Transition-metal Complexes of the n-$B_{18}H_{20}^{2-}$ Ion

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Summary The n-$B_{18}H_{20}^{2-}$ ion reacts with $Co_2(CO)_8$, $(Ph_3P)_2NiCl_2$, and $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ to form $(CO)_2Co(n\text{-}B_{18}H_{20})^-$, $(Ph_3P)_2Ni(n\text{-}B_{18}H_{20})$, and $(Ph_2PCH_2CH_2PPh_2)Ni(n\text{-}B_{18}H_{20})$ respectively.

IN recent years a large number of hetero-atom-boranes have been synthesized which have twelve or less atoms in the cage structure.[1] We report the preparation of a series of hetero-atom-boranes containing nineteen atoms in the cage framework. A mixture of $Na_2(n\text{-}B_{18}H_{20})$ and $Co_2(CO)_8$ in tetrahydrofuran was kept at room temperature until gas evolution ceased (3 h). After removal of solvent, the residues were dissolved in water and treated with tetramethylammonium chloride to give a red-brown precipitate. The solids were subjected to column chromatography on silica gel with methylene chloride as eluent to give red, $Me_4N[(CO)_3Co(n\text{-}B_{18}H_{20})]$ in 20% yield.[†] The i.r. spectrum of this complex (KBr disc) exhibits λ_{max} at 2525 (B–H) 2075, 2035, and 2020 (CO) cm^{-1}. The 32MHz boron-11 n.m.r. spectrum of the cobalt derivative is grossly similar

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[†] All compounds gave satisfactory elemental analyses.

to that of n-$B_{18}H_{22}$. In an analogous manner $(Ph_3P)_2NiCl_2$ or $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ and n-$B_{18}H_{20}^{2-}$ reacted to form red $(Ph_3P)_2Ni$(n-$B_{18}H_{20}$) (I) and purple $(Ph_2PCH_2CH_2PPh_2)Ni$(n-$B_{18}H_{20}$) (II) in 27 and 32% yield respectively. The i.r. spectrum (KBr disc) of (II) contained λ_{max} at 2533 (B–H) and 1943 (B–H–B) cm^{-1}. The electronic spectrum of (II) (acetonitrile solution) exhibits λ_{max} (ϵ) at 368 (12,450) and 557 μm (1038). The solubility of (II) in $ClCH_2CH_2Cl$ was insufficient to obtain an accurate osmometric molecular weight (calc. 672, found 800) but is qualitatively in accord with the formula suggested.

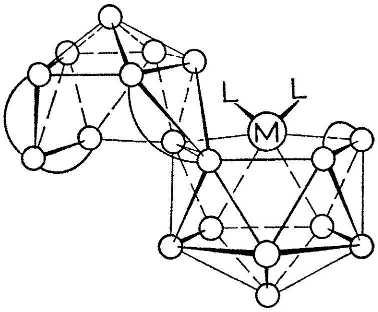

FIGURE. *Suggested structure of* $(Ph_3P)_2Ni$(n-$B_{18}H_{20}$).

Recently a series of transition-metal complexes like $Me_4N[(CO)_3Co(B_{10}H_{12})]$ have been prepared and characterized.[2] From the similarities in structure of $B_{10}H_{14}$ and n-$B_{18}H_{22}$, we suggest (see Figure) that the metal–borane bonding in both the n-$B_{18}H_{20}^{2-}$ and $B_{10}H_{12}^{2-}$ complexes is similar. Preliminary experiments suggest that i-$B_{18}H_{20}^{2-}$ also forms metal complexes.

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[1] E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, 1968, ch. 5.

[2] F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1968, 7, 2072.