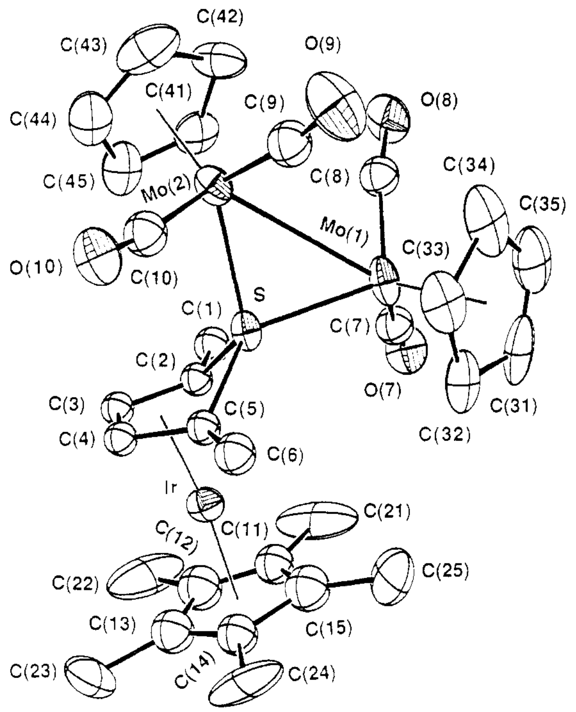

Figure 1. ORTEP drawing of $(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)(IrCp^*)[Mo(CO)_2Cp]_2$ (**3**). Selected bond distances (Å) and angles (deg): C(2)-S = 1.81 (2), C(5)-S = 1.83 (1), C(2)-C(3) = 1.44 (2), C(3)-C(4) = 1.48 (2), C(4)-C(5) = 1.40 (2), C(1)-C(2) = 1.55 (2), C(5)-C(6) = 1.52 (2), Mo(1)-S = 2.342 (3), Mo(2)-S = 2.343 (5), Mo(1)-Mo(2) = 3.144 (2), Mo(1)-C(7) = 1.92 (2), Mo(1)-C(8) = 1.95 (2), Mo(2)-C(9) = 1.90 (2), Mo(2)-C(10) = 1.97 (1), Ir-C(2) = 2.12 (2), Ir-C(3) = 2.14 (2), Ir-C(4) = 2.13 (2), Ir-C(5) = 2.14 (2); C(2)-S-C(5) = 81.7 (6), C(1)-C(2)-C(3) = 122 (1), C(4)-C(5)-C(6) = 124 (1), C(7)-Mo(1)-C(8) = 81.8 (8), C(9)-Mo(2)-C(10) = 80.3 (6), Mo(1)-S-Mo(2) = 84.3 (1), S-Mo(1)-Mo(2) = 47.9 (1), S-Mo(2)-Mo(1) = 47.9 (1).

crystals[10] in 38% yield after recrystallization of the residue from hexane/CH_2Cl_2 at −80 °C.

The structure of **3** determined by X-ray crystallography (Figure 1) contains a thiophene that is coordinated via the four ring carbon atoms (η^4) to the iridium and through its sulfur to the two Mo atoms. The structural features of the $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ portion of **3** are nearly the same as that of free $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**1**),[4] except the C-S bond distances (1.81 (2), 1.83 (1) Å) in **3** are slightly longer than the corresponding distances (1.76 (2), 1.79 (2) Å) in **1**. The thiophene ring is folded with an angle of 43.6 (8)° between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes, as compared with a 42° angle in **1**. The methyl carbons, C(1) and C(6), are in the C(2)-C(3)-C(4)-C(5) plane within experimental error, and the sulfur is 0.95 Å out of this plane. The S-Mo(1)-Mo(2) plane is essentially perpendicular to both the C(2)-C(3)-C(4)-C(5) (92.4 (5)°) and C(2)-S-C(5) (91.2 (5)°) planes. The Mo(1)-Mo(2) distance (3.144 (2) Å) is slightly shorter than that (3.235 (1) Å)[12] in $Cp(CO)_3MoMo(CO)_3Cp$, but not nearly as short a the metal-metal bond in $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (2.448 (1) Å).[9,13] The CO ligands in **3** are terminal, unlike those in $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$,[9] in which there are semibridging CO groups. Thus, it appears that the sulfur in **3** acts as a formal four-electron donor to the molybdenum dimer.

The formation of **3** from the reaction of **1** and $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ appears to be promoted by the strong donor ability of the sulfur in **1**; this donating character has already been demonstrated[4,14] in the reaction of **1** with $Me_2S{\cdot}BH_3$ to form the sulfur adduct $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T{\cdot}BH_3)$. Clearly, the η^4-coordination of thiophene to the iridium activates the thiophene to react with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$, since there is no reaction between the molybdenum dimer and either thiophene or 2,5-Me_2T under the conditions used to prepare **3**.

Rather remarkably, the ring-opened isomer **2** (Scheme I) (25 mg, 0.057 mmol) also reacts with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (30 mg, 0.069 mmol) in 30 mL of THF to give **3** in 44% isolated yield. This reaction occurs at 0-15 °C over an 8-h period, conditions even milder than those used in the reaction of **1**. At this point, the mechanisms of the reactions of the molybdenum dimer with **1** and **2** are not understood, but it is possible that the known[7] isomerization of **1** to **2** is involved. Further studies of **3** and related derivatives are in progress.

Acknowledgment. We thank Dr. Lee M. Daniels for the crystal structure determination of **3**. The loan of $IrCl_3$ from Johnson Matthey, Inc., is greatly appreciated.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes and dihedral angles (16 pages); a listing of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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[10] Anal. Calcd for $C_{30}H_{33}O_4SIrMo_2$: C, 41.24; H, 3.81. Found: C, 41.46; H, 3.86. IR (CH_2Cl_2, ν(CO)): 1910 s, 1870 vs, 1828 s, 1805 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.29 (s, 5 H, Cp), 5.16 (s, 5 H, Cp), 4.73 (s, 1 H), 4.62 (s, 1 H), 1.98 (s, 15 H, Cp*), 0.947 (s, 3 H, CH_3), 0.873 (s, 3 H, CH_3). EIMS: *m/e* 878 (M^+, based on ^{98}Mo). Melting point: >230 °C dec.

[11] Crystal data for **3**: dark green crystal, 0.19 × 0.15 × 0.08 mm, monoclinic, $C2/c$, $a = 30.767$ (8) Å, $b = 9.670$ (1) Å, $c = 26.952$ (6) Å, $\beta = 124.05$ (1)°, $V = 6644$ (2) Å^3, $Z = 8$, $\rho_{calcd} = 1.917$ g/cm^3, μ(Mo Kα) = 49.64 cm^{-1}. Diffraction data: Enraf-Nonius CAD4 diffractometer, Mo radiation (λ = (Kα) = 0.71073 Å), graphite monochromator, range 4.0° < 2θ < 45.0°, 4431 reflections, 4335 unique data, 2712 observed data ($I > 3\sigma(I)$), crystal temperature −20 (1) °C, ω-2θ scans, corrected for absorption, Lorentz, and polarization effects. Solution and refinement: centric space group indicated by intensity statistics; Ir and Mo positions given by direct methods, other atoms taken from difference maps; hydrogen atoms not included; one molecule of CH_2Cl_2 in the lattice refined as a disordered model of two independent units with the total occupancy restrained to unity; refinement of 294 parameters converged with $R_F = 0.0465$, $R_{wF} = 0.0609$, and goodness of fit 1.05; largest peak in the final difference Fourier map 1.4 (1) e/Å^3.

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Easy Double Metalation of a Diphosphinomethane Ligand: Structure of the Remarkable Octagold Cage Complex $[Au_8Cl_2\{\mu_3\text{-}(MeO)_2PCHP(OMe)_2\}_2\{\mu_4\text{-}(MeO)_2PCP(OMe)_2\}_2]{\cdot}CHCl_3$

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Summary: Reaction of AuCC-*t*-Bu with $(MeO)_2PCH_2P(OMe)_2$ (dmopm), followed by recrystallization first from CH_2Cl_2 and then from $CHCl_3$, gave the title cage complex, which contains four fused nine-membered rings and the first structurally characterized example of a $[\mu_4\text{-}R_2PCPR_2]^{2-}$ ligand, formed by easy deprotonation of dmopm.

The ligands $R_2PCH_2PR_2$ (R = alkyl, aryl, alkoxy, aryloxy) are often used as binucleating ligands and have been

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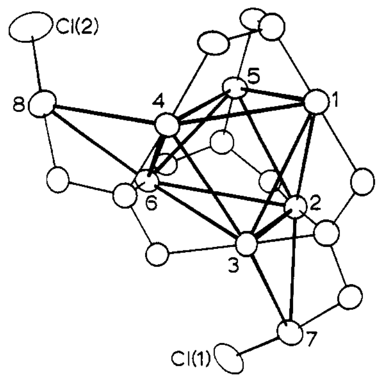


Figure 1. View of the structure of complex 3. The gold atoms are numbered 1–8. Bonds are drawn between all adjacent gold atoms to emphasize the dicapped-octahedral geometry, but only the distances Au(2)–Au(3) = 2.938 (1) Å and Au(4)–Au(6) = 2.951 (1) Å are considered bonding. Other Au–Au distances are 3.351 (1)–4.085 (1) Å. For the diphosphine ligand geometry, see Figure 2, where the gold atom numbering is the same as in Figure 1.

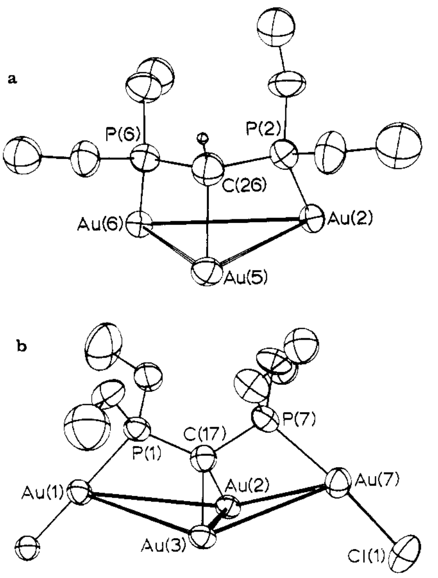
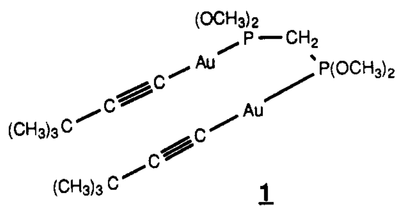


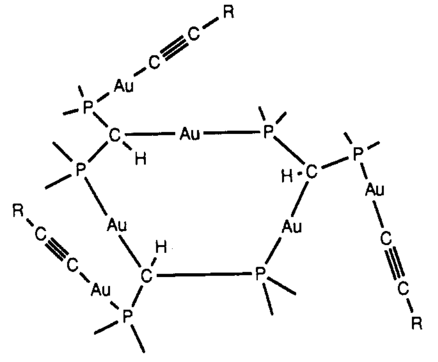
Figure 2. A singly deprotonated μ_3-(MeO)$_2$PCHP(OMe)$_2$ ligand (a) and a doubly deprotonated μ_4-(MeO)$_2$PCP(OMe)$_2$ ligand (b).

of great significance in developing the organometallic chemistry of binuclear and cluster complexes.[1] It is well-known that these ligands can be deprotonated to give $[R_2PCHPR_2]^-$, which can act as monodentate (C donor), chelate (P,P donors), μ_2 (P,P or P,C donors), or μ_3 (P,C,P donors) ligands, but strong bases are usually required in such reactions.[1-3] This paper reports the very easy deprotonation of the ligand $R_2PCH_2PR_2$ (R = MeO)[4] by reaction with AuCC-*t*-Bu,[5] which gives the title cage complex, containing the first structurally characterized example of a $[\mu_4\text{-}R_2PCPR_2]^{2-}$ ligand.[2i]

The reaction in CH_2Cl_2 solvent of AuC≡C-*t*-Bu with $(MeO)_2PCH_2P(OMe)_2$ (dmopm) in a 2:1 ratio at room temperature is complex. It is probable that the first-formed complex is $[CH_2\{P(OMe)_2AuC{\equiv}C\text{-}t\text{-}Bu\}_2]$ (1), but

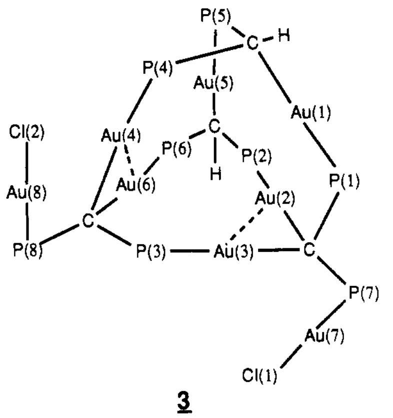


1



2

R = C(CH3)3 ; P = P(OMe)2



3

this was an oil and decomposed in solution.[6] Slow crystallization of 1 from CH_2Cl_2/pentane gave in high yield (70–80%) a single colorless product, characterized as $[Au_2(CC\text{-}t\text{-}Bu)\{\mu_3\text{-}(MeO)_2PCHP(OMe)_2\}]_n$ (2), for which a likely structure with $n = 3$ is shown.[7] The crystals of 2 were not suitable for X-ray diffraction, so a further slow

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(5) Coates, G. E.; Parkin, C. *J. Chem. Soc.* **1962**, 3220.

(6) NMR data for 1 (CD_2Cl_2): ^1H, δ 1.21 [s, 18 H, *t*-Bu] 2.67 [t, 2 H, J(PH) = 11 Hz, CH_2], 3.88 [m, 12 H, ^3J(PH) + ^5J(PH) = 15 Hz, *Me*O]; ^{31}P, δ 166.6 [s, P]. The corresponding complex (1) of $Ph_2PCH_2PPh_2$ is more stable and has been characterized crystallographically: Payne, N. C.; Ramachandran, R. Unpublished work.

(7) Data for 2: Anal. Calcd for $(C_{11}H_{22}Au_2O_4P_2)_n$: C, 19.6; H, 3.5. Found: C, 19.6; H, 3.4. NMR (CD_2Cl_2): ^1H, δ 1.13 [s, 9 H, t-Bu], 3.64–4.05 [4 d, 12 H, *Me*O], 4.34 [dt, 1 H, ^2J(PH) = 15 Hz, ^3J(PH) = 10 Hz, CHP$_2$]; ^{31}P, δ 161.6 [m, P^A], 152.0 [m, P^X]. The ^{31}P NMR spectrum was simulated as an AA′XX′ spin system but is consistent with $[AX]_n$, where $n \geq 2$ and probably $n = 3$.

recrystallization from $CHCl_3$/pentane was carried out and gave colorless crystals in 70% yield of $[Au_8Cl_2\{\mu_3\text{-}(MeO)_2PCHP(OMe)_2\}_2\{\mu_4\text{-}(MeO)_2PCP(OMe)_2\}_2]$ as the $CHCl_3$ solvate (3).[8]

The structure of 3 was determined by X-ray diffraction[9] and is a new type of cage containing four fused nine-membered rings. Each ring may be viewed as forming one face of a tetrahedron; Au atoms 1–6 are thus held in a proximity approaching octahedral (Au···Au ranging from 2.938 (1) to 4.085 (1) Å, Figure 1). Each of the four dmopm ligands has lost either one or two methylene protons. The atom order in two of the rings is AuPCAuPCAuPC, as proposed for 2, while in the other two AuPCAuPCPAuC is found. Each ring contains at least one Au–P–CH–Au fragment (structure 3 and Figure 2a) and at least one of the hitherto unknown Au–P–C*–Au fragments (structure 3 and Figure 2b). The phosphorus atom of each of the doubly deprotonated ligands that is not involved in ring formation is bonded to an exocyclic Au–Cl unit. There is Au–Au bonding between the pairs of gold atoms bound to doubly deprotonated C*, as is clear from the distances Au(2)–Au(3) = 2.938 (1) Å and Au(4)–Au(6) = 2.951 (1) Å and the angles Au(2)–C(17)–Au(3) = 87.8 (9)° and Au(4)–C(38)–Au(6) = 88.4 (9)°.[10] This secondary bonding between Au(I) centers is a common phenomenon.[3e]

Given the structure of 3 and formula of 2, it is possible to understand the complex chemistry involved. It seems that the alkynyl ligand in 1 is sufficiently basic to deprotonate the dmopm ligand with formation of *t*-BuCCH and "$Au_2(CC\text{-}t\text{-}Bu)\{(MeO)_2PCHP(OMe)_2\}$", which oligomerizes to the crystalline 2. Further conversion of 2 to 3 in $CHCl_3$ involves additional condensation by loss of *t*-BuCCH, leading to formation of the new $[\mu_4\text{-}(MeO)_2PCP(OMe)_2]^{2-}$ ligand, along with a parallel reaction in which AuCC-*t*-Bu groups react with chloroform to give Au–Cl bonds.[11] It is likely that the very easy double deprotonation of the $(MeO)_2PCH_2P(OMe)_2$ ligand is aided by the electronegative methoxy substituents on phosphorus, which may increase the acidity of the CH_2P_2 protons compared to those of the more common $R_2PCH_2PR_2$ ligands with R = alkyl or aryl.[6] In turn, this promises a rich chemistry of the ligands $(RO)_2PCH_2P(OR)_2$ in forming and stabilizing unusual cage and cluster complexes of other elements.

Acknowledgment. We thank the NSERC (Canada) for financial support to N.C.P. and R.J.P. and the University of Western Ontario for a fee bursary to R.R.

Supplementary Material Available: A description of the crystal structure data collection and refinement and tables of atomic positional and thermal parameters, anisotropic thermal parameters, hydrogen atom parameters, selected torsion angles, selected bond distances and bond angles, and least-squares planes (12 pages); a listing of observed and calculated structure amplitudes (43 pages). Ordering information is given on any current masthead page.

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[8] Data for 3: Anal. Calcd for $C_{21}H_{51}Au_8Cl_5O_{16}P_8$: C, 9.85; H, 2.0. Found: C, 9.8; H, 2.1. NMR (CD_2Cl_2): ^1H, δ 3.02 [dt, 1 H, $^2J(PH) = 17$ Hz, $^3J(PH) = 8$ Hz, CHP_2], 3.10 [dt, 1 H, $^2J(PH) = 17$ Hz, $^3J(PH) = 8$ Hz, CHP_2], 3.70–4.03 [m, *Me*O]; ^{31}P, δ 157.7 [m, 1 P], 155.1 [m, 1 P], 150.4 [m, 1 P], 149.9 [m, 1 P] 148.4 [m, 1 P], 145.6 [m, 1 P], 126.4 [m, 2 P].

[9] Crystal data for 3: $C_{21}H_{51}Au_8Cl_5O_{16}P_8$, $M_r = 2560.4$, triclinic, $P\bar{1}$, $a = 14.152$ (2) Å, $b = 18.373$ (2) Å, $c = 12.151$ (2) Å, $\alpha = 91.17$ (1)°, $\beta = 114.77$ (1)°, $\gamma = 108.16$ (1)°, $V = 2684$ (2) Å, $Z = 2$, $D_m = 3.158$ (2) Mg m^{-3}, $D_c = 3.168$ Mg m^{-3}, $F(000) = 2282$ e, $\lambda(\text{Mo K}\bar{\alpha}) = 0.71073$ Å, $\mu = 214.8$ mm^{-1}, $T = 295$ K. Intensity data were collected on an Enraf-Nonius CAD4F diffractometer by the θ–2θ technique with use of graphite-monochromatized Mo radiation. The structure was solved with SHELXS-86 software. Full-matrix least-squares refinement on F (SHELX76 software, 5677 unique observations with $I > 2.5\sigma(I)$, 436 variables, H atom contributions included but not refined) converged at $R = 0.0355$ and $R_w = 0.0371$. Full details of the structure determination are given in the supplementary material.

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Unambiguous Example of a η^2-Benzyl Group Functioning as a Formal Three-Electron Ligand: Solid-State Molecular Structure of $Cp^*Mo(NO)(CH_2SiMe_3)(\eta^2\text{-}CH_2C_6H_5)$[1]

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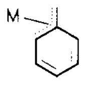
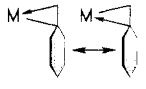
Received October 3, 1989

Summary: Sequential treatment at 20 °C of $Cp^*Mo(NO)(\eta^2\text{-}CH_2Ph)Cl$ in Et_2O first with an equimolar amount of Me_3SiCH_2MgCl and then water affords $Cp^*Mo(NO)(CH_2SiMe_3)(\eta^2\text{-}CH_2Ph)$, which is isolable in 82% yield as red, prismatic crystals. A single-crystal X-ray crystallographic analysis of the product complex has confirmed its formulation and has determined that it possesses a "three-legged piano stool" molecular structure. The chemically most interesting result of this analysis is the establishment of the intramolecular dimensions of the Mo–(η^2-CH_2Ph) grouping, which indicate that the η^2-benzyl group functions as a three-electron ligand via C–Moσ bonds involving its methylene and ipso carbon atoms.

When a benzyl group functions as a formal three-electron donor to a transition-metal center, it usually attaches to the metal in a η^3 fashion to form a linkage that may be represented as shown in A. The first example of such a link was invoked for $CpMo(CO)_2(\eta^3\text{-}CH_2Ph)$ (Cp = η^5-C_5H_5)[2] and was confirmed by a single-crystal X-ray crystallographic analysis of its *p*-methylbenzyl analogue, whose molecular structure reveals the existence of the localized bonding within the phenyl ring indicated in A.[3] We now wish to report that a benzyl ligand coordinated in a η^2 manner to a transition metal can also provide three electrons to the metal center in a rather unusual way. Specifically, we wish to describe the synthesis and characterization of $Cp^*Mo(NO)(CH_2SiMe_3)(\eta^2\text{-}CH_2Ph)$ (Cp^* = η^5-C_5Me_5), a diamagnetic 18-valence-electron complex in which the metal–benzyl linkage is best represented by the resonance hybrid B (M = Mo).



A



B

$Cp^*Mo(NO)(CH_2SiMe_3)(\eta^2\text{-}CH_2Ph)$ is preparable by the sequential treatment of $Cp^*Mo(NO)(\eta^2\text{-}CH_2Ph)Cl$[4] in Et_2O

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