equilateral triangle which is symmetrically bound to the Re resulting in a tetrahedral framework. The conversion of **3** to **4** represents the first structural rearrangement of a four-metal core simply upon protonation.[14] Also noteworthy is the fact that protonation converts the meridional arrangement of PMe_2Ph ligands in **3** to a facial array in **4**.

In summary, the reaction of Ph_3PAuOR with transition-metal hydrides proceeds smoothly and rapidly at room temperature to give one product in essentially quantitative yield. The number of hydrides can also be increased by simple addition of H^+ and such protonation, which does not change the total valence electron count, can nevertheless cause reconstruction of the metal polyhedron. One feature of dinuclear reductive elimination (eq 2)

$$\text{M-X} + R_3\text{PAuY} \rightarrow R_3\text{PAuM} + \text{X-Y} \qquad (2)$$

as a synthetic procedure for Au/other metal(M) compounds is that it occurs without change in charge on the species containing M; it is thus particularly suitable for (but not limited to) the synthesis of uncharged molecules. This sets the methodology apart from procedures which *add* $AuPR_3^+$. Finally, the observation that proton transfer within $[(PhMe_2P)_3ReH_3(AuPPh_3)_3]OR$ completes what is stoichiometrically a dinuclear reductive elimination (even in a nonpolar solvent) emphasizes the Brønsted acidity of certain transition-metal polyhydrides.[15] Consequently, reductive elimination is not a concerted extrusion of the molecule X–Y in certain of the reactions reported here.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for $(PhMe_2P)_3ReH_2(AuPPh_3)_3$ and $[(PhMe_2P)_3ReH_3(AuPPh_3)_3]BF_4$ (3 pages). Ordering information is given on any current masthead page.

(14) Note that metal framework rearrangement has been observed when protonation causes a CO ligand to take up a π-CO function. See: Horwitz, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8147.
(15) Edidin, R. T.; Longato, B.; Martin, B. D.; Matchett, S. A.; Norton, J. R. In *Organometallic Compounds: Synthesis, Structure and Theory*; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1983; p 260.

New Dimeric Quadruply Metal–Metal Bonded Molybdenum(II) Derivative with a Dibenzotetraaza[14]annulene Ligand: Access to New Mixed Valence Complexes and Structural Characterization of the Mo^{II}/Mo^{III} Dimer

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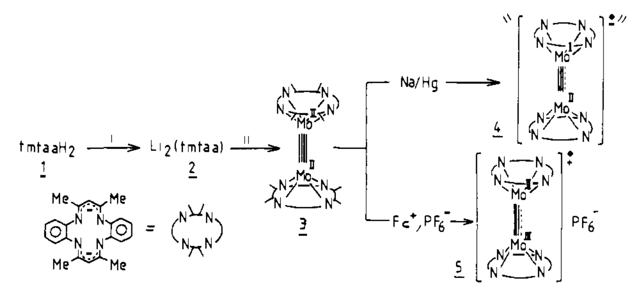
Coordination of small macrocycles such as tetraazaannulenes to transition metals is of current interest due to the complementaries of these ligands with other well-known N_4 macrocyclic derivatives such as porphyrins and phtalocyanines. The dibenzotetramethyltetraaza[14]annulene dianionic ligand[1,2] ($tmtaa^{2-}$ = $C_{22}H_{22}N_4^{2-}$; see Scheme I), although resembling porphyrins, shows important differences relative to electronic delocalization, core size, and framework flexibility.[3]

Scheme I[a]



[a] (i) 2 equiv of BuLi; (ii) 0.5 equiv of $Mo_2(OAc)_4$.

With hopes that some of them would be used as catalysts in redox processes, or would mimic naturally occurring systems, many "$[M^{II}$(tmtaa)]-type" complexes have been synthesized.[4] However, facing the wide field of the metalloporphyrin chemistry — especially the new class of dinuclear $[ML_4]_2$ metal complexes recently reported[5-8] —chemistry of $[M^{II}(tmtaa)]_2$ dimers with nonbridging macrocycles remains still undeveloped in spite of the promising reactivity of dimeric Ru–Ru bonded complexes.[9] This lack may be attributed to the difficulties encountered in the synthesis of such nonbridged dimers.

The in situ formation of an organic dianionic species by abstraction of two protons from the neutral macrocycle $tmtaaH_2$ may be involved in complexation processes leading to $[M^{II}$-(tmtaa)]-type complexes, but so far, isolation of such an intermediate has not been reported.[10] Furthermore, with M = Mo and W, tetradentate coordination of $tmtaa^{2-}$ is not observed, the only known species being the M^0 carbonyl monomers $M(CO)_4$-(η^2-$tmtaaH_2$) obtained from $M(CO)_6$ and $tmtaaH_2$.[11]

Thus to obtain $[Mo^{II}$(tmtaa)]-type complexes, a new synthetic approach was necessary. We report a convenient and high-yield synthesis of complex **3**, $[Mo(tmtaa)]_2$, involving (i) the isolation of the lithium salt Li_2tmtaa **2** and (ii) the reaction of **2** with $Mo_2(OAc)_4$.[12] We also describe some of the redox properties of **3** and the first X-ray crystal structure of a mixed-valence Mo^{II}/Mo^{III} macrocyclic complex, compound **5**, obtained by chemical oxidation of **3** (see Scheme I).

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(1) Jäger, E. G. *Z. Anorg. Allg. Chem.* **1969**, *364*, 177.
(2) Goedken, V. L.; Weiss, M. C. *Inorg. Synth.* **1980**, *20*, 115.
(3) See, for instance: Goedken, V. L.; Pluth, J. J.; Peng, S. M.; Bursten, B. *J. Am. Chem. Soc.* **1976**, *98*, 8014.
(4) See, for instance: Bailey, C. L.; Bereman, R. D.; Rillema, D. P.; Nowak, R. *Inorg. Chem.* **1984**, *23*, 3956. Bailey, C. L.; Bereman, R. D.; Rillema, D. P.; *Inorg. Chem.* **1986**, *25*, 3149 and many references therein.
(5) (a) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869. (b) Setsune, J.; Yoshida, Z.; Ogoshi, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 983.
(6) (a) Wayland, B. B.; Newman, A. R. *Inorg. Chem.* **1981**, *20*, 3093. (b) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (c) Del Rossi, K. J.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1653.
(7) (a) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030. (b) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684. (c) Collman, J. P. Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 2592. (d) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500. (e) Collman, J. P.; Kim, K. *J. Am. Chem. Soc.* **1986**, *108*, 7847. (f) Collman, J. P.; Kim, K.; Garner, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1711.
(8) Yang, C. H.; Dzugan, S. J.; Goedken, V. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1313.
(9) Warren, L. F.; Goedken, V. L. *J. Chem. Soc., Chem. Commun.* **1978**, 909.
(10) The Li_2(tmtaa) salt has been recently postulated in some synthetic pathways but never isolated. See: Ciurli, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1401.
(11) Bell, L. G.; Dabrowiak, J. C. *J. Chem. Soc.; Chem. Commun.* **1975**, 512.
(12) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. Cotton, F. A. *Chem. Soc. Rev.* **1983**, *12*, 35.

0002-7863/87/1509-3490$01.50/0

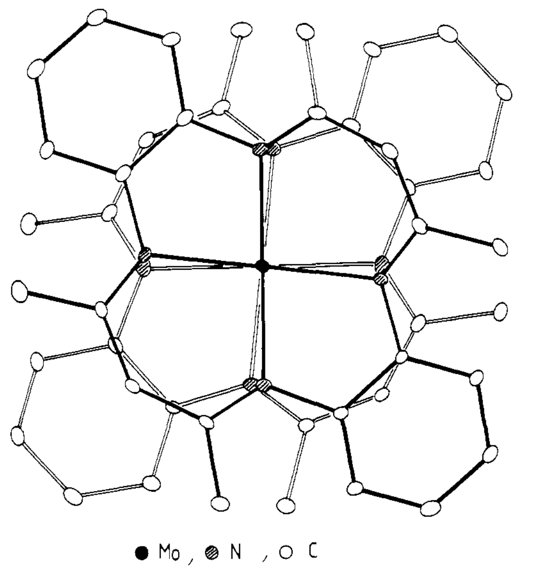

Figure 1. ORTEP plot of $[\{Mo(tmtaa)\}_2]^{\cdot+}$ viewed down the Mo–Mo bond axis illustrating the almost eclipsed configuration of the two MoN_4 moieties.

Treatment at low temperature of a THF solution of $tmtaaH_2$ with 2 equiv of *n*-BuLi affords, after warming up at 20 °C and crystallization (THF/n-hexane), pyrophoric bright red THF-solvated crystals of Li_2tmtaa (**2**) (see Scheme I). The diamagnetic compound **2** (ν(N═C═C═C═N) = 1545 cm^{-1}) is obtained in nearly quantitative yield.

At −30 °C, a THF solution of **2** reacts with 0.5 equiv of $Mo_2(OAc)_2$, affording, after extraction and crystallization (CH_2Cl_2/Et_2O), brown-black crystals of $[Mo(tmtaa)]_2$ (**3**) in 70% yield.

It is noteworthy that compound **3**, which is slightly air sensitive and unstable in solution, could not be obtained by reaction of $Mo_2(OAc)_4$ with $tmtaaH_2$ in various solvents, even in the presence of bases such as DBU.[13]

The cyclic voltammetry of **3** in acetonitrile (0.1 M Bu_4NPF_6; 200 mV/s) shows four redox processes corresponding to two reductions and two oxidations. The first reduction ($E^{1/2} = -0.90$ V/Fc) and the firt oxidation ($E^{1/2} = -0.44$ V/Fc) are associated with chemically and electrochemically reversible one-electron transfer steps. The second reduction wave ($E^{1/2} = -2.48$ V/Fc) is irreversible (both chemically and electrochemically) whereas the second oxidation at $E^{1/2} = +0.42$ V/Fc is an electrochemically reversible process. The magnitude of the second oxidation peak current suggests it is due to a two-electron transfer step. These results indicate that access to mixed-valence Mo^{II}/Mo^{III} and Mo^{I}/Mo^{II} complexes may be expected by chemical redox processes. Indeed the CV of **5** starting from 0 V/Fc is identical with that of **3** except that the redox process at −0.44 V/Fc is now a reduction wave.

Characterization of the unstable reduced species **4**, obtained by reduction of **3** with Na-Hg (toluene, −10 °C, 2 h), has been carried out by ESR spectroscopy. Evidence for the electron being delocalized over two molybdenum nuclei comes from the observation at room temperature of low-intensity 6- and 11-line spectra near the intense central signal ($g = 1.964$; $A_{Mo} = 23.3 \times 10^{-4}$ cm^{-1}).

Room-temperature oxidation of **3** with ferricinium salts is easily realized, quantitatively yielding the dark-purple cationic paramagnetic Mo^{II}/Mo^{III} species **5** as a thermally and air stable complex. ESR spectroscopy measurements (CH_2Cl_2; room temperature) are indicative of a $S = {}^1/_2$ metal-centered radical ($g = 1.959$; $A_{Mo} = 32.2 \times 10^{-4}$ cm^{-1}).

The X-ray crystal structure of **5** (Figure 1) confirms the dimeric nature of this species.[14] The two "saddle-shaped" ligands are rotated by nearly 90° relative to one another with the molybdenum atoms displaced 0.57 Å from the N_4 coordination mean plane. The eclipsed configuration of the two MN_4 moieties and the Mo–Mo distance of 2.221 (1) Å are consistent with a metal bond order of 3.5.[12] These parameters may be compared with those of the recently structurally characterized metalloporphyrin dimer, $[Mo(TPP))_2$, in which the Mo–Mo distance is 2.239 (1) Å, the Mo atoms are displaced 0.46 Å from the plane, and the two porphyrin moieties are rotated 18° relative to one another.[8]

In conclusion we would emphasize that use of the reactive species Li_2tmtaa instead of $tmtaaH_2$ constitutes an excellent approach for the synthesis of new tmtaa–metal derivatives. Further examples are presently under study.

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Supplementary Material Available: Details for the X-ray structure determination of **5** including a listing of positional and thermal parameters and tables of bond lengths and angles, some analytical and spectroscopic (IR, ^{1}H NMR, ESR, MS) data for **2**, **3**, and **5** and ESR data for **4** (8 pages); table of structure factors for **5** (14 pages). Ordering of information is given on any current masthead page.

(13) Kerbaol, J. M., unpublished results. DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene.

(14) $[Mo(C_{22}H_{22}N_4)]_2PF_6$, CH_2Cl_2. Crystals are monoclinic, space group $C2/c$ with $a = 34.483$ (8) Å, $b = 15.749$ (5) Å, $c = 16.991$ (7) Å, $\beta = 101.06$ (6)°, $V = 9056$ (2) A^3, $Z = 8$, $d_c = 1.625$ g cm^{-3}, $\mu = 7.61$ cm^{-1}. Intensity data were collected on a CAD-4 Enraf Nonius automated diffractomer with Mo $K\alpha$ radiation up to a 2θ limit of 50°. The structure was solved by Patterson and Fourier methods and refined to present discrepancy indices R and R_w of 0.054 and 0.063, respectively, for 4599 independent reflections with $I > 4\sigma(I)$ out of 8836 unique data collected. The PF_6 anion and the CH_2Cl_2 solvate molecule are distributed on the same two general positions with a statistical occupancy of 0.5; then the PF_6 anion appears with a strongly distorted octahedral symmetry.

A Novel Route to Allenyl Fluorides. Synthesis of 4-Amino-7-fluorohepta-5,6-dienoic Acid, the First Fluoroallenyl Amino Acid[1]

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Although both fluorine and allene chemistry are active areas of research, there are few documented examples of fluoroallenes,[2,3]

$$-\underset{|}{C}=C=\underset{|}{C}-F$$

This type of functional group is not only of fundamental chemical interest but could also have important applications in the design of enzyme-activated irreversible inhibitors[4] and other biologically active species. It is well-known, for example, that the replacement of a hydrogen by a fluorine atom at saturated and unsaturated carbon centers of enzyme substrates[5,6] and inhibitors[7] can have profound metabolic consequences.

However, the lack of a practical route to fluoroallenes has limited their availability. We wish to report a simple and efficient means of preparing fluoroallenes that avoids the use of highly

(1) Contribution no. 257 from the Institute of Bioorganic Chemistry.
(2) Dolbier, W. R., Jr.; Burkholder, C. R.; Piedrahita, C. A. *J. Fluorine Chem.* **1982**, *20*, 637.
(3) Zens, A. P.; Ellis, P. D.; Ditchfield, R. *J. Am. Chem. Soc.* **1974**, *96*, 1309 and references therein.
(4) Seiler, N.; Jung, M. J.; Koch-Weser, J. *Enzyme-Activated Irreversible Inhibitors*; Elsevier/North-Holland: New York, 1978.
(5) Peters, R. A. *Adv. Enzymol.* **1957**, *18*, 113–142.
(6) Heidelberger, C. In *Antineoplastic and Immunosuppressive Agents*; Sartorelli, A. C.; Johns, D. G., Eds.; Handbuch der Experimenteller Pharmakologie; Springer-Verlag: Berlin, 1975, Part II, Vol. 38, pp 193–231.
(7) Bey, P. ref 4, pp 27–41.

0002-7863/87/1509-3491$01.50/0