Novel Ligand Rearrangement of *closo*-Nickelacarbaboranes

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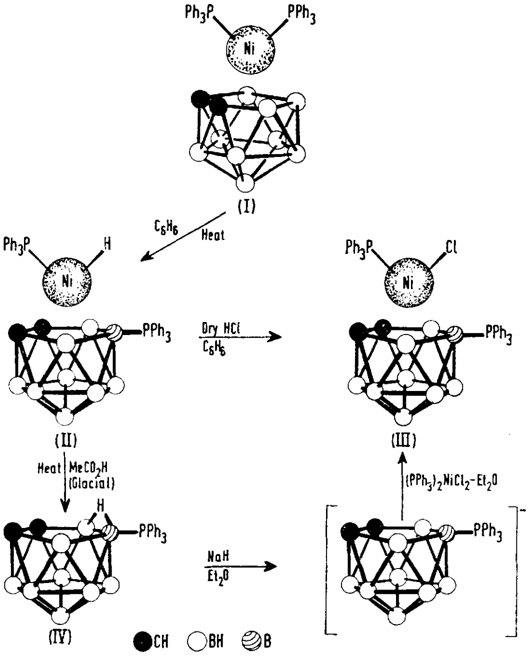
Summary Thermal rearrangement under mild conditions of *closo*-3,3-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{11}$ yields the hydrido-species, *closo*-3,8-$(PPh_3)_2$-3-H-3,1,2-$NiC_2B_9H_{10}$ in quantitative yield.

WE report the formation of *closo*-nickelacarbaboranes containing metal–hydride linkages through a novel ligand rearrangement of seemingly unreactive *closo*-nickelacarbaborane triarylphosphine complexes.

Treatment[1] of 7,8-$C_2B_9H_{11}^{2-}$ with 1 equiv. of $(PPh_3)_2NiCl_2$ in tetrahydrofuran at room temperature produces olive-green *closo*-3,3-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{11}$ (I) in high yield (Scheme). The structure of (I) has been confirmed by elemental analysis and ^1H and ^{11}B n.m.r., i.r. and mass spectroscopy.

When (I) is heated at reflux in dry benzene under argon for several hours, it is converted quantitatively into the red-orange hydrido-species, *closo*-3,8-$(PPh_3)_2$-3-H-3,1,2-$NiC_2B_9H_{10}$ (II). Compound (II) can also be obtained directly by reaction of $(PPh_3)_2NiCl_2$ with 7,8-$Tl_2C_2B_9H_{11}$[2] in benzene at reflux in $>90\%$ yield. The overall charge of the carbaborane cage in this compound is reduced from

-2 to -1 by the presence of the Ph_3P substituent in the 8-position and it is believed that the metal–hydride linkage is formed from the terminal B–H displaced from this position. The i.r. spectrum of (II) shows a sharp absorption at ν 1984 (Ni–H) cm^{-1} and the 100 MHz ^1H n.m.r. spectrum (CD_2Cl_2) exhibits a pair of doublets centred at τ 28·4 (J_{P-H} 89·0, $J_{P'-H}$ 7·5 Hz). The proton decoupled 80·5 MHz ^{11}B n.m.r. spectrum (CH_2Cl_2) consists of three poorly resolved resonances of relative area 5 : 3 : 1 at +15·30, +16·89, and +23·38 p.p.m. respectively, relative to external standard $BF_3{\cdot}OEt_2$. The boron–phosphorus coupling is not resolved in this spectrum. The mass spectrum of (II) reveals a molecular ion as a weak series of peaks with a mass cut-off at *m/e* 718 corresponding to $^{12}C_{38}{}^{1}H_{42}{}^{11}B_9{}^{31}P_2{}^{59}Ni_1$. A very intense envelope is also observed for the carbaborane fragment with a mass cut-off at *m/e* 395 corresponding to $^{12}C_{20}{}^{1}H_{25}{}^{11}B_9{}^{31}P_1$.



Scheme

Treatment of (II) with dry HCl in benzene at room temperature results in the loss of H_2 and the formation of the bright lavender chloro-derivative, *closo*-3,8-$(PPh_3)_2$-3-Cl-3,1,2-$NiC_2B_9H_{10}$ (III) in high yield (Scheme). The ^{11}B n.m.r. spectrum (CH_2Cl_2) of (III) exhibits four multiplets of relative area 1 : 2 : 2 : 4 at +1·75, +9·11, +10·70, and +19·84 p.p.m., respectively, relative to external standard $BF_3{\cdot}OEt_2$. While the other multiplets collapse, the doublet of area one remains intact upon proton decoupling and is assigned to the unique phosphorus-bearing boron (J_{B-P} 128 Hz). Compound (III) may also be obtained in 38% yield from the reaction of $(PPh_3)_2NiCl_2$ with 7,8-$C_2B_9H_{13}$[3] in benzene at reflux along with some (II). Compound (III) is formed from (II) by the action of HCl generated *in situ*.

Compound (II) is degraded by warming in glacial acetic acid to Ph_3P, $Ni(OAc)_2$, and the neutral ligand-adduct carbaborane species, *nido*-10-PPh_3-7,8-$C_2B_9H_{11}$ (IV), in quantitative yield. Compound (IV) is identical by i.r. and ^{11}B n.m.r. spectra and m.p. to the symmetrical isomer obtained by oxidative substitution[4] of Ph_3P on 7,8-$C_2B_9H_{12}{}^-$ in the presence of $FeCl_3$. This degradation reaction clearly proves the location of the carbon atoms and the Ph_3P adduct in compound (II). It is to be noted that the rearrangement of (I) to (II) is highly selective yielding only one isomer in contrast to the oxidative substitution reaction (*vide infra*) which produces mixtures of ligand adduct isomers.

Treatment of (IV) with NaH in ether removes the B–H–B bridge and produces *nido*-Na(10-PPh_3-7,8-$C_2B_9H_{10}$) which, on treatment with 1 equiv. of $(PPh_3)_2NiCl_2$ in ether, produces (III) in quantitative yield. This lends further support to the structures of (II) and (III).

The analogous compounds *closo*-1,1-$(PPh_3)_2$-1,2,3-$NiC_2B_8H_{10}$ and *closo*-3-CO-3-PPh_3-3,1,2-$NiC_2B_9H_{11}$ also appear to rearrange to hydrido-species in a similar manner. In fact, this rearrangement appears to be general for nickel compounds of this type and proceeds with high selectivity and without migration of the carbon atoms, a common result in many thermal rearrangements of metallocarbaboranes.[5]

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[5] There are numerous examples of these rearrangements: see 'Boron Hydride Chemistry,' ed. E. L. Muetterties, Academic Press, New York, 1975, and references therein.