

**Preliminary communication**

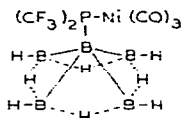
**[1-Pentaboryl-bis(trifluoromethyl)phosphine] nickel tricarbonyl**

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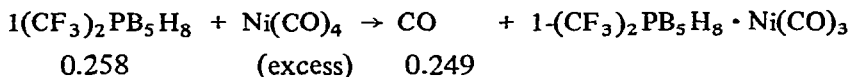
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A compound having the structural formula



was formed quantitatively from the previously-reported ligand  $1-(\text{CF}_3)_2\text{PB}_5\text{H}_8$ <sup>1</sup> in excess liquid  $\text{Ni}(\text{CO})_4$ , easily at 25°. The pertinent stoichiometry (with mmole quantities) is represented as follows.



After the removal of the excess  $\text{Ni}(\text{CO})_4$  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

	$1-(\text{CF}_3)_2\text{PB}_5\text{H}_8$ <sup>1</sup>		$1-(\text{CF}_3)_2\text{PB}_5\text{H}_8 \cdot \text{Ni}(\text{CO})_3$	
	$\delta$ (ppm)	$J$ (cps)	$\delta$ (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 <sub>1</sub>	68.8	(70)	67.0	137
B <sub>2,3,4,5</sub>	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  $\delta$  values were measured upfield from the standard:  $(\text{CH}_3)_4\text{Si}$  for H,  $\text{Cl}_3\text{CF}$  for F,  $\text{H}_3\text{PO}_4$  for P, and  $(\text{CH}_3\text{O})_3\text{B}$  for B.

Especially noteworthy is the increase of  $J(\text{PB}_1)$  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)<sup>1</sup>. In the complex, however, the 1-B atom appears as a clear doublet. The reason for the increase in  $J(\text{PB}_1)$  is not difficult to recognize: whereas the phosphorus lone-pair electrons in  $1-(\text{CF}_3)_2\text{PB}_5\text{H}_8$  would have mostly  $3s$  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  $3s$  character to the P-B bond. Similar increases in  $J$  values have been observed for other such complexes, for the same reason<sup>2</sup>.

The infrared spectrum of  $1-(\text{CF}_3)_2\text{PB}_5\text{H}_8 \cdot \text{Ni}(\text{CO})_3$  (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  $2090\text{ cm}^{-1}$  and a somewhat more intense doublet at  $2029$  and  $2019\text{ cm}^{-1}$ . There was an unexplained satellite at  $2001\text{ cm}^{-1}$  and a trace of  $\text{Ni}(\text{CO})_4$  was observed at  $2047\text{ cm}^{-1}$  (literature<sup>3</sup> for the cyclohexane solution,  $2044.7\text{ cm}^{-1}$ ).

The clean formation of the  $\text{LNi}(\text{CO})_3$  type complex, showing no tendency to disproportionate, may be in part due to the steric difficulty of forming the  $\text{L}_2\text{Ni}(\text{CO})_2$  type with the two  $1-(\text{CF}_3)_2\text{PB}_5\text{H}_8$  ligands mutually adjacent on a tetrahedral nickel atom. However, we have not attempted actually to make  $[1-(\text{CF}_3)_2\text{PB}_5\text{H}_8]_2\text{Ni}(\text{CO})_2$ . We did try to make a nickel complex from  $\mu\text{-CH}_3\text{CF}_3\text{PB}_5\text{H}_8$ <sup>1</sup> and  $\text{Ni}(\text{CO})_4$  in a sealed tube at temperatures as high as  $100^\circ$ , 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  $\text{LNi}(\text{CO})_3$ , including the cost of removing one CO.

#### ACKNOWLEDGEMENT

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#### REFERENCES

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