Study of the Fixation of Nitrogen. Isolation of Tris(triphenylphosphine)cobalt Complex Co-ordinated with Molecular Nitrogen

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IN the course of an attempt to isolate alkyltransition-metal compounds from mixed systems containing transition-metal compounds, organoaluminium compounds, and various ligands such as bipyridyl[1] and phosphines in an atmosphere of nitrogen, we have discovered a cobalt–triphenylphosphine complex in which molecular nitrogen is bound to cobalt. This complex, to our knowledge, represents the first example of an isolated single transition-metal compound in which molecular nitrogen is fixed. Fixation of nitrogen by mixed systems composed of transition-metal compounds and organometallic compounds has been reported by Vol'pin and Shur,[2] but so far no complex containing nitrogen has been isolated from the mixed systems.

Ruthenium[3] and iridium[4] complexes co-ordinated with molecular nitrogen have recently been isolated by the reactions of the transition-metal compounds with hydrazine hydrate[3] and with acid azides,[4] but not by fixation of nitrogen.

The cobalt complex was prepared in an atmosphere of nitrogen by the reaction of cobalt(III) acetylacetonate with diethylaluminium monoethoxide in the presence of triphenylphosphine in ether or toluene.

$$\mathrm{Co(acac)_3 + 3AlEt_2OEt + 3PPh_3 + N_2 \rightarrow [(Ph_3P)_3Co{\cdot}N_2]}$$

Yellow crystals isolated from the reaction mixture and recrystallized from toluene at low temperature contained one molecule of nitrogen per cobalt atom. (Analysis: Calc. for $C_{54}H_{45}N_2P_3Co$: C, 74·3; H, 5·2; N, 3·2; Co, 6·7%. Found: C, 74·0; H, 5·8; N, 3·0; Co, 6·9%.) The complex is moderately stable in the absence of air. Thermal decomposition over 80° liberated the calculated amount of nitrogen from the complex, as proved by mass spectrometry.

The infrared spectrum of the complex shows a sharp strong band at 2088 cm.$^{-1}$ which is assigned to the co-ordinated N–N stretch. This band is not observed in a tris(triphenylphosphine)cobalt complex prepared in a similar way but in an atmosphere of argon. Similar bands have been observed in the 2095—2195 cm.$^{-1}$ region in the spectra of ruthenium[3] and iridium[4] complexes co-ordinated with molecular nitrogen.

The reduction of $Co(acac)_3$ with $AlEt_2OEt$ to the zerovalent cobalt complex probably proceeds through the formation of unstable ethylcobalt complexes.[1] The methyl–cobalt bond is more stable compared with the ethyl–cobalt bond and $[MeCo(Ph_3P)_3]$ was isolated as brown crystals by the reaction of $Co(acac)_3$, $AlMe_2OEt$, and triphenylphosphine in an argon atmosphere.

Experiments are in progress to explore the possibility of reducing the co-ordinated nitrogen and of applying this type of complex to the catalytic fixation of nitrogen under mild conditions.

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