Preparation of a Cobalt Complex Coordinated by Molecular Nitrogen and Triphenylphosphine

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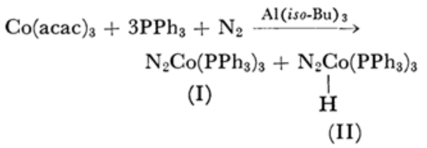
Fixation of molecular nitrogen under mild conditions has become one of the most interesting subjects in the field of coordination chemistry since the works of Vol'pin and Shur.⁽¹⁾ Chemical bonding of molecular nitrogen to transition metals has been proved by means of infrared spectroscopy in the cases of metallic nickel,⁽²⁾ metallic cobalt,⁽³⁾ and ruthenium salt⁽⁴⁾. Recently ruthenium⁽⁵⁾ and iridium⁽⁶⁾ complexes coordinated by molecular nitrogen were reported. During the course of the studies on the alkyl transition metal complexes having stabilizing ligands,⁽⁷⁾ Yamamoto and Ikeda discovered the formation of a cobalt complex coordinated by molecular nitrogen and triphenylphosphine.⁽⁸⁾

We have prepared a cobalt complex by the reaction of cobalt(III) acetylacetonate, triphenylphosphine, and triisobutylaluminum in a nitrogen gas stream in toluene solutions at −5—15°C. The complex was separated from the reaction mixture as precipitate and after repeated washing with petroleum ether, was recrystallized from toluene.



$$\mathrm{Co(acac)_3 + 3PPh_3 + N_2 \xrightarrow{Al(\mathit{iso}\text{-}Bu)_3} \underset{(I)}{N_2Co(PPh_3)_3} + \underset{(II)}{\underset{\overset{|}{H}}{N_2Co(PPh_3)_3}}}$$

Found: C, 74.07; H, 5.76; N, 3.08; Co, 6.80%. Calcd for $C_{54}H_{45}N_2P_3Co$: C, 74.22; H, 5.19; N, 3.20; Co, 6.74%. Calcd for $C_{54}H_{46}N_2P_3Co$: C, 74.14; H, 5.30; N, 3.20; Co, 6.73%.

The complex is an orange-colored crystal and rather sensitive to oxygen but fairly stable to water. It dissolves in such organic solvents as aromatic hydrocarbons and ether. When heated in vacuum, it decomposes at about 80°C evolving molecular nitrogen and hydrogen in a ratio of *ca.* 9 : 1, and a small amount of benzene. The decomposition products were identified and quantitatively analyzed by means of gas chromatography and mass spectroscopy. The infrared spectrum of the complex gives a sharp strong band at 2088 $\mathrm{cm^{-1}}$, and several other bands due to triphenylphosphine. The 2088 $\mathrm{cm^{-1}}$ band is assigned to the $N\equiv N$ stretching of the coordinated nitrogen molecule, since it is very near the reported wave numbers for the several transition metal complexes of molecular nitrogen.⁽⁴⁻⁶⁾ However, no hydride band has so far been detected. From the experimental results described above, the product is probably a mixture of complexes I and II. The reactions of the coordinated nitrogen with metal hydrides, molecular hydrogen, metal alkyls, *etc.* are now being investigated.

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