Polyhedral Transition Metal Complexes Containing the $B_9H_9CHP^{2-}$ and $B_9H_9CHPCH_3^-$ Ligands

Sir:

We wish to report the preparation of a new class of sandwich-bonded transition metal complexes utilizing the (3)-1,2- and (3)-1,7-carbaphosphollide(2−) ions as ligands, and the X-ray analysis of one member of this class.

Reaction of the recently reported 1,7-$B_{10}H_{10}CHP$[1] in excess piperidine at reflux for several hours results in removal of one boron atom from the cage structure to form the piperidinium salt of (3)-1,7-$B_9H_{10}CHP^-$ (I) in 82% yield. *Anal.* Calcd for $C_5H_{10}NH_2B_9H_{10}CHP$: C, 30.38; H, 9.76; N, 5.89. Found: C, 30.22; H, 9.57; N, 5.88. Reaction of the tetramethylammonium salt of I with methyl iodide gave sublimable (3)-1,7-$B_9H_{10}CHPCH_3$ (II), mp 112–113°, in high yield. *Anal.* Calcd for $B_9H_{10}CHPCH_3$: C, 14.44; H, 8.48; P, 18.61; mol wt, 167. Found: C, 14.69; H, 8.30; P, 18.66; mol wt, 175 (osmometric in acetone). The ^1H nmr spectrum of II contains a doublet (3 H) at τ 8.03 (J_{PCH} = 10 cps), suggesting that the methyl group is attached to the phosphorus atom. The carborane CH resonance is a broad singlet at τ 7.6.

The (3)-1,2-$B_9H_{10}CHP^-$ (III) ion and (3)-1,2-$B_9H_{10}CHPCH_3$ (IV) have been obtained from 1,2-$B_{10}H_{10}CHP$ employing methods similar to those described above. Since these four molecules (I–IV) are isoelectronic with the known (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions,[2] the possibility of generating the corresponding $B_9H_9CHP^{2-}$ and $B_9H_9CHPCH_3^-$ "carbaphosphollide" ions was investigated.

Table I. Analyses

Compound	Calculated, % C	H	N	B	Metal	Found, % C	H	N	B	Metal
$[(CH_3)_4N]_2Fe[(3)\text{-}1,7\text{-}B_9H_9CHP]_2$	23.79	8.78	5.55	38.55	11.06	24.22	8.62	5.37	...	11.03
$[(CH_3)_4N]Co[(3)\text{-}1,7\text{-}B_9H_9CHP]_2$	16.61	7.44	3.23	44.85	13.58	16.60	7.25	3.00	...	13.30
$Fe[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]_2$ (VI)	12.43	6.78	...	50.33	14.44	12.57	6.52	...	...	14.63
$Co[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]_2$[a]	12.33	6.72	...	49.93	15.12	12.68	6.66	...	...	14.86
$Co[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]_2$[b]	12.33	6.72	...	49.93	15.12	12.60	6.66	...	48.69	14.96
$Ni[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]_2$	12.33	6.72	...	49.96	15.07	12.26	6.84	...	...	14.76
$(CO)_3Mn[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]$	19.73	4.30	...	31.96	18.06	19.52	4.21	...	31.40	17.82
$Fe[(3)\text{-}1,2\text{-}B_9H_9CHPCH_3]_2$	12.43	6.78	...	50.33	14.44	12.61	6.72	...	...	14.32
$C_5H_5Fe[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]$	29.36	6.34	...	33.98	19.51	29.76	6.32			19.67

[a] The melting point of this isomer is 278–279°. [b] The melting point of this isomer is 231.5–233.5°.

Treatment of I with sodium hydride and then ferrous chloride formed the red-violet compound, $[(3)\text{-}1,7\text{-}B_9H_9CHP]_2Fe^{2-}$ (V). Alkylation of V with methyl iodide produced two isomeric sublimable compounds, $[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]_2Fe$ (VI), brown, mp 239.5–240.5°; (VII) red, mp 233–234°. A *d,l* pair of $B_9H_{10}CHP^-$ (I) ions would be generated by base abstraction of either of two equivalent boron atoms adjacent to both the carbon and phosphorus atoms of 1,7-$B_{10}H_{10}CHP$. The two isomeric iron complexes would then be a *d,d–l,l* racemate and a *d,l meso* form. The brown (VI) isomer could be partly resolved by passage through a lactose hydrate column employing heptane as eluent to give a rotation $[\alpha]^{25}{}_{5000}$ +69°.

A cocrystallite containing both isomers forms deep red prisms by sublimation. Crystals are orthorhombic with a = 13.66, b = 13.96, and c = 20.36 Å (Mo Kα, λ 0.7107 Å). The unit cell volume is 3882 × 10^{-24} cm^3 and there are eight molecules of $Fe(B_9H_9CHPCH_3)_2$ (mol wt 386.7) in the unit cell (ρ_{measd} = 1.27 g cm^{-3}; ρ_{calcd} = 1.32 g cm^{-3}). The space group is uniquely determined as Pbca ($D_{2h}{}^{15}$, no. 61) on the basis of systematic absences.

Levels of data, *h0l* to *h10l*, were collected on an equi-inclination Weissenberg camera with Co Kα radiation (λ 1.792 Å) and estimated visually. A total of 1297 independent reflections was obtained. At the present stage of refinement with isotropic temperature factors, the *R* factor is 0.135 on all observed reflections. An idealized view of the molecular structure is given in Figure 1.

After separation of the mixture, cell dimensions and the space group were determined for both the red and brown isomers. While the crystals of the brown form were of poor quality, the space group is Pbca and it appears that the unit cell dimensions are virtually identical with those of the cocrystallite. The space group of the red form is also Pbca, but the cell parameters have changed considerably with a = 14.44, b = 13.79, and c = 19.51 Å. The crystal used in the structure analysis was identified as a cocrystallite both by thin-layer chromatographic separation and by the results of the X-ray analysis. In one of the cages, the carbon atom could be readily identified from a difference map and by examination of bond lengths; in the other cage, however, no unambiguous assignment could be made, and it is probable that the carbon atom occupies two sites in the crystal on an approximately statistical basis. The five atoms in the open face of each cage are coplanar. The two rings which are π-bonded to the iron atom are within 2° of being parallel.[3] There is a greater deviation from parallelism (4.5°) of the open-face five-membered ring and the other nearly parallel five-membered ring (Figure 1) in the same cage. The two rings have an average angle of twist of 107° from the position where the two phosphorus atoms would be eclipsed.

Initial experiments indicate that bis-ligand complexes of iron, cobalt, and nickel, all with 2+ formal oxidation states, can be formed with carbaphosphollide ions derived from II and bases. The (3)-1,2-$B_9H_9CHPCH_3^-$ ion also forms bis-ligand complexes with Fe(II)

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(3) The deviation from exact planarity can be detected by the phosphorus atom and the two adjacent boron atoms in each open face being slightly further from the iron atom (2.16 Å) than are the other two atoms of the face (2.11 Å).

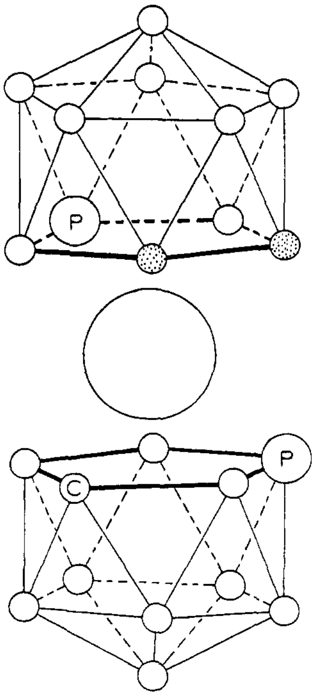

Figure 1. An idealized view of the molecular structure; the exocyclic methyl groups are not shown. The established position for the carbon atom in one of the complexing rings is marked. The partial carbon sites in the other ring are dotted. The perpendicular distance of the iron atom from the ring is 1.47 Å; the average P–C, P–B, B–B, and B–C distances are 1.80, 1.90, 1.81, and 1.71 Å, respectively.

and Co(II). The neutral mixed ligand compounds, π-$C_5H_5Fe[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]$ and $[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]Mn(CO)_3$ have been obtained by procedures similar to those described previously.[4] Analyses of representative compounds are given in Table I. A large family of these compounds probably exists, and an extensive study of this area is in progress.

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A New Method for Peptide Synthesis by Oxidation–Reduction Condensation

Sir:

This communication reports a new and useful method for the synthesis of peptides by the use of sulfenamide as an amino component. It is known that the sulfenamide group obtained from sulfenyl chloride and amines can be employed as a useful protecting group in peptide synthesis.[1,2] The sulfenyl group can be readily removed by treatment with mercaptan.[3] The enhanced reactivity of mercaptan toward sulfenamide is believed to be owing to the "soft" nucleophilicity of mercaptan and, of equal importance, to the ability to protonate the nitrogen atom of the sulfenamide. The latter was ascertained by the following experiments. A rapid reaction took place to yield amine, mercaptan or sulfide, and phosphine oxide when sulfenamide was treated with another "soft" nucleophile, triphenylphosphine, in the presence of either water or alcohol. On the contrary, no detectable change was observed when the reaction was carried out in the absence of these active hydrogen compounds. On this basis, it was found that carboxamide was formed when carboxylic acid was used in the above-mentioned reaction. Unfortunately, this reaction is not sufficiently quantitative for the preparative method of carboxamide because of the undesirable side reaction of mercaptan produced with sulfenamide. This difficulty was overcome by the use of carboxylic acid as its copper(II) salt, by which the mercaptide anion is captured as copper mercaptide.

$$(R^1CO_2)_2Cu + 2R^2SNR^3R^4 + 2Ph_3P \longrightarrow 2R^1CONR^3R^4 + [(R^2S)_2Cu] + 2Ph_3P{=}O$$

In a typical experiment, N-*n*-butylbenzenesulfenamide (10 mmol) in methylene chloride was added at room temperature to a stirred mixture of copper(II) *n*-capronate (5 mmol) and triphenylphosphine (10 mmol) in methylene chloride. After stirring for an additional 3 hr, the precipitated copper mercaptide was filtered off and the solvent was evaporated *in vacuo*. From the residue triphenylphosphine oxide resulted as crystals, mp 154–156°, 2.60 g (93%), and N-*n*-butyl-*n*-capronamide was obtained by distillation as a colorless liquid, bp 95–98° (0.05 mm), 1.63 g (95%).

On the other hand, when N-benzyl-*o*-nitrobenzenesulfenamide (10 mmol) was allowed to react with copper(II) benzoate (5 mmol) and triphenylphosphine (10 mmol) in methylene chloride at room temperature, N-benzylbenzamide could not be detected in tlc. However, the reaction began to take place rapidly by the further addition of 10 mmol of the phosphine to the reaction mixture, resulting in the formation of N-benzylbenzamide in 90% yield along with about 15 mmol of triphenylphosphine oxide.

Next, this method was applied to peptide synthesis by treating copper(II) benzyloxycarbonyl-L-phenylalaninate (5 mmol) and N-(*o*-nitrophenylsulfenyl)glycine ethyl ester (10 mmol) with triphenylphosphine (20 mmol) in methylene chloride at room temperature. The reaction took place soon after the addition of phosphine; NPS-glycine ester disappeared within 3 hr and only three spots of metallic compound, dipeptide derivative, and phosphine oxide were detected on tlc. After removal of the solvent the residue was dissolved in methanol–ether. Then the addition of petroleum ether gave 2.60 g (68%) of benzyloxycarbonyl-L-phenylalanylglycine ethyl ester, which was recrystallized from ethyl acetate–petroleum ether, mp 109–112°, $[\alpha]^{20}D$ −17.0° (*c* 2, EtOH) [lit.[4] mp 110–113°, $[\alpha]^{25}D$ −16.6° (*c* 2, EtOH)]. An additional 1.10 g of dipeptide

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