Nuclear Magnetic Resonance Evidence for the Presence of a Hydridic Hydrogen in the Nitrogen Complex of Cobalt

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WE have previously reported[1] that a nitrogen-co-ordinated complex of cobalt is prepared by the reaction of cobalt(III) acetylacetonate, triphenylphosphine, and tri-isobutylaluminium under nitrogen; the complex is probably a mixture of $CoN_2(PPh_3)_3$ and a small amount of $CoHN_2(PPh_3)_3$. Yamamoto *et al.*[2] prepared a nitrogen complex of cobalt by a similar method and formulated it as $CoN_2(PPh_3)_3$. On the other hand, Sacco *et al.*[3] obtained the nitrogen complex, $CoHN_2(PPh_3)_3$, by the reaction of $CoH_3(PPh_3)_3$ with nitrogen. The presence of a hydridic hydrogen in the complex was postulated from the results of its thermal decomposition, and its reactions with hydrochloric acid, iodine, carbon tetrachloride, and 1,2-bis(diphenylphosphino)ethane. Recent *X*-ray structural analysis[4] of the nitrogen complex prepared by the method of Yamamoto *et al.* indicates that the co-ordination about cobalt is best described as trigonal bipyramidal with one apical site vacant, in which a hydridic hydrogen may be located.

^{1}H n.m.r. spectra of the complexes (tetrahydrofuran solution) prepared by either method show identical quartet structures (J 50 c./sec.) at τ 29 with intensity ratios 1 : 3 : 3 : 1 for the four equally-spaced bands. An interaction with phosphorus-31 (spin $\frac{1}{2}$) and equivalence of the three co-ordinated phosphines are indicated, implying that a hydridic hydrogen does occupy an apical site in the trigonal bipyramidal structure suggested by Ibers *et al.*[4]

Furthermore, the i.r. spectra of the two complexes are identical, and the elemental analysis of the complex prepared by the method of Sacco *et al.* is in accord with the formula $CoHN_2(PPh_3)_3$.

From these results, it may be reasonable to conclude that both nitrogen complexes are the same compound, correctly formulated as $CoHN_2(PPh_3)_3$. The structure of the complex is described as trigonal bipyramidal, in which a hydridic hydrogen occupies an apical site *trans* to the nitrogen ligand.

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