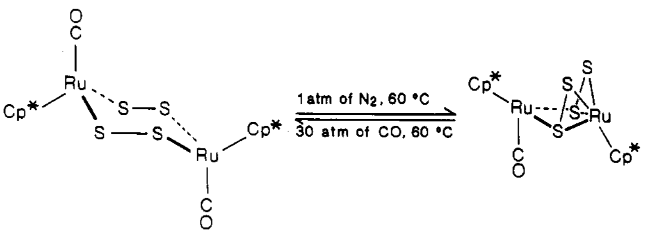
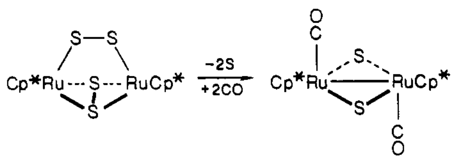


(1)

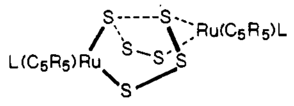
a solution of 21.3 μL of $(n\text{-Bu})_3P$ (2.3 equiv) in 10 mL of CO-saturated toluene was slowly added dropwise to a solution of 24.4 mg of 1 in 25 mL of CO-saturated toluene. The phosphine discharges the intense blue color characteristic of 1 resulting in a pale yellow solution. After several hours, the golden brown product was purified by filtration through silica gel and recrystallization from CH_2Cl_2/hexane. Elemental analysis and FDMS indicate the formulation $Cp^*{}_2Ru_2S_2(CO)_2$ (yield 60%).[11] ^1H NMR and IR spectroscopy indicate a centrosymmetric molecule which suggests the following structure (eq 2).[11] We note



(2)

that this $S_2(CO)_2$ compound would have the same number of valence electrons as Roussin's red anion $Fe_2S_2(NO)_4{}^{2-}$. The latter has a planar M_2S_2 core with a short Fe···Fe contact.[12] So far we have been unsuccessful in obtaining X-ray-quality single crystals of the dicarbonyl. Obviously the phosphine-induced carbonylation of 1 follows a different pathway than the thermal process. When 1 is treated with the phosphine in the absence of CO, a red compound is formed which is itself unreactive toward CO. These results parallel our study of the phosphine-induced reaction of 1 and acetylenes that leads to the formation of dithiolene complexes $Cp^*{}_2Ru_2S_2C_2R_2$.[2]

Several of the compounds described above are also formed in variable yields in both the photochemical and thermal (60 °C) syntheses of 1 from $Cp^*{}_2Ru_2(CO)_4$ and 0.5–1 equiv of S_8 (toluene solvent). We observed the following new compounds after standard chromatographic workup:[13] red $Cp^*{}_2Ru_2S_5(CO)$[14] (13% yield), black-green $Cp^*{}_2Ru_2S_6(CO)_2$[15] (variable amounts), and traces of a turquoise isomer of $Cp^*{}_2Ru_2S_2(CO)_2$.[16] On the basis of the ^1H NMR spectra, the penta- and hexasulfides are chiral; the latter possesses equivalent Cp* ligands while the former has no symmetry (eight methyl singlets). Both species can be quantitatively converted to 1 by photolysis in toluene. The spectroscopic data indicate that the hexasulfide is structurally analogous to 1,5-$[(MeCp)Ru(PPh_3)]_2S_6$.[8]



1,5-$[(C_5R_5)RuL]_2S_6$ (L = CO, PPh_3; $R_5 = H_5$ or Me_4Et)

In summary, the carbonylation of 1 represents the first example of a metal-centered ligand addition to a cyclopentadienyl metal sulfide. The metal centers in $1(CO)_x$ are good π donors and therefore provide the driving force for the carbonylation of 1 despite the relatively high formal oxidation state of Ru(III). The carbonylation of 1 involves the stepwise unfolding of the M_2S_4 core and demonstrates the facultative nature of the μ-S_2 ligand. Lastly, desulfurization reagents permit the carbonylation of 1 to proceed under very mild conditions. This pattern is reminiscent of the proposed role of anion vacancies in heterogeneous metal sulfide catalysis.[17]

Acknowledgment. This research was supported by the National Science Foundation. Field desorption mass spectra were recorded on a MAT 731 supported by NIH (GM27029). We thank Dr. J. Wachter for communication of results prior to publication.

Registry No. 1, 101953-49-5; *trans*-$1(CO)_2$, 115226-90-9; *trans*-1(CO), 115226-91-0; *cis*-1(CO), 115268-39-8; $Cp^*{}_2Ru_2S_2(CO)_2$, 115226-92-1; $Cp^*{}_2Ru_2(CO)_4$, 115226-93-2; $Cp^*{}_2Ru_2(CO)_2$, 115226-94-3.

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[10] Chanaud, H.; Ducourant, A. M.; Gianotti, C. *J. Organomet. Chem.* **1980**, *190*, 201. For an update on this chemistry see: Weberg, R.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 1315. Brunner, H.; Janietz, N.; Meier, W.; Sergeson, G.; Wachter, J.; Zahn, T.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1060.

[11] Anal. Calcd: C, 46.41; H, 5.52. Found: C, 46.18; H, 5.44. FDMS (m/z, ^{102}Ru): 622 (P^+). ^1H NMR (C_6D_6): δ 2.24 (q, 4 H), 1.69 (s, 12 H), 1.56 (s, 12 H), 0.74 (t, 6 H). IR (CH_2Cl_2): 1941 cm^{-1}.

[12] Lin, X.; Huang, J.; Lu, J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, C232.

[13] Flash chromatography was carried out by using 32–63-μm Merck silica gel eluting with toluene.

[14] Anal. Calcd: C, 40.07; H, 4.98. Found: C, 40.60; H, 5.19. FDMS (m/z, ^{102}Ru): 690 (P^+), 658 ($P^+ - S$), 722 ($P^+ + S$), 630 ($P^+ - COS$). ^1H NMR (C_6D_6): δ 2.05 (q, 2 H), 1.86 (q, 2 H), 1.62 (s, 3 H), 1.60 (s, 3 H), 1.58 (s, 3 H), 1.56 (s, 3 H), 1.43 (s, 3 H), 1.40 (s, 3 H), 1.37 (s, 3 H), 1.33 (s, 3 H), 0.85 (t, 3 H), 0.71 (t, 3 H). IR (CH_2Cl_2): 1970 (sh), 1945 cm^{-1}. The (C_5Me_5) derivative of this compound has been isolated by J. Wachter and his group in Regensburg.

[15] FDMS (m/z, ^{102}Ru): 750 (P^+), 690 ($P^+ - COS$), 658 ($P^+ - COS_2$). ^1H NMR (C_6D_6): δ 2.09 (q, 4 H), 1.61 (s, 6 H), 1.59 (s, 6 H), 1.54 (s, 6 H), 1.51 (s, 6 H), 0.75 (t, 6 H). IR (CH_2Cl_2): 1963 cm^{-1}.

[16] FDMS (m/z, ^{102}Ru): 622 (P^+), 594 ($P^+ - CO$). ^1H NMR (C_6D_6): δ 2.31 (q, 4 H), 1.79 (s, 12 H), 1.72 (s, 12 H), 0.88 (q, 6 H).

[17] Gellman, A. J.; Bussell, M. E.; Somorjai, G. A. *J. Catal.* **1987**, *107*, 103 and references therein.

[18] **Note added in proof**: The structure of *trans*-1,4-$[Cp^*Ru(CO)]_2S_4$ has been confirmed by single-crystal X-ray diffraction. The molecule very closely resembles *trans*-1,4-$[(MeCp)Ru(PPh_3)]_2S_4$.

An Appraisal of the Steric versus Electronic Requirements of Gold(I) Phosphine Substituents in Clusters: The Crystal Structure of $[HFe_4(CO)_{12}\{AuPEt_3\}_2B]$

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Summary: The elucidation of the crystal structure of one isomer of the mixed metal boride $[HFe_4(CO)_{12}\{AuPEt_3\}_2B]$ illustrates that the geometry of the hexametal atom core and the location of the endo-hydrogen atom depend upon the steric, rather than electronic, requirements of the gold(I) phosphine substituents. Electronic effects, however, are responsible for the $AuPR_3$ fragment interacting with Fe–B rather than Fe–Fe bonds of the core cluster.

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Recently, via a structural investigation[1,2] of the auraferraborane $[Fe_4(CO)_{12}\{AuPPh_3\}_2BH]$ (II) complimented by a Fenske–Hall molecular orbital analysis of the bonding in this cluster,[2] we presented the idea that the rather unusual metal core geometry observed in this compound may be brought about, at least in part, by the advantages of the gold(I) phosphine fragments bridging Fe–B rather than Fe–Fe edges. While electronic effects may well be the root cause of the endo group (H or $AuPPh_3$) "migrating" toward the boron atom in going from $[HFe_4(CO)_{12}BH_2]$[3] (III) to II, these said effects do not account for the exact geometry of the metal framework in the heterometallic–main-group element cluster; there are other geometries available for the Fe_4Au_2B core which are more symmetrical than that observed in II and in which Fe–(AuL)–B still predominate over Fe–(AuL)–Fe interactions. Since the steric strain imparted by triphenylphosphine substituents is significant, we decided to investigate the consequences of reducing this strain and, thereby, attempt to partition steric from electronic effects. In terms of steric effects, for all metal frameworks, it has been shown that substituting two PPh_3 groups for one $Ph_2PCH_2CH_2PPh_2$ ligand in the compounds $[Au_2Ru_4(\mu_3\text{-}H)(CO)_{12}L_2]$ and $[Au_3Ru_4(\mu\text{-}H)(CO)_{12}(PPh_3)L_2]$ ($L_2 = (PPh_3)_2$ or $(Ph_2PCH_2CH_2PPh_2)$) does, indeed, result in structural reorganization.[4-6]

We have previously reported the preparation of the bis(triethylphosphine) derivative $[Fe_4(CO)_{12}\{AuPEt_3\}_2BH]$ (I). Room-temperature spectroscopic (^1H, ^{31}P, and ^{11}B NMR and infrared) characterization implied that I was isostructural with II.[7] A crystal of I, suitable for X-ray diffraction, was grown from CH_2Cl_2 layered with hexane. The structure[8] determined for I, and shown in Figure 1, proved to be inconsistent with the previously recorded NMR data for this compound.[7] The tetrairon atom butterfly framework is, as expected, the basic building block of the cluster, and the boron atom is located interstitially within the unit, 0.31 (1) Å above the Fe(2)–Fe(2a) axis.[9] Each Fe_{wing}–B edge is bridged by an $Au(PEt_3)$ fragment, and the molecule thereby possesses a twofold axis passing through the boron atom and the midpoint of the Fe(1)–Fe(1a) bond. The Au–B distances of 2.262 (11) Å (~0.1 Å shorter than those found in II) are clearly bonding contacts, and thus, the boron atom is rendered six-coordinate with respect to boron–metal interactions. Each P–Au bond vector points toward the middle of an Fe_{wing}–B edge and thus implies the presence of a three-center bonding interaction. This is consistent with the primary bonding interaction of the $AuPEt_3$ fragment utilizing the largely sp-hybrid orbital on gold which is directed colinearly along the P–Au axis.[2,10] The endo-hydrogen atom was not located directly, but the orientations of the carbonyl ligands on Fe(1) and Fe(1a) imply that it bridges the Fe(1)–Fe(1a) bond.[11]

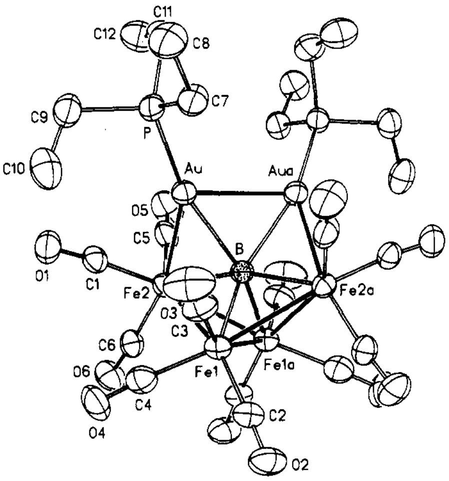
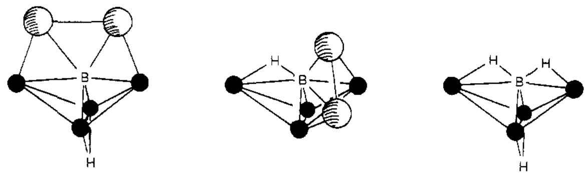


Figure 1. Molecular structure and labeling scheme for I: Au–Au(a) = 2.880 (1), Au–Fe (2) = 2.615 (1), Au–P = 2.293 (3), Fe(1)–Fe(1a) = 2.621 (2), Fe(1)–Fe(2) = 2.690 (2), Fe(1)–Fe(2a) = 2.689 (2), Au–B = 2.262 (11), Fe(1)–B = 2.065 (11), Fe(2)–B = 1.989 (3) Å; Au–B–Au(a) = 79.1 (5), Fe(1)–B–Fe(1a) = 83.1 (3), Fe(2)–B–Fe(2a) = 162.1 (8), Fe(2)–Fe(1)–Fe(2a) = 93.9 (1)°. Iron–butterfly internal dihedral angle = 113.5 (3)°.

Chart I



I II III

In the light of the structural data collected for I, and considering the spectroscopic data that we have detailed previously, it is clear that two isomers of I exist (Chart I) but that the isomer which predominates in solution is not that which we have crystallographically characterized. The proton NMR spectrum is perhaps the best indicator of an equilibrium between two isomers. We have reexamined the 250-MHz ^1H NMR spectrum and have observed that the broad resonance at δ −10.4,[12] which persists at 298 K and appears to indicate the presence of only an Fe–H–B bridging hydrogen atom, shifts[13] to δ −9.2 at 200 K.[14] This is accompanied by the appearance of a weak, but sharp, hydride signal at δ −25.0. These observations are consistent with the presence of two isomers of I, the minor one being

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(1) Housecroft, C. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 6420.

(2) Housecroft, C. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1332.

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(6) Adatia, T.; McPartlin, M.; Salter, I. D. *J. Chem. Soc., Dalton Trans.* **1988**, 751.

(7) Harpp, K. S.; Housecroft, C. E. *J. Organomet. Chem.* **1988**, *340*, 389.

(8) Crystal data for I: monoclinic, $I2/a$, a = 17.783 (5) Å, b = 11.277 (3) Å, c = 18.084 (7) Å, β = 106.26 (3)°, V = 3481.3 (17) Å^3, Z = 4, D(calcd) = 2.291 g cm^{-3}, μ(Mo Kα) = 101.5 cm^{-1}, and T = 23 °C. A Nicolet R3m diffractometer was used to collect 4333 reflections (4° ≤ 2θ ≤ 55°) on a black specimen (0.28 × 0.28 × 0.33 mm). Of these, 4001 were independent, R_{int} = 2.1%, and 2965 were observed ($5\sigma(F_o)$) and empirically corrected for absorption. The Au atom was located by heavy-atom methods. The structure possesses a crystallographic twofold axis containing B and bisecting the Au–Au(a) and Fe(1)–Fe(1a) bonds. All non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were included as idealized contributions. $R(F)$ = 4.75%, $R(wF)$ = 6.03%, GOF = 1.344, Δ/σ(final) = 0.047, $\Delta(\rho)$ = 2.62 e Å^{-3} (0.86 Å from Au), and N_o/N_v = 14.46. All computations used SHELXTL(5.1), G. Sheldrick, Nicolet XRD, Madison, WI.

(9) The boron atom lies 0.37 and 0.31 Å above the Fe_{wing}–Fe_{wing} axis in II and III, respectively.

(10) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171.

(11) In III, a hinge bridging hydride was located[3] and the hinge iron carbonyl orientations for III reflect those found in I; we have emphasized previously for II that endo-hydrogen (or gold(I) phosphine) location and carbonyl orientation are mutually dependent.[2]

(12) All NMR spectra were recorded in CD_2Cl_2.

(13) In our experience, a ^1H NMR shift for an Fe–H–B proton is relatively insensitive to temperature, and we would not attribute such a significant change in chemical shift as that observed to simply a change in temperature.

(14) In II, the ^1H NMR resonance for the Fe_{wing}–H–B proton is δ −9.1.[1,2]

in ~8% abundance and having the structure shown in Figure 1 and the major isomer being isostructural with II. The room-temperature ^1H NMR resonance at δ −10.4 is therefore a coalesence signal produced by interconversion of the two isomers. Variable-temperature ^{31}P and ^{11}B NMR spectra proved to be unhelpful in illustrating the presence of the minor isomer.[15]

The structurally characterized isomer of I exhibits two gold(I) phosphine units in positions which are probably sterically unacceptable to the $AuPPh_3$ fragments. Although the P···P distances in I and II are similar (5.401 and 5.307 Å, respectively) and thereby imply that substitution of phenyl for ethyl groups in I might well be sterically allowed with respect to *inter*-phosphine interactions, it is in fact difficult to find orientations of the Ph_3P substituents that allow the phenyl H atoms to be at reasonable distances *both* from the carbonyl O atoms of the $Fe_4(CO)_{12}$ framework and from the H atoms of the second triphenyl phosphine unit. Thus, in the case of II, the isomer equilibrium swings wholly in favor of the asymmetrical geometry in which one $AuPPh_3$ is forced down toward the iron framework and the endo-hydrogen atom migrates toward the boron atom (Chart I). It is significant, however, that in I, neither isomer exhibits a $AuPEt_3$ unit interacting completely with the tetrairon framework.[17] Thus, electronic factors[2] appear to drive the gold(I) phosphine units toward interaction with the boron atom, and steric factors then control the heavy metal atom assembly about the boron atom. These observations illustrate the limitations of applying the isolobal analogy to heterometallic- and mixed-metal–main group systems and underline the subtle balance existing between the steric and electronic effects that govern cluster geometry. For both isomers of $Fe_4(CO)_{12}(AuPEt_3)_2BH$ to be observed by using NMR spectroscopy, the energy difference between the two must be small. It is likely, therefore, that crystal packing forces are important when it comes to determining which structure is preferred in the solid state.

Further evidence to support the above postulate comes from a study of the compound $[Fe_4(CO)_{12}\{Au_2(Ph_2PCH_2CH_2PPh_2\}BH]$ which appears to exhibit the same solution equilibrium as I, but with the two isomers being approximately *equally* populated.[18] Work on this system is in progress, as are studies with other phosphine gold(I) substituents.

Acknowledgment. We thank the Cambridge Commonwealth Trust (to M.S.S.) and the Royal Society for a 1983 Research Fellowship (to C.E.H.). NSF is acknowledged for a grant towards the purchase of the diffractometer at the University of Delaware.

Registry No. I, 114465-57-5; Fe, 7439-89-6.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, thermal parameters, and H-atom fractional coordinates (5 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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[15] Low-temperature ^{11}B NMR signals are broad,[16] and no new resonance could be detected on cooling. The ^{31}P NMR resonance (298 K) at δ 51.6 gave rise to signals (197 K) of roughly equal intensity (δ 52.9 and 51.5);[7] since the minor isomer possesses phosphorus atoms in an environment similar to one of the P atoms in the major isomer, we suggest that the resonance for the minor isomer coincides with one of those observed for the major isomer of I.

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[17] Compare with the structure of $[Fe_4(CO)_{13}(AuPEt_3)]^-$: Horowitz, C. P.; Holt, E. M.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8136.

[18] Harpp, K. S.; Housecroft, C. E., unpublished results.

An Unusual Trigonal-Bipyramidal Coordination of Aluminum by an Open-Chain Tetradentate Amine. Synthesis and Molecular Structure of $[Al(CH_3)][C_8H_{19}N_4][Al(CH_3)_2]$

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Summary: Reaction of trimethylaluminum with the tetradentate open-chain amine *N*,*N'*-bis(3-aminopropyl)ethylenediamine affords the crystalline product $[Al(CH_3)][C_8H_{19}N_4][Al(CH_3)_2]$. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 8.193 (6) Å, b = 9.235 (7) Å, c = 12.094 (8) Å, α = 96.05 (6)°, β = 111.15 (5)°, γ = 107.18 (6)°, and D_{calcd} = 1.13 g cm^{-3} for Z = 2. Least-squares refinement based on 1739 observed reflections with intensities $I \geq 3\sigma(I)$ in the range $0.0° \leq 2\theta \leq 50.0°$ converged at R = 0.041 (R_w = 0.059). The title compound contains a pentacoordinate aluminum atom in a trigonal-bipyramidal environment.

Principally due to its ability to form stable complexes with such transition-metal ions as Ni(II),[1] Co(III),[2,3] and Rh(III),[3,4] the macrocyclic tetradentate secondary amine 1,4,8,11-tetraazacyclotetradecane, [14]aneN_4 (commonly referred to as cyclam), has proven to be particularly useful in inorganic chemistry. Recently, we initiated an investigation into the main-group chemistry of [14]aneN_4 by exploring its interactions with organoaluminum species.[5–7] Although the tetradentate open-chain amine *N*,*N'*-bis(3-aminopropyl)ethylenediamine, $C_8H_{22}N_4$, has been employed in the Ni–template synthesis of [14]aneN_4,[8] its coordination chemistry has remained largely unexplored. Herein, we report the synthesis[9] and structure of $[Al(CH_3)][C_8H_{19}N_4][Al(CH_3)_2]$ isolated from reaction of trimethylaluminum with *N*,*N'*-bis(3-aminopropyl)ethylenediamine. In addition to representing the first examination of the main-group organometallic coordination chemistry of this important open-chain amine, the title compound is unusual in that it contains a pentacoordinate aluminum atom in a trigonal-bipyramidal environment. The X-ray crystal structure of $[Al(CH_3)][C_8H_{19}N_4][Al(CH_3)_2]$ is shown in Figure 1.

X-ray intensity data were collected on a Nicolet R3m/V diffractometer by using an $\omega/2\theta$-scan technique with Mo Kα radiation (λ = 0.71073 Å) at 26 °C. The title com-

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[7] Robinson, G. H.; Appel, E. S.; Sangokoya, S. A.; Zhang, H.; Atwood, J. L. *J. Coord. Chem.*, in press.

[8] Barefield, E. K. *Inorg. Chem.* **1972**, *11*, 2273.

[9] A 50-mL reaction vessel was charged with *N*,*N'*-bis(3-aminopropyl)ethylenediamine (8.2 mmol) and trimethylaluminum (16.4 mmol) in a 2:1 pentane/methylene chloride solution in the drybox. Reaction was immediate; the evolution of gas was observed. The system was allowed to react at room temperature for several hours at which point a multitude of colorless extremely air-sensitive crystals were obtained. ^1H NMR ($CDCl_3$); δ −0.99 (s, 3 H, AlCH_3), −0.94 (s, 3 H, AlCH_3), −0.89 (s, 3 H, AlCH_3); The propano and ethano fragments of the amine consist of a pair of complex multiplets centered at δ 1.76 and 2.98.

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