Copper(I), Silver(I), and Gold(I) Complexes with *nido*-Pentaborane Anions

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The 16-electron copper(I) complexes [Cu(μ-1-BrB$_5$H$_7$)(PPh$_3$)$_2$] and [Cu(μ-B$_5$H$_8$)(dppe)] (dppe = Ph$_2$PCH$_2$-CH$_2$PPh$_2$) have been prepared and shown to be similar to [Cu(μ-B$_5$H$_8$)(PPh$_3$)$_2$] whose structure has recently been established by single-crystal *X*-ray analysis. The corresponding silver(I) complex [Ag(μ-B$_5$H$_8$)(PPh$_3$)$_2$] has been prepared as a colourless photosensitive solid which decomposes fairly rapidly in solution even in the absence of light; however, ^{11}B n.m.r. spectroscopy shows that the complex is non-fluxional in dichloromethane. A gold complex, possibly [Au(B$_5$H$_8$)(PPh$_3$)], is formed at −78 °C but is too unstable to isolate.

THE recently reported complex [Cu(μ-B$_5$H$_8$)(PPh$_3$)$_2$] [1-3] provided the first example of a transition-metal atom coordinated by a *nido*-pentaborane ligand *via* a three-centre two-electron bond. The structure in the solid state was unequivocally established by means of single-crystal *X*-ray analysis [4] and confirmed that previously indicated by ^{1}H n.m.r. spectroscopy.[2] We report here the preparation and properties of a number of similar Group IB metal complexes in which the anions [B$_5$H$_8$]$^-$ or [1-BrB$_5$H$_7$]$^-$ act as μ-bonded ligands to copper and silver, *viz.* [Cu(μ-1-BrB$_5$H$_7$)(PPh$_3$)$_2$], [Cu(μ-B$_5$H$_8$)-(dppe)] [dppe = 1,2-bis(diphenylphosphino)ethane], and [Ag(μ-B$_5$H$_8$)(PPh$_3$)$_2$]. A gold complex, possibly [Au(B$_5$H$_8$)(PPh$_3$)], was formed at −78 °C but was too unstable to isolate.

RESULTS AND DISCUSSION

The reaction of K[1-BrB$_5$H$_7$] with an equimolar quantity of [CuCl(PPh$_3$)$_3$] in tetrahydrofuran (thf)–dichloromethane solution yielded an off-white solid [Cu(μ-1-BrB$_5$H$_7$)(PPh$_3$)$_2$] which decomposed without melting at 110 °C. It could be recrystallized from warm benzene solution as colourless needles. The complex [Cu(μ-B$_5$H$_8$)(dppe)] was prepared by a ligand-replacement reaction involving [Cu(μ-B$_5$H$_8$)(PPh$_3$)$_2$] and an equimolar amount of dppe in dichloromethane at low temperature. The photosensitive complex [Ag(μ-B$_5$H$_8$)(PPh$_3$)$_2$] was prepared from equimolar quantities of K[B$_5$H$_8$] and [AgCl(PPh$_3$)$_3$] in thf–CH$_2$Cl$_2$ solution in the absence of light. Analytical data are in the Experimental section.

The new copper complexes are very similar to the known [Cu(μ-B$_5$H$_8$)(PPh$_3$)$_2$]. The 1-bromoheptahydropentaborato-complex is less stable than the parent complex: in the atmosphere, decomposition is apparent within 12 h, as indicated by the appearance of a shoulder near the original B–H stretching frequency in the i.r. spectrum. On the other hand, the dppe complex is at least as stable as [Cu(μ-B$_5$H$_8$)(PPh$_3$)$_2$] in the solid and is more stable than this complex in solution as might be expected from the presence of a five-membered chelate ring. Thus, the ^{11}B n.m.r. spectrum of [Cu(μ-B$_5$H$_8$)-(dppe)] is essentially unchanged after 4 d at room temperature under nitrogen in dichloromethane whereas [Cu(μ-B$_5$H$_8$)(PPh$_3$)$_2$] decomposes completely under similar conditions.

Infrared bands of these complexes in the B–H (terminal) stretching region are recorded in the Table which also compares the 28.9-MHz ^{11}B n.m.r. spectra obtained from solutions in dichloromethane at room temperature. The n.m.r. data are recorded relative to [BF$_3$(OEt$_2$)] using the sign convention that chemical shifts to low frequency (high field) of the standard are negative. For the 1-bromoheptahydropentaborato-complex there is a high-field singlet of relative area 1 at −42.5 p.p.m. due to the bromine-substituted apical boron atom B(1) and a broad unresolved resonance of relative area 4 at −14.6 p.p.m. due to the basal boron atoms B(2)—B(5). On cooling the solution to −30 °C the singlet is little affected but the basal resonance becomes appreciably broader. A possible explanation for this type of behaviour in terms of quadrupolar relaxation of the copper nuclei has been proposed.[2] The ^{11}B n.m.r. spectrum of [Cu(μ-B$_5$H$_8$)-(dppe)] is similar except that the B(1) resonance is now a doublet with *J*(B–H) 145 Hz.

TABLE

Infrared and ^{11}B n.m.r. data at room temperature

Complex	ν(B–H) [a]/cm^{-1}	^{11}B N.m.r.[b]
[Cu(μ-B$_5$H$_8$)(PPh$_3$)$_2$]	2 570vs, 2 555vs 2 520s, 2 495m	−48.0, *J* 146 (1) −14.3 (br, 4)
[Cu(μ-1-BrB$_5$H$_7$)(PPh$_3$)$_2$]	2 550vs 2 500s, 2 490m	−42.5 (singlet, 1) −14.6 (br, 4)
[Cu(μ-B$_5$H$_8$)(dppe)]	2 560vs, 2 535s 2 500s, 2 490w	−46.6, *J* 145 (1) −13.6 (br, 4)
[Ag(μ-B$_5$H$_8$)(PPh$_3$)$_2$]	2 565vs, 2 555vs 2 515s, 2 500m	−48.0, *J* 140 (1) −14.0, *J ca.* 130 (2) −8.0, *J ca.* 130 (2)

[a] s = Strong, m = medium, w = weak, and v = very [b] In p.p.m. relative to [BF$_3$(OEt$_2$)]; *J* in Hz, areas in parentheses; br = broad.

The complex [Ag(μ-B$_5$H$_8$)(PPh$_3$)$_2$] is colourless when initially prepared but is photosensitive and turns beige and eventually black on exposure to light. In the absence of light the solid remains white for longer periods but in solution, even in the dark and under an inert atmosphere, decomposition is extensive after 1 h. The i.r. spectrum in the B–H(terminal) stretching region was very similar to that of the copper analogue, the fine structure again

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indicating the presence of a co-ordinated $[B_5H_8]^-$ ligand. The molecular structure is considered to be the same as that of the copper analogue [4] and this is also consistent with the observed ^{11}B n.m.r. spectra (see Table). The 28.9-MHz ^{11}B n.m.r. spectrum of $[Ag(\mu\text{-}B_5H_8)(PPh_3)_2]$ in dichloromethane at room temperature consists of a high-field doublet of relative intensity 1 at −48.0 p.p.m. (*J* 140 Hz) and a low-field multiplet of intensity 4 centred at −11.0 p.p.m. The high-field doublet can be assigned to the apical B(1) atom and collapses to a singlet on proton decoupling, as expected. The low-field multiplet arises from two overlapping doublets of equal intensity at −14.0 (*J ca.* 130) and −8.0 p.p.m. (*J ca.* 130 Hz) as shown by proton decoupling. The system is therefore non-fluxional on the ^{11}B n.m.r. time scale and resembles $[Cu(\mu\text{-}B_5H_8)(PPh_3)_2]$ [2,4] and $[Cd(\mu\text{-}B_5H_8)Cl(PPh_3)]$.[5] Comparison with B_5H_9 itself suggests that the doublet at lowest field can be assigned to the basal boron atoms B(2) and B(3) that are involved in the μ bonding to silver. The silver atom in $[Ag(\mu\text{-}B_5H_8)(PPh_3)_2]$ has trigonal-planar co-ordination, being σ-bonded to two PPh_3 ligands and μ-bonded *via* a three-centre two-electron bond to $[B_5H_8]^-$. The Ag^I is thus formally a 16-electron species as is Cu^I in the analogous complex, although both are synthesized from 18-electron complexes $[MCl(PPh_3)_3]$.

Equimolar quantities of $[AuCl(PPh_3)]$ and $K[B_5H_8]$ reacted in thf–CH_2Cl_2 at low temperature. After removal of potassium chloride, addition of pentane to the filtrate at −78 °C yielded a white precipitate which was filtered off under nitrogen. At low temperatures the product remained white but on approaching room temperature the solid turned brown and eventually black. It was spontaneously flammable in air. No further investigation of this reaction was undertaken since the desired product $[Au(B_5H_8)(PPh_3)]$, if formed at all, was too unstable to be isolated.

It was clear that, in this series of complexes, the sequence of stability is $Cu > Ag \gg Au$; this parallels the stability sequence found for the corresponding series of $[B_3H_8]^-$ complexes,[6] in which no phosphinegold(I) derivatives sufficiently stable for isolation and characterization were found.

EXPERIMENTAL

All the manipulations were carried out in a nitrogen-filled glove-box or on the vacuum line. Potassium hydride (Alpha Products Ltd.) was freed from trace amounts of mineral oil by washing with dry pentane. 1-Bromopentaborane(9) was prepared by the direct bromination of pentaborane(9) in the presence of aluminium trichloride.[7] The complexes $[CuCl(PPh_3)_3]$,[8] $[AgCl(PPh_3)_3]$,[8] and $[AuCl(PPh_3)]$ [9] were prepared according to the literature. The chelating ligand 1,2-bis(diphenylphosphino)ethane was obtained from B.D.H.

Preparations.— (1-*Bromoheptahydropentaborato*)*bis*(*triphenylphosphine*)*copper*(I). Potassium hydride (0.285 g, 70% active equivalent to 5.0 mmol of KH) was weighed in a glove-box into a flask (100 cm³) equipped with a Teflon-covered stirring bar and a tipper-tube side arm. The complex $[CuCl(PPh_3)_3]$ (4.0 g, 4.5 mmol) was weighed into the tipper tube, the apparatus was assembled, removed to the vacuum line, and evacuated. 1-Bromopentaborane(9) (0.72 g, 5 mmol) and thf (10 cm³) were condensed into the flask at −196 °C and $K[1\text{-}BrB_5H_7]$ was prepared as described in the literature.[10] The metal complex was added from the tipper tube and dichloromethane (10 cm³) was condensed in at −196 °C. The contents of the flask were stirred at −40 °C for 4 h and then at −78 °C overnight. The addition of pentane to the filtered solution at −78 °C yielded the product as a white *precipitate*. The solid was filtered off under nitrogen, washed with diethyl ether (3 × 10 cm³), and dried *in vacuo*. The yield was 45% (Found: C, 58.9; H, 5.2; B, 7.2; Br, 10.6; Cu, 8.4; P, 8.4. $C_{36}H_{37}B_5BrCuP_2$ requires C, 59.3; H, 5.1; B, 7.4; Br, 10.9; Cu, 8.7; P, 8.5%).

[1,2-*Bis*(*diphenylphosphino*)*ethane*](*octahydropentaborato*)-*copper*(I). The complex $[Cu(\mu\text{-}B_5H_8)(PPh_3)_2]$ (0.65 g, 1 mmol) and dppe (0.4 g, 1 mmol) were weighed in a glove-box into a flask (50 cm³) equipped with a stirring bar. The flask was capped, removed to the vacuum line, and evacuated. Dichloromethane (10 cm³) was distilled into the flask at −196 °C which was then warmed to −40 °C and the contents stirred at this temperature for 6 h. Pentane (50 cm³) was added to the solution at −78 °C and the resulting white *precipitate* of $[Cu(\mu\text{-}B_5H_8)(dppe)]$ was filtered off under nitrogen, washed with diethyl ether, and dried *in vacuo*. The yield was 40% (Found: C, 59.5; H, 6.3; B, 10.1; Cu, 12.4; P, 11.7. $C_{26}H_{32}B_5CuP_2$ requires C, 59.6; H, 6.2; B, 10.3; Cu, 12.2; P, 11.8%).

$[Ag(\mu\text{-}B_5H_8)(PPh_3)_2]$. The procedure outlined above for the preparation of $[Cu(\mu\text{-}1\text{-}BrB_5H_7)(PPh_3)_2]$ was followed, using $K[B_5H_8]$ and $[AgCl(PPh_3)_3]$ on the 3 mmol scale, except that the reaction was carried out with the exclusion of light at all stages. Yield *ca.* 20% (Found: C, 60.1; H, 5.2; B, 7.1. $C_{36}H_{38}AgB_5P_2$ requires C, 62.3; H, 5.5; B, 7.8%).

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer using Nujol mulls between KBr plates. Spectra were calibrated against a polystyrene film and the quoted values are accurate to within ±5 cm⁻¹. The ^{11}B n.m.r. spectra at 28.87 MHz were recorded on a Bruker HFX4 spectrometer modified for use in the Fourier-transform mode by Bruker-Datasystem BNC 12. Chemical shifts were accurate to ±0.5 p.p.m. and are quoted using the newly adopted convention that resonances to low frequency (high field) of the standard, $[BF_3(OEt_2)]$, are negative.

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