(cf. **1** and **2**) for the planar form, whereas a B–P bond length of 1.91 Å is predicted for the most stable ground state, which has a pyramidal phosphorus, a 0° twist angle, and a dihedral angle of 124°. The HPH angle was calculated to be 103.4°. The corresponding angles and distances in the title compound show it to be somewhat nearer the planar form than the ground state of BH_2PH_2. However further variations of an R'_2BPR_2 molecule may show a range of these parameters. It is also interesting to note that when calculations were carried out on the orthogonal form (i.e. twist angle = 90°) of BH_2PH_2, a much longer BP distance of 1.98 Å was calculated.[11]

In summary the structure of Mes_2BPPh_2 further supports the largely double B–P bond assignment in compounds **1** and **2**. The pyramidal phosphorus should still be capable of ligand behavior. Complexes involving the title compound as a ligand and other variations involving its arsenic and antimony analogues are under investigation.

Acknowledgment. We thank the NSF (Grant CHE-8116355) for financial support.

Note Added in Proof. Professor Nöth has informed us that the structure of $[\{B(PEt_2)_3\}_2]$, a dimer, has been solved. This also has pyramidal phosphorus centers in the terminal positions.

Supplementary Material Available: A table summarizing the data collection and refinement and tables of atom coordinates, bond distances, angles, anisotropic thermal parameters, and hydrogen coordinates and thermal parameters (7 pages); a table of structure factors (19 pages). Ordering information is given on any masthead page.

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A Fluxional High-Nuclearity Gold–Platinum Cluster: Structure of $[Au_6Pt(CC\text{-}t\text{-}Bu)(PPh_3)_7]^+[Au(CC\text{-}t\text{-}Bu)_2]^-$

Sir:

Both platinum and gold form high-nuclearity cluster complexes, with fascinating structures and unique bonding patterns.[1,2] We now report that the properties of the first high-nuclearity platinum–gold cluster suggest an equally rich field for the heteronuclear clusters formed by these elements.[3,4]

Reaction of $[Pt(PPh_3)_3]$ with [AuCC-*t*-Bu] in toluene in a 1:1 molar ratio followed by cooling to −20 °C gave crystals of an air stable cluster complex in about 20% yield. Since the NMR data[5] did not define the structure, an X-ray diffraction study was undertaken[6] and proved the title complex to be ionic.

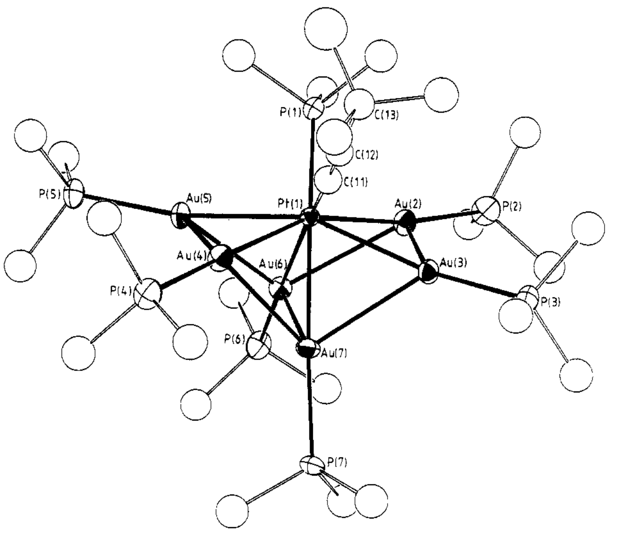

Figure 1. Perspective view (ORTEP, 50% probability thermal ellipsoids) of the caton $[\{Au(PPh_3)\}_6Pt(PPh_3)(CC\text{-}t\text{-}Bu)]^+$, with only the ipso C atoms of the phenyl rings and no H atoms shown. Important distances (Å): Pt(1)–Au(2), 2.6712 (15); Pt(1)–Au(3), 2.6933 (15); Pt(1)–Au(4), 2.6726, (15); Pt(1)–Au(5), 2.6920 (16); Pt(1)–Au(6), 2.6382 (15); Pt(1)–Au(7), 2.6249 (15); Au(2)–Au(3), 2.8537 (16); Au(2)–Au(6), 2.8788 (16); Au(3)–Au(7), 2.8324 (16); Au(4)–Au(5), 2.8472 (16); Au(4)–Au(7), 2.8430 (16); Au(5)–Au(6), 2.8496 (16); Au(6)–Au(7), 2.8748 (16).

The $[(t\text{-}BuCC)_2Au]^-$ ion has the expected near-linear backbone. Figure 1 shows a perspective view of the cation, demonstrated by the crystallographic analysis to be $[\{Au(PPh_3)\}_6Pt(PPh_3)(CC\text{-}t\text{-}Bu)]^+$, the identities of the metal atoms being assigned in conjunction with the NMR data.[5]

The central core of the cation may be described as comprising two $PtAu_4$ square-based pyramids (Pt apical) fused about a common triangular face. As far as we are aware such an arrangement for a seven-atom cluster is without precedent. The metal core has access to 90 valence electrons and so cannot be rationalized by the condensed polyhedra principle,[10] which requires a cluster of this shape to have 148 − 48 = 100 electrons. However, it is well established that general electron counting patterns do not hold for Au- or Pt-based polyhedra.[1-3]

The internal angle between the basal planes of the cation (which are slightly distorted from square) is 103.7°. The Pt atom is ca. 0.05 Å closer to the bridgehead than the peripheral Au atoms, and the P(1)C(11)Pt(1)Au(6)Au(7) moiety is approximately planar with a P(1)–Pt(1)–C(11) angle of 87.1 (6)°. This may

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(1) Clark, H. C.; Jain, V. K. *Coord. Chem. Rev.* **1984**, *55*, 151.

(2) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 281.

(3) $PtAu_2$, Pt_2Au, and Pt_2Au_2 clusters have been reported recently. (a) Braunstein, P.; Lehner, H.; Matt, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Angew. Chem.* **1984**, *96*, 307. (b) Gilmour, D. I.; Mingos, D. M. P. *J. Organomet. Chem.* **1986**, *302*, 127.

(4) Several other Pt group element–Au clusters have been reported. (a) Casalnuovo, A. L.; Pignolet, L. H.; van der Velden, J. W. A.; Bour, J. J.; Steggerda, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 5957. (b) Casalnuovo, A. L.; Laska, T.; Nilsson, P. V.; Oloffson, J.; Pignolet, L. H.; Bos, W.; Bour, J. J.; Steggerda, J. J. *Inorg. Chem.* **1985**, *24*, 182.

(5) NMR data in acetone-d_6: ^1H, $\delta = 1.06$ [s, 18 H, t-*Bu*CCAu], 0.44 [s, 9 H, t-*Bu*CCPt]; ^{31}P, $\delta = 59.0$ [septet, $^3J(P^aP^b) = 41$ Hz, $^1J(PtP^a) = 2154$ Hz, PtP^a], 42.5 [d, $^3J(P^aP^b) = 41$ Hz, $^2J(PtP^b) = 444$ Hz, AuP^b]. The ^{31}P NMR was unchanged at −20 °C, but low solubility prevented spectra at lower temperatures from being obtained.

(6) Crystal data: $[C_{132}H_{114}Au_6P_7Pt]^+[C_{12}H_{18}Au]^-$, dark-red blocks, monoclinic, $a = 27.838$ (7) Å, $b = 17.107$ (4) Å, $c = 28.484$ (7) Å, $\beta = 97.192$ (21)°, $V = 13458$ Å^3, $Z = 4$ ion pairs, $D_c = 1.803$ g cm^{-3}, $F(000) = 6928$ electrons, μ(Mo Kα) = 87.6 cm^{-1}, space group Cc from systematic absences, E statistics, and successful refinement. A total of 8987 intensities, from a crystal of approximate dimensions 0.2 × 0.3 × 0.4 mm, were recorded (θ–2θ scans) at 185 K to θ_{max} 22.5° (graphite-monochromated Mo Kα X-radiation, $\lambda = 0.71069$ Å) on an Enraf-Nonious CAD4 diffractometer. An empirical absorption correction[7] was applied (correction factors between 0.931 and 1.055). The structure was solved by direct methods (Au, Pt atoms) (SHELX84[8]) and difference-Fourier techniques and refined by full-matrix least-squares techniques (SHELX76[9]) to an R value of 0.0364 for 7805 reflections with $F > 3\sigma F$. Pt, Au, and P atoms were allowed anisotropic thermal motion. Phenyl groups were treated as rigid, planar hexagons (C–C = 1.395 Å), with phenyl H atoms set in idealized positions (C–H = 1.08 Å). Overall isotropic thermal parameters were used for phenyl C [0.0438 (5) Å^2] and phenyl H [0.075 (7) Å^2]. The CC-*t*-Bu ligand of the cation was refined by using individual isotropic thermal parameters. There is evidence for substantial disorder in the anion, which has been modeled with a combination of isotropic and anisotropic vibration parameters and variable site occupation factors. Full details will be published elsewhere.

(7) Walker, N. G.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(8) Sheldrick, G. M., University of Gottingen, 1984.

(9) Sheldrick, G. M., University of Cambridge, 1976.

(10) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

suggest a formal partitioning of oxidation states within the cation as $(Au^0)_6Pt^{II}$.

The ^{31}P NMR spectrum was inconsistent with the static structure of Figure 1 since it contained only two resonances,[5] a septet for the Pt*P*Ph$_3$ atom and a doublet for the Au*P*Ph$_3$ atoms due to PP coupling.[11] Hence the cation is fluxional and the time-averaged structure appears to be a hexagonal pyramid with equivalent AuPPh$_3$ units at the base and the Pt(PPh$_3$)(CC-*t*-Bu) unit, rapidly rotating with respect to the Au$_6$ hexagon, at the apex. The mechanism of fluxionality most reasonably involves rotation of the Pt(PPh$_3$)(CC-*t*-Bu) unit with respect to the Au$_6$ unit (Figure 1) in 60° steps, which, with flexing of the Au$_6$ unit, interconverts pairs of bridgehead and peripheral gold atoms. Both the structure of the cluster and the nature of the fluxionality appear to be unprecedented.

Acknowledgment. D.E.S. thanks the SERC for a maintenance grant, and R.J.P. thanks the NSERC (Canada) for financial support.

Supplementary Material Available: Atom coordinates (Table I), thermal parameters (Table II), interatomic distances (Table III), and interbond angles (Table IV) (6 pages). Ordering information is given on any current masthead page.

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[11] This observation, together with the easy assignment of PtP and AuP resonances from the different magnitudes of ^1J(PtP) and ^2J(PtAuP) couplings[5], allows the number of AuPPh$_3$ and PtPPh$_3$ groups in a cluster to be determined. It also shows that the fluxional process does not involve reversible fragmentation of the cluster cation.

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Reversible Double Addition of H_2 on a Bis(μ-sulfido) Binuclear Rhodium Complex

Sir:

We report on a dinuclear rhodium species with a central Rh$_2$S$_2$ ring that may alternatively add or release 2 mol of molecular hydrogen.

Reaction of H$_2$S with (triphos)RhCl(C$_2$H$_4$)[1] (**1**) in CH$_2$Cl$_2$/DMF solution (triphos = MeC(CH$_2$PPh$_2$)$_3$) followed by addition of NaBPh$_4$ in *n*-butanol gives pink crystals of [(triphos)HRh(μ-SH)$_2$RhH(triphos)](BPh$_4$)$_2$·3DMF (**2**) in 95% yield (IR (Nujol mull) 2540 (ν(S–H)), 2010 cm^{-1} (ν(Rh–H)); ^{1}H NMR (Me$_2$SO, 293 K) δ 2.12 (multiplet, S-H), 6.06 (J(H–P$_{trans}$) = 95 Hz, doublet of multiplets, Rh–H)) (Scheme I). Compound **2** is fluxional in solution as evidenced by its $^{31}P\{^1H\}$ NMR spectra in DMF/CD$_3$COCD$_3$ for the temperature range 223–328 K. In any case, the resonance of the P atom trans to H consists of a doublet of triplets at −4.04 ppm (J(P–P) = 23.0 Hz, J(P–Rh) = 71.3 Hz), −5.23 ppm (J(P–P) = 22.0 Hz, J(P–Rh) = 71.8 Hz), and −5.77 ppm (J(P–P) = 22.1 Hz, J(P–Rh) = 71.5 Hz) for the spectra recorded at 223, 293, and 328 K, respectively. At 293 K the resonances of the phosphorus atoms cis to H appear as a broad, unique band centered at ca. 23 ppm, which is split into two unresolved multiplets at 23.04 and 19.94 ppm at 328 K. Each of the last two resonances is further split into two multiplets at 31.55 and 9.97 ppm when the temperature is lowered to 223 K.

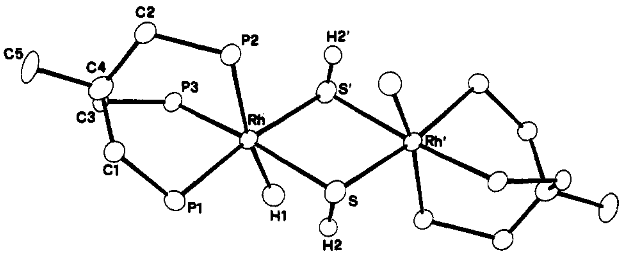
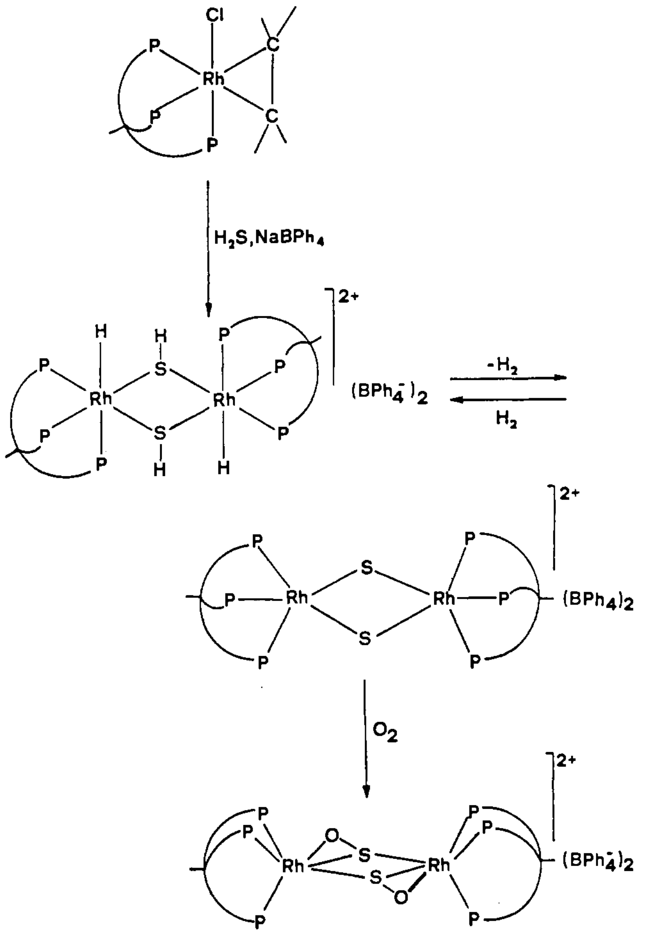


Figure 1. ORTEP drawing of the [(triphos)HRh(μ-SH)$_2$RhH(triphos)]$^{2+}$ complex cation. Some pertinent bond lengths (Å) and angles (deg) are as follows: Rh–Rh' = 3.617 (2), Rh–S = 2.395 (3), Rh–S' = 2.390 (3), Rh–P(1) = 2.288 (3), Rh–P(2) = 2.407 (3), Rh–P(3) = 2.312 (3), Rh–H(1) = 1.70 (11); S–Rh–S' = 81.9 (1), Rh–S–Rh = 98.2 (2), Rh–S–H (av) = 92 (6).

Scheme I



In the X-ray structure of **2**[2] each rhodium atom of the dimeric cation is coordinated by three terminal phosphine ligands, one hydride ligand, and two shared SH groups (see Figure 1). The Rh–S–Rh–S ring is planar, similar to analogous dimers having the [(triphos)M(μ-S)$_2$M(triphos)] framework (M = Co, Ni)[3,4] or to the closely related complex (PPh$_3$)$_2$ClHRh(μ-SH)$_2$RhHCl(PPh$_3$)$_2$.[5] In the latter complex, as well as in **2**, the S–H vectors are almost perpendicular to the Rh$_2$S$_2$ plane and are almost parallel with the Rh–H vectors (the torsion angles H–

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[1] Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* **1986**, 778.

[2] Crystal data: C$_{130}$H$_{122}$B$_2$P$_6$Rh$_2$S$_2$·3(CH$_3$)$_2$NCHO; M_r = 2381.1; monoclinic, $P2_1/n$; a = 14.848 (4), b = 31.145 (9), c = 14.244 (3) Å; β = 105.17 (2)°; Z = 2; D_{calcd} = 1.24 g cm^{-3}; μ(Mo Kα) = 4.1 cm^{-1}. X-ray data were collected on a Philips PW1100 diffractometer. Structure solution and least-squares refinement were based on 3715 absorption-corrected reflections with $I > 3\sigma(I)$ (2θ = 45°). The current R factor is 0.071 (R_w = 0.077). The hydride and SH hydrogen atoms, located from a ΔF map, behaved well during refinement.

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