiMe_3)$ at −160 °C: space group = $P2_12_12_1$, a = 20.884 (9) Å, b = 13.734 (5) Å, c = 16.842 (6) Å, Z = 4, d_{calcd} = 1.46 g cm^{-3}. Of 6120 unique intensities, the 5579 having $F > 2.33\sigma(F)$ were used in the least-squares refinement. The hydrogen atoms were used as fixed-atom contributors in idealized positions. The final residuals are F_F = 0.052 and R_{wF} = 0.050.

(5) Formation of a μ-$CR^1CR^2CR^3$ ligand has been observed previously in the reaction between an alkyne and a μ_2-CR ligand[1f] and more recently in the reaction between an alkyne and a μ_3-CR ligand; Beanan, L. R.; Rahman, Z. A.; Keister, J. B. *Organometallics* **1983**, *2*, 1062–1064.

exchange between the 1- and 2-positions of the μ-C(Me)C(Me)CSiMe$_3$ ligand is occurring on the NMR time scale (see Figure 2). From the coalescence temperature of +55 °C, $\Delta G^{\ddagger}$ ca. 15 Kcal mol^{-1} can be estimated. The exchange process does not involve a scrambling of the CSiMe$_3$ group nor does it involve the CH$_2$SiMe$_3$ ligands. Though some changes in the ^{1}H spectra do occur with changing temperature all changes other than the CMe scrambling can be understood in terms of chemical shift variations with temperature. Thus, though 1,2-CMe site exchange is quite rapid on the NMR time scale, the asymmetry imposed by the C(Me)C(Me)CSiMe$_3$ ligand straddling the W–W bond is retained.

The slow formation of II from I (R = Me) appears to preclude a fluxional process involving II $\rightleftharpoons$ I. This, taken together with the likelihood that a rapid reversible insertion of the alkyne moiety would scramble the CSiMe$_3$ groups, leads us to propose an alternate mechanism involving the interconversion of the μ-1,3-dimetallaallyl ligand with a μ-metallacyclopropenyl ligand as shown in Scheme I. Here by a series of 60° twists and bond openings and closings it is possible to achieve scrambling of all (1, 2, and 3) carbon sites. This would allow for formation of the μ-C(H)CSiMe$_3$C(H) ligand without invoking an acetylene metathesis-like reaction in which a C$_2$ unit was extruded from the μ-C$_3$ ligand. Also, if for steric or electronic reasons the μ-C(R)C(R)CSiMe$_3$ ligand has a marked preference for the CSiMe$_3$ group in the 3-position, then only a facile 1 $\rightleftharpoons$ 2 site exchange of CR groups would occur.

Interestingly, $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$,[6] which is a structural analogue of the tungsten derivative but is a d^0–d^0 dimer, does not react with alkynes at ambient temperatures. Many questions are raised by these observations, and further studies are in progress.[7]

Supplementary Material Available: Fractional coordinates and isotropic thermal parameters for the $(Me_3SiCH_2)_4W(\mu\text{-}C_3Ph_2SiMe_3)(\mu\text{-}CSiMe_3)$ molecule (1 page). Ordering information is given on any current masthead page.

(6) Mowat, W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1120–1124.

(7) We thank the National Science Foundation for financial support.

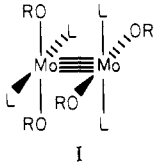
Quadruple Bonds between Molybdenum Atoms Supported by Alkoxide Ligands. Structural Effects and Reactivity Patterns

Malcolm H. Chisholm,* Kirsten Folting, John C. Huffman, and Robert J. Tatz

Department of Chemistry and Molecular Structure Center, Indiana University Bloomington, Indiana 47405

Received October 24, 1983

We wish to report the preparation of a series of compounds of formula $Mo_2(OR)_4L_4(M\overset{4}{-}M)$ and structural type I. These are



I

the first compounds containing the $(Mo\overset{4}{-}Mo)^{4+}$ unit supported by alkoxy ligands and show interesting structural parameters and reactivity patterns not previously observed in the chemistry of compounds containing Mo–Mo quadruple bonds.[1]

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

Alcoholysis reactions[2] of 1,2-Mo_2-*i*-$Bu_2(NMe_2)_4$ in hexane reveal a marked dependence on steric factors of the alcohol. Reaction employing *t*-BuOH yields Mo_2-*t*-Bu(O-*t*-Bu)$_5$, isobutane, and dimethylamine (4 equiv), whereas with *t*-BuCH$_2$OH, the purple crystalline compound $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(HNMe_2)_4(M\overset{4}{-}M)$ is obtained with liberation of 1 equiv of isobutylene and isobutane. Reactions employing *i*-PrOH yield purple solutions that contain a mixture of species, including $Mo_2(O\text{-}i\text{-}Pr)_4(HNMe_2)_4$ as determined by ^{1}H NMR spectroscopy. This purple solution is reactive toward ethylene to give $Mo_2Et(O\text{-}i\text{-}Pr)_5(M{\equiv}M)$ and toward neutral donor ligands to give $Mo_2(O\text{-}i\text{-}Pr)_4L_4(M\overset{4}{-}M)$ compounds where L = py, H$_2$NMe, and PMe$_3$. Rather interestingly, in the presence of excess *i*-PrOH, the solvent complex $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$ crystallizes from the reaction mixture [Mo_2-*i*-$Bu_2(NMe_2)_4$ + *i*-PrOH] at −20 °C. The latter compound is unstable at room temperature, slowly decomposing to $Mo_2(O\text{-}i\text{-}Pr)_6$ along with other as yet uncharacterized products. However, when freshly prepared, it may be used to synthesize new $(Mo\overset{4}{-}Mo)^{4+}$ containing compounds. With CO$_2$ and acacH (2,4-pentanedione), $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$ reacts in hydrocarbon solvents to give $Mo_2(O_2CO\text{-}i\text{-}Pr)_4$ and $Mo_2(acac)_4$, respectively. Addition of HNMe$_2$ (4 equiv) and ethylene affords $Mo_2Et(O\text{-}i\text{-}Pr)_5$ with a return to the $(Mo{\equiv}Mo)^{6+}$ unit, but addition of H$_2$NMe and ethylene yields only the substituted product $Mo_2(O\text{-}i\text{-}Pr)_4(H_2NMe)_4$. Except for the thermally unstable compound $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$, satisfactory elemental analyses have been obtained for the new compounds reported.

These reactions may be understood in the following manner. Alcoholyses of $Mo_2R'_2(NMe_2)_4$ compounds (R′ = a β-hydrogen containing alkyl) proceed by β-hydrogen atom transfer and reductive elimination to give alkene, alkane, and "$Mo_2(OR)_4$", as was suggested earlier on the basis of labeling experiments.[3] The "$Mo_2(OR)_4$" species may be trapped and isolated as an $Mo_2(OR)_4L_4$ compound *only* if steric factors are favorable, otherwise an oxidative-addition reaction will regenerate the $(Mo{\equiv}Mo)^{6+}$ unit: "$Mo_2(OR)_4$" + ROH + alkene → $Mo_2R'(OR)_5$. The importance of steric factors in stabilizing $Mo_2(OR)_4L_4$ compounds is evident from the reaction of $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$ with HNMe$_2$ and H$_2$NMe in the presence of ethylene, which lead to $Mo_2Et(O\text{-}i\text{-}Pr)_5(M{\equiv}M)$ and $Mo_2(O\text{-}i\text{-}Pr)_4(H_2NMe)_4(M\overset{4}{-}M)$, respectively. This leads us to suggest that the oxidative-addition step involves reaction of a coordinatively unsaturated $(Mo\overset{4}{-}Mo)^{4+}$ speceis such as $Mo_2(O\text{-}i\text{-}Pr)_4(HNMe_2)_3$.

A comparison of pertinent structural parameters[4] for $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(HNMe_2)_4$, $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(PMe_3)_4$, $Mo_2(O\text{-}i\text{-}$

(2) All reactions and manipulations were carried out in dry and oxygen-free solvents (hexane or toluene) and atmospheres (N$_2$).

(3) Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2075.

(4) Crystal data: (1) for $Mo_2(O\text{-}i\text{-}Pr)_4(py)_4$ at −167 °C, space group $P\bar{1}$, a = 18.254 (6) Å, b = 10.327 (2) Å, c = 10.076 (2) Å, α = 70.92 (1)°, β = 103.08 (1)°, γ = 104.38 (1)°, Z = 2, d_{calcd} = 1.44 g cm^{-3}. 4492 unique reflections, 3765 having $F > 2.33\sigma(F)$ were used in full least squares refinements, including isotropic hydrogen atom positions. Final residual are R_F = 0.031 and R_{wF} = 0.033; (2) for $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(HNMe_2)_4$ at −160 °C, space group *I*4*cm*, a = 22.064 (5) Å, b = 22.064 (5) Å, c = 16.985 (4) Å, Z = 8, d_{calcd} = 1.16 g cm^{-3}. Of 1480 unique reflections, 1433 having $F > 2.33\sigma(F)$ were used in the refinement. Hydrogen atoms were located in a difference Fourier and were placed in idealized calculated positions for the final three cycles. Final residuals are R_F = 0.063 and R_{wF} = 0.065; (3) for $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(PMe_3)_4$ at −160 °C, space group *Pa*, a = 19.441 (10) Å, b = 11.619 (5) Å, c = 9.906 (4) Å, β = 106.41 (2)°, Z = 2, d_{calcd} = 1.31 g cm^{-3}. Of the 2828 unique reflections, the 2463 having $F > 2.33\sigma(F)$ were used in the least-squares refinement. At the present stage of refinement, hydrogen atoms have not been included. Current residuals are R_F = 0.062 and R_{wF} = 0.063; (4) for $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$ at −162 °C: probable space group based on extinctions *P*4/*nmm* with a = 12.810 (5) Å, c = 9.869 (5) Å, Z = 2, d_{calcd} = 1.37 g cm^{-3}. The total number of reflections collected was 2287, of which 637 were unique and 599 had $F > 2.33\sigma(F)$. The molecule was found to be disordered about the crystallographic fourfold axis. Hydrogen atom positions were calculated and were used as fixed atom contributors in the least-squares refinement. Current residuals are R_F = 0.083 and R_{wF} = 0.100. While each end of the molecule appears different, this may be an artifact of the disorder. Attempts to place the molecule in lower symmetry space groups yielded equivalent results.

0002-7863/84/1506-1153$01.50/0