$(SAr)_3]^-$,[17] while bidentate ligands displace oxo groups to give species of the general types $[MoO(NNR_2)(LL)_2]$ and $[Mo_2O_2(NNR_2)_2(\mu\text{-}OR)_2(LL)_2]$. Synthetic studies are in progress to exploit the potential of I as a precursor and to test the persistence of the *cis*-$[MoO(NNR_2)]^{2+}$ unit, a moiety with structural and chemical characteristics related to those of the well-characterized *cis*-dioxomolybdate $[MoO_2]^{2+}$ core.

Acknowledgment. This research was supported by a grant from the National Science Foundation (No. CHE8514634).

Supplementary Material Available: Tables of experimental details for the data collections, atomic positional parameters, bond lengths, bond angles, and anisotropic temperature factors for Ia and II and a table of calculated hydrogen atom positions for $[Bu_4N]_2[Mo_4O_{10}(OCH_3)_2(NNPh_2)_2]$ (19 pages); tables of observed and calculated structure factors for Ia and II (37 pages). Ordering information is given on any current masthead page.

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Structure of a Monomeric Phosphinoborane: Synthesis and X-ray Crystal Structure of (Diphenylphosphino)dimesitylborane

Sir:

A recent report from this laboratory has detailed the synthesis and structural characterization of the complexes $[Li(Et_2O)_2PRBMes_2]$ (**1**) and $[Li(12\text{-crown-}4)_2][RPBMes_2]$ (**2**) (Mes = 2,4,6-$Me_3C_6H_2$; R = Ph, C_6H_{11}, or Mes), which were formulated to have a large degree of double bonding between boron and phosphorus with B–P distances of 1.82–1.83 Å.[1] This disclosure begs the following question. Would a molecule of formula R'_2BPR_2 (R or R′ = alkyl or aryl group) also have a double bond between boron and phosphorus? If this is the case, then such a molecule should have a B–P distance similar to **1** and **2** and a planar geometry at phosphorus in addition to a substantial B–P rotation barrier. In effect the structure should be very close to those seen for similar aminoborane compounds such as Me_2BNMe_2, which has a planar C_2BNC_2 array with a short BN bond.[2] The closest approaches to such a compound are the recently published structures of the aminophosphinoboranes $[\{MesPB(tmp)\}_2]$[3] (**3**), $[Mes(H)PB(Cl)(tmp)]$[3] (**4**), and $[\{Et_3CPB(tmp)\}_2]$[4] (**5**) (tmp = 2,2,6,6-tetramethylpiperidine). However in these compounds the competitive dative interaction to boron is dominated by the nitrogen ligand tmp. This gives rise to short B–N distances, pyramidal phosphorus centers, and B–P bond lengths of 1.916 (3) Å for **3**, 1.948 (3) Å for **4**, and 1.933 (2) and 1.916 (2) Å for **5**, consistent with B–P single bonds. For $R_2'BPR_2$ compounds, substituted by essentially noninteracting alkyl or aryl substituents, ring structures of formula $[(R_2'BPR_2)_n]$ are generally found[5] with *n* having a value of 2, 3, or 4. In order to study the P–B dative interaction in the absence of oligomerization or significantly competitive ligands the monomeric compound Mes_2BPPh_2 (**6**) has been synthesized and characterized by ^{31}P and ^{11}B NMR spectroscopy[6] in addition to X-ray crystallography.[7]

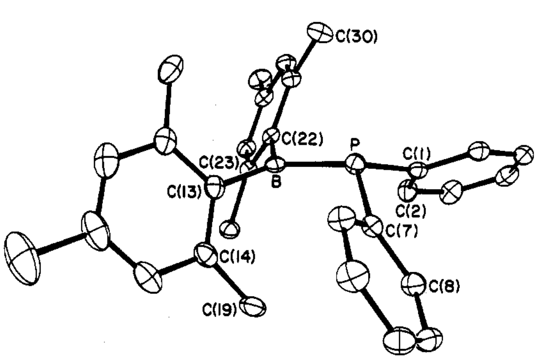

Figure 1. Computer-generated thermal ellipsoid plot of Mes_2BPPh_2. Important bond distances (Å) and angles (deg): B–P = 1.859 (3), B–C(13) = 1.584 (4), B–C(22) = 1.580 (4), P–C(1) = 1.811 (3), P–C(7) = 1.815 (3); C(1)PC(7) = 106.9 (1), C(1)PB = 116.0 (1), C(7)PB = 116.5 (1), PBC(13) = 116.2 (2), PBC(22) = 117.9 (2), C(13)BC(22) = 125.2 (2).

The molecular structure of **6** is shown in Figure 1. It can be seen that the molecule is monomeric with planar boron and pyramidal phosphorus coordination. The main features of interest concern the B–P bond length, 1.859 (3) Å, and the degree of pyramidicity at phosphorus, which are the most sensitive indications of the nature of the B–P bond. The bond length may be compared to 1.82–1.83 Å seen in complexes **1** and **2**,[1,8] distances indicative of multiple bonds and to 1.93–1.96 Å for a B–P single bond. The sum of the angles at phosphorus is 339.4°. However, this is significantly greater than the sum of the angles in PPh_3 (ca. 310°)[9] or in **4** (ca. 307°). Even in the very crowded and distorted diphosphaboretane **3** the sum of the angles at P is ca. 329°. The twist angle between the BP C(13)C(22) plane and the C(1)PC(7) plane is 1.6°, and the dihedral angle is 140.2°. The configuration Mes_2BPPh_2 therefore conveys a bonding picture intermediate between a totally planar B–P system with maximized P→B dative bonding and an alternative arrangement that has relatively acute angles at phosphorus and a smaller interaction between its lone pair and the acceptor p orbital on boron.

This view of the bonding receives some support from dipole moment data[10] and a theoretical study of the hypothetical molecule BH_2PH_2.[11] These calculations reveal a bond distance of 1.83 Å

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(6) The synthesis of the title compound was straightforward. Solid Mes_2BF (1.04 g, 3.9 mmol) was added slowly to a solution of $LiPPh_2$ formed from the addition of *n*-BuLi (2.4 mL of a 1.63 M *n*-hexane solution) to $PHPh_2$ (0.73 g, 3.9 mmol) in Et_2O (20 mL). The resultant orange yellow solution was stirred for 2 h, and the volatiles were removed in vacuo. The residue was redissolved in toluene (10 mL), and the yellow solution was filtered, reduced to ca. 5 mL, and cooled to −20 °C, which afforded the product as yellow crystals in ca. 40% yield (0.7 g), mp 172–174 °C. ^{31}P NMR: $\delta = 30.2$. ^{11}B NMR: $\delta = 51.7$.

(7) Mes_2BPPh_2, $C_{30}H_{32}PB$. Crystal data at 130 K: yellow needles, 0.15 × 0.30 × 0.50 mm, $a = 13.341$ (6) Å, $b = 9.689$ (4) Å, $c = 20.311$ (5) Å, $\beta = 106.21$ (5)°, monoclinic, $P2_1/c$, $Z = 4$. Data collection: Syntex $P2_1$ diffractometer, graphite monochromator, Mo Kα radiation, $0° < 2\theta < 50°$, $+h,+k,\pm l$; 4934 reflections collected of which 4449 were unique, $R(\text{merge}) = 0.024$; $\mu = 1.1$ cm^{-1}, absorption correction applied (program XABS). The structure was solved by direct methods, with 3207 data with $I > 2\sigma(I)$ in final refinement, 307 parameters for 32 nonhydrogen atoms (anisotropic), and 32 hydrogen atoms riding on the bonded carbon; $R = 0.049$.

(8) See: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 289. This reference suggests that the covalent radius of boron is not well-defined but probably lies between 0.85 and 0.90 Å. Huheey (Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; Table 6.1, p 258) gives 0.9 Å as the radius of boron. Using 1.1 Å as the radius of phosphorus and assuming the range of 0.85–0.90 Å for B, we may estimate a P–B single-bond length to be 1.94–1.98 Å. With an 8–9% reduction for double bonding, a P–B double bond is predicted to be 1.79–1.84 Å. These methods also predict a value of ca. 1.74–1.77 Å for a B–P multiple bond, which might be possible in a monomer of formula RPBR.

(9) Daly, J. J.; Zuerich, S. A. *Z. Kristallogr.* **1963**, *118*, 332.

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(12) Fellow of the A. P. Sloan Foundation, 1985–1987.

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(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.

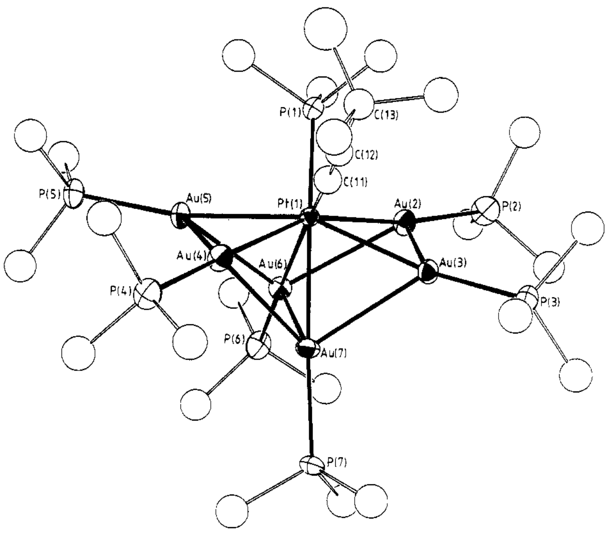

Figure 1. Perspective view (ORTEP, 50% probability thermal ellipsoids) of the caton $[\{Au(PPh_3)\}_6Pt(PPh_3)(CC\text{-}t\text{-}Bu)]^+$, with only the ipso C atoms of the phenyl rings and no H atoms shown. Important distances (Å): Pt(1)–Au(2), 2.6712 (15); Pt(1)–Au(3), 2.6933 (15); Pt(1)–Au(4), 2.6726, (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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(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, Pt*P*ᵃ], 42.5 [d, $^3J(P^aP^b) = 41$ Hz, $^2J(PtP^b) = 444$ Hz, Au*P*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.

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