20 min) gave a single hydroxy ester **14**, mp 78–79 °C (65% from **12**). Conversion of **14** to the tetracyclic dilactone **15** was accomplished by the sequence (1) mesylation (1.5 equiv of triethylamine, 3 equiv of mesyl chloride at −20 °C in CH_2Cl_2 for 30 min, yield 94%) and (2) methyl ester hydrolysis (0.1 N lithium hydroxide in THF–water at 23 °C for 2 h) and acidification (84% yield). The short and simple synthesis of **15** illustrates the synthetic potential of the methodology described herein.

The widely different rates of the carbolactonization reaction with keto acids **2**, **7**, **9**, and **11** would seem to indicate that cyclization rather than α-deprotonation may be rate limiting in these cases. If this is indeed so, it must also be true that the reactive intermediate in the C–C bond-forming step of the carbolactonization is not a conventional free radical but a Mn-stabilized "radicaloid" species, perhaps that derived by deprotonation of a bridged acetate in $Mn_3O(OCOCH_3)_7$.

The extension of this methodology and its application to the synthesis of gingkolides will be described in subsequent papers.[13]

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(i-PrO)₃Mo≡Mo(CH₂Ph)₂(O-i-Pr)(PMe₃): The First Example of a Compound Containing a Triple Bond Uniting Three- and Four-Coordinate Molybdenum Atoms and the Observation of Phosphine-Promoted, Reversible Benzyl–Alkoxy Migrations at the (M≡M)⁶⁺ Center

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Of all the compounds containing multiple bonds between metal atoms,[1] the d^3–d^3 dimers of molybdenum and tungsten show the most varied and fascinating coordination chemistry. There are compounds with M–M triple bonds of configuration $\sigma^2\pi^4$ in which the metal atoms are each coordinated to three, four, five, and even six ligand atoms.[2,3] Though *ligand* atoms may span the two metal atoms, there are no bridging *atoms* in this group of d^3–d^3 dimers. However, compounds with bridging atoms are known as in $W_2Cl_6(py)_4$[4] and the salts containing $M_2X_9{}^{3-}$ ions (X = Cl, Br)[5] which adopt structures based on edge- and face-shared octahedra, respectively. Within the former group of compounds of formula $X_nM≡MX_n$ or $X_nY_mM≡MX_nY_m$, where X and Y = a ligand atom and n or (n + m) = 3 → 6, there has been no example of a compound where the coordination number at each metal atom has been different, e.g., in $Mo_2(NMe_2)_6$, $Mo_2(O-i-Pr)_6(py)_2$, $W_2Me_2(O_2CNEt_2)_4$, and $W_2(O_2CNMe_2)_6$ n or (n + m) = 3, 4, 5, and 6, respectively. The apparent desire of the metal atoms to maintain this equality in coordination number is exemplified

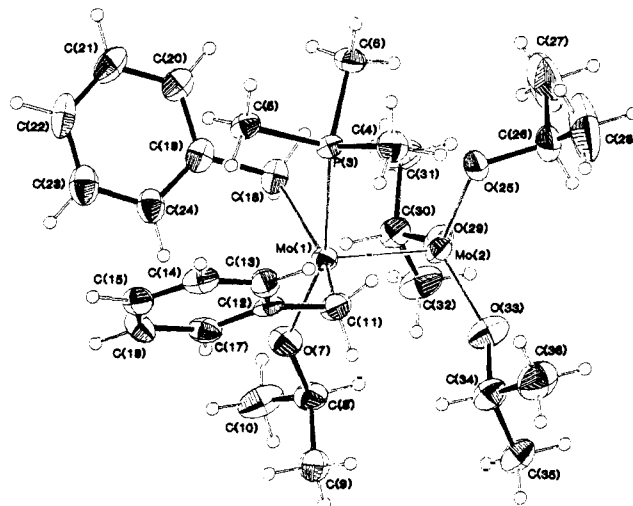
Figure 1. ORTEP view of the (i-PrO)₃Mo≡Mo(CH₂Ph)₂(O-i-Pr)(PMe₃) molecule. Some pertinent bond distances (Å) and angles (°) (averaged where appropriate): Mo–Mo = 2.235 (1) Mo–C = 2.22 (1), Mo(1)–O-(7) = 1.920 (4), Mo(2)–O = 1.89 (2), Mo–P = 2.581 (2); Mo–Mo–C = 101.3 (6), Mo(2)–Mo(1)–O(7) = 106.5 (1), Mo–Mo–P = 94.65 (4), Mo(1)–Mo(2)–O = 107.2 (20), Mo–C–C = 114.4 (11).

by the pair-wise insertion of CO_2 into OR[6] and NMe_2[7] ligands and the cooperative binding of Lewis bases to $M_2(OR)_6$ compounds:[8] $M_2(OR)_6 + 2L \rightarrow M_2(OR)_6L_2$. We report here the first example of a compound having a central $(M≡M)^{6+}$ unit in which the metal atoms have different coordination numbers, namely, 3 and 4.

Hexane solutions of $1,2-Mo_2(CH_2Ph)_2(NMe_2)_4$[9] react with i-PrOH (4 equiv) to yield $1,2-Mo_2(CH_2Ph)_2(O-i-Pr)_4$.[10] The ^{1}H NMR spectra[11] confirm the 1,2-dibenzyl substitution pattern and are consistent with a rapidly interconverting (NMR time scale) mixture of anti and gauche rotamers, through the presence of only the anti rotamer cannot be excluded: the benzyl methylene protons appear as a singlet, and there is only one type of O-i-Pr ligand which contains diastereotopic methyl groups.

Addition of PMe_3 (2 equiv) to a hexane solution of $1,2-Mo_2$-$(CH_2Ph)_2(O-i-Pr)_4$ yields (i-PrO)₃Mo≡Mo(CH₂Ph)₂(O-i-Pr)-(PMe_3) as red crystals upon cooling. The molecular structure, deduced from an X-ray study,[12] is shown in Figure 1. The Mo–Mo distance, 2.235 (1) Å, is comparable to those in Mo_2-$(OCH_2-t-Bu)_6$[13] 2.222 (2) Å, and $Mo_2Me_2(O-t-Bu)_4(py)_2$[14] 2.256

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(10) Dry and oxygen free solvents and atmospheres (N_2) were used throughout.

(11) ^{1}H NMR data obtained from toluene-d_8 at 360 MHz for $1,2-Mo_2$-$(CH_2Ph)_2(O-i-Pr)_4$ (+20 °C): δ (CH_2Ph) 4.13 (s); (CH_2Ph) o 7.05 (d, J = 7.6 Hz), m 6.99 (dd, J = 7.6 Hz), p 6.79 (t, J = 7.6 Hz); (CHMe₂) 5.39 (sept, J = 5.8 Hz); (CHMe_2) 1.32 (d, J = 5.8 Hz), 1.26 (d, J = 5.8 Hz). (i-PrO)₃Mo≡Mo (CH₂Ph)₂(O-i-Pr)(PMe₃) (−20 °C): δ (CH_2Ph) 4.63 (2 H, dd, $^2J_{H-H'}$ = 11.8 Hz; $^3J_{H-P}$ = 15.5 Hz), 4.46 (2 H, dd, $^2J_{H'-H}$ = 11.8 Hz, $^3J_{H-P}$ = 11.8 Hz); (CH₂Ph) o 7.07 (4 H, d, J = 7.6 Hz), m 6.96 (4 H, d, J = 7.6 Hz), p 6.71 (2 H, d, J = 7.6 Hz); (OCHMe₂) 6.08 (1 H, sept, J = 5.8 Hz); (OCHMe_2) 1.83 (6 H, d, J = 5.8 Hz); (OCHMe₂)′ 4.68 (3 H, sept, J = 5.8 Hz); (OCHMe_2)′ 1.30 (18 H, d, J = 5.8 Hz).

(12) Crystal data at −159 °C: a = 16.779 (3) Å, b = 10.104 (1) Å, c = 19.555 (4) Å, β = 90.59 (1)°, Z = 4 and space group P2₁/c. Of the 4823 reflections collected using Mo Kα, 6° < 2θ < 45°, the 3665 having F > 3σ(F) were used in the full-matrix least-squares refinement. All the H atoms were located and refined. Final residuals were R(F) = 0.037 and R_w(F) = 0.041. For general operating procedures and listings of programs employed at the IUMSC, see: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C., *Inorg. Chem.* **1984**, *23*, 1021.

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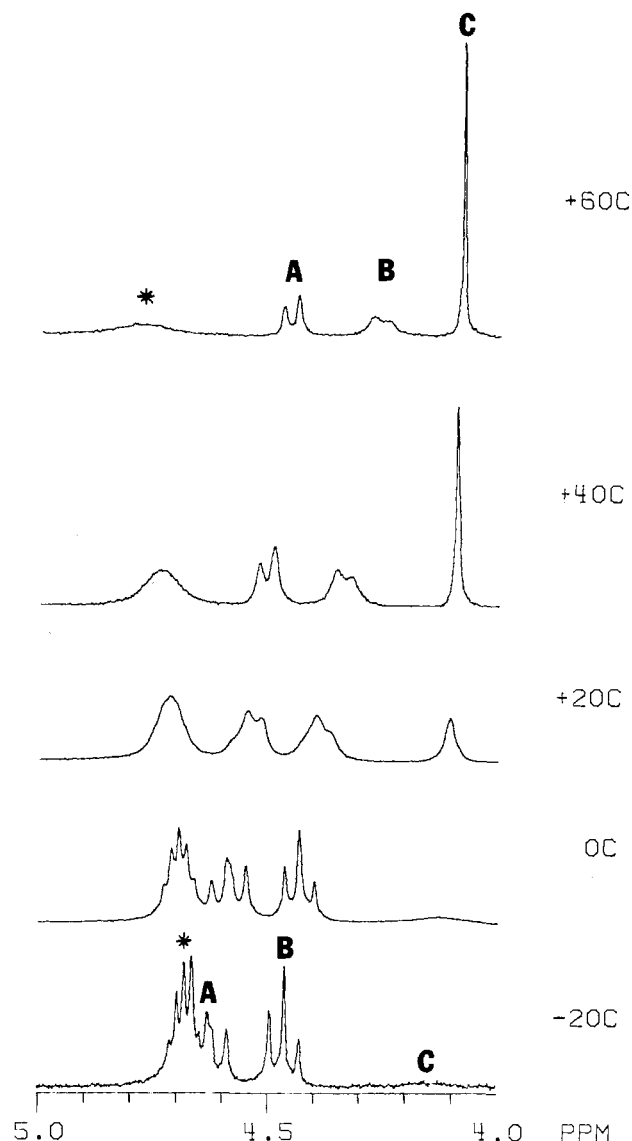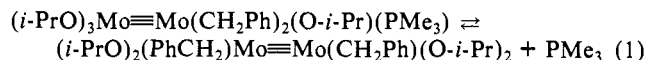
Figure 2. ^{1}H NMR spectra of the PhCH_2 protons as a function of temperature of a crystalline sample of (*i*-PrO)$_3$Mo≡Mo(CH$_2$Ph)$_2$(O-*i*-Pr)(PMe$_3$) dissolved in toluene-d_8. At −20 °C the PhCH_2 protons appear as an ABX spectrum (X = ^{31}P) with the downfield portion of the spectrum partially obscured by the septet of the (*i*-PrO)$_3$Mo≡ methyne protons (*). Upon raising the temperature the growth of the singlet (C) at ca. 4.1 ppm corresponds to the increase in concentration of (*i*-PrO)$_2$(PhCH$_2$)Mo≡Mo(CH$_2$Ph)(O-*i*-Pr)$_2$. The signals arising from the PhCH_2 protons of the (*i*-PrO)$_3$Mo≡Mo(CH$_2$Ph)$_2$(O-*i*-Pr)(PMe$_3$) molecule decrease in intensity as the former grows (C) and coupling of A/B to ^{31}P is lost indicating rapid reversible loss of PMe$_3$ at +60 °C. Spectra were recorded at 360 MHz.

(1) Å. Also the Mo–O distances at the 3- and 4-coordinate ends of the molecule are comparable to those seen in Mo$_2$(OCH$_2$-*t*-Bu)$_6$ and Mo$_2$(O-*i*-Pr)$_6$(py)$_2$, respectively. The long Mo–P distance is consistent with its lability toward PMe$_3$ dissociation (vide infra). The Mo–C distances are longer than those in 1,2-Mo$_2$-(CH$_2$Ph)$_2$(NMe$_2$)$_4$,[9] but the increase in Mo–C distance is comparable to that seen previously in going from 3- to 4-coordinate molybdenum, c.f., , Mo–C = 2.16 (1) Å in 1,2-Mo$_2$Et$_2$(NMe$_2$)$_4$[15] and Mo–C = 2.21 (1) Å in Mo$_2$Et$_2$(NMe$_2$)$_2$(PhN$_3$Ph)$_2$.[16]

The ^{1}H NMR spectrum[11] of a crystalline sample of (*i*-PrO)$_3$Mo≡Mo(CH$_2$Ph)$_2$(O-*i*-Pr)(PMe$_3$) dissolved in toluene-d_8 at -20 °C is entirely consistent with expectations based on the

observed molecular structure allowing for rapid rotation about the Mo–Mo bond. Ther are two types of O-*i*-Pr ligands in the ratio 1:3, and the methylene protons of the benzyl ligand are diastereotopic and appear as part of an ABX spin system (X = ^{31}P). When the temperature is raised, the spectrum changes and is interpretable in terms of PMe$_3$ dissociation and the equilibrium shown in eq 1.

$$(i\text{-PrO})_3\text{Mo}≡\text{Mo}(\text{CH}_2\text{Ph})_2(\text{O-}i\text{-Pr})(\text{PMe}_3) \rightleftharpoons$$
$$(i\text{-PrO})_2(\text{PhCH}_2)\text{Mo}≡\text{Mo}(\text{CH}_2\text{Ph})(\text{O-}i\text{-Pr})_2 + \text{PMe}_3 \quad (1)$$

The temperature dependence of the equilibrium is easily followed in the PhCH_2 region of the NMR spectrum as shown in Figure 2. It is tempting to attribute the stability of the PMe$_3$ adduct to the favorable binding of the soft P donor ligand to the soft (i.e., bis-alkylated) molybdenum center.

The present findings provide the first observation of facile, reversible alkyl/alkoxy exchange at a (Mo≡Mo)$^{6+}$ center. These are of obvious relevance to previous findings of Rothwell and co-workers[17,18] and are of potential importance when one considers viable mechanisms for dinuclear reductive eliminations[19] which convert M–M triple to M–M quadruple bonds.[20,21]

Further studies are in progress.[22]

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Dibenzyl- and Dineopentyltetrakis(propionato)ditungsten($M≡M$). Axial Ligation and Unprecedentedly Short W–W Distances for the RW≡WR Unit

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Of all the compounds containing multiple bonds between metal atoms,[1] the d^3–d^3 dimers of molybdenum and tungsten show the most varied and fascinating coordination chemistry. There are compounds with M–M triple bonds of configuration $\sigma^2\pi^4$ in which the metal atoms are each coordinated to three, four, five, and even six ligand atoms.[2,3] Though *ligands* may span the two metal atoms, there are no bridging *atoms* in this group of d^3–d^3 dimers. However, compounds with bridging atoms are known as in

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