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Preliminary communication

[1-Pentaboryl-bis(trifluoromethyl)phosphine] nickel tricarbonyl

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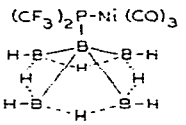
A compound having the structural formula



was formed quantitatively from the previously-reported ligand 1-$(CF_3)_2PB_5H_8$ [1] in excess liquid $Ni(CO)_4$, easily at 25°. The pertinent stoichiometry (with mmole quantities) is represented as follows.

$$1(CF_3)_2PB_5H_8 + Ni(CO)_4 \rightarrow CO + 1\text{-}(CF_3)_2PB_5H_8 \cdot Ni(CO)_3$$
$$0.258 \quad (excess) \quad 0.249$$

After the removal of the excess $Ni(CO)_4$ and a trace of fine brown sediment, the product appeared as a colorless non-volatile liquid, apparently quite stable at 25°. Its high purity was indicated by the cleanness of the four-element NMR spectra (recorded both before and after removal of the excess nickel carbonyl, with the same results), shown in Table 1.

TABLE 1

NMR COMPARISON OF LIGAND AND COMPLEX

	1-$(CF_3)_2PB_5H_8$ [1]		1-$(CF_3)_2PB_5H_8 \cdot Ni(CO)_3$	
	δ (ppm)	*J* (cps)	δ (ppm)	*J* (cps)
H (terminal)	−2.74	169	−2.75	169
H (bridge)	1.87	–	1.95	–
F	49.9	72	57.8	75
P	25.1	70	26.7	(?)
B_1	68.8	(70)	67.0	137
B_{2345}	30.4	168	30.6	170

These results were obtained by means of the Varian HA-100 instrument, at 100 Mc for H, 94.1 Mc for F, 40.5 Mc for P, and 32.1 Mc for B. All positive δ values were measured upfield from the standard: $(CH_3)_4Si$ for H, Cl_3CF for F, H_3PO_4 for P, and $(CH_3O)_3B$ for B.

Especially noteworthy is the increase of $J(PB_1)$ when the phosphorus atom forms the bonds to nickel. For the free ligand this J cannot be determined from the boron spectrum (wherein the 1-B atom is seen as a very broad singlet); it was estimated rather from the phosphorus spectrum (an overlapping quartet of septets appearing as a pseudo-dectet)[1]. In the complex, however, the 1-B atom appears as a clear doublet. The reason for the increase in $J(PB_1)$ is not difficult to recognize: whereas the phosphorus lone-pair electrons in $1\text{-}(CF_3)_2PB_5H_8$ would have mostly 3*s* character (so that the P—B bond would use mostly P_{3p} character), the P—Ni bond would use those phosphorus electrons more in the $3sp^3$ manner, giving more 3*s* character to the P—B bond. Simular increases in J values have been observed for other such complexes, for the same reason[2].

The infrared spectrum of $1\text{-}(CF_3)_2PB_5H_8 \cdot Ni(CO)_3$ (solution in cyclohexane) was recorded in the C—O stretching region by a well calibrated Beckman IR-7 instrument. The two expected modes appeared as a sharp singlet at 2090 cm^{-1} and a somewhat more intense doublet at 2029 and 2019 cm^{-1}. There was an unexplained satellite at 2001 cm^{-1} and a trace of $Ni(CO)_4$ was observed at 2047 cm^{-1} (literature[3] for the cyclohexane solution, 2044.7 cm^{-1}).

The clean formation of the $LNi(CO)_3$ type complex, showing no tendency to disproportionate, may be in part due to the steric difficulty of forming the $L_2Ni(CO)_2$ type with the two $1\text{-}(CF_3)_2PB_5H_8$ ligands mutually adjacent on a tetrahedral nickel atom. However, we have not attempted actually to make $[1\text{-}(CF_3)_2PB_5H_8]_2Ni(CO)_2$. We did try to make a nickel complex from $\mu\text{-}CH_3CF_3PB_5H_8$ [1] and $Ni(CO)_4$ in a sealed tube at temperatures as high as 100°, but there was no reaction beyond a slight evolution of non-condensable gas, and no change in the boron NMR spectrum. For the intended result, of course, the P atom would have to be moved from its B—P—B bridging position to a B—P terminal position, at an energy cost which evidently would be greater than could be supplied by the formation of the $LNi(CO)_3$, including the cost of removing one CO.

ACKNOWLEDGEMENT

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