

## Organo-nitrile Analogues of the Nitrogen Complex of Cobalt, $\text{CoHN}_2(\text{PPh}_3)_3$

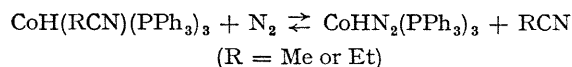
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For the complex  $\text{CoHN}_2(\text{PPh}_3)_3$ ,<sup>1</sup> X-ray analysis<sup>2</sup> indicates that the Co-N≡N linkage is nearly linear. This linkage is analogous to the M-N≡C-R linkage in organonitrile complexes in which the organo-nitrile is bonded to the metal through the nitrogen lone-pair. We have prepared organo-nitrile analogues of the nitrogen complex by treating it with organonitriles.

The dark-red acetonitrile complex, prepared by addition of acetonitrile to a toluene solution of  $\text{CoHN}_2(\text{PPh}_3)_3$  at room temperature, is air-sensitive. Its elemental analysis is in accord with the formula  $\text{CoH}(\text{MeCN})(\text{PPh}_3)_3$ , and its i.r. spectrum shows a sharp absorption at  $2210 \text{ cm}^{-1}$  assignable to the C≡N stretching vibration, which is about  $45 \text{ cm}^{-1}$  lower than that of free acetonitrile. This may be attributed to a degree of back donation from the low-valent metal to the  $\pi$ -antibonding C≡N ligand. Benzonitrile complexes of ruthenium(II) also show a lowering of  $\nu_{\text{CN}}$  resulting from coordination of monodentate organo-nitriles to a metal cation.<sup>3</sup> No absorption assignable to the Co-H stretching vibration was observed in the i.r. spectrum of  $\text{CoH}(\text{MeCN})(\text{PPh}_3)_3$ . However, the presence of a hydridic hydrogen is suggested by the following results. The acetonitrile complex decomposes *in vacuo* above *ca.*  $120^\circ$  to give acetonitrile and

benzene. Its reaction with carbon monoxide yields carbonyl complexes,  $\text{CoH}(\text{CO})(\text{PPh}_3)_4$ <sup>3</sup> and  $[\text{Co}(\text{CO})_3\text{PPh}_3]_2$ .<sup>5</sup> When nitrogen was bubbled through a solution of the acetonitrile complex in toluene at room temperature, the original dark red colour became lighter and the i.r. spectrum of the solution showed a sharp absorption at  $2088 \text{ cm}^{-1}$  characteristic of the N≡N stretching vibration in the nitrogen complex,  $\text{CoHN}_2(\text{PPh}_3)_3$ . This indicates that the coordinated acetonitrile can readily be displaced by molecular nitrogen.



The reaction of the nitrogen complex with propionitrile gives a dark red crystalline complex,  $\text{CoH}(\text{EtCN})(\text{PPh}_3)_3$ , which also reacts with nitrogen gas at room temperature to give  $\text{CoHN}_2(\text{PPh}_3)_3$ . However, the dark brown solutions obtained by adding acrylonitrile and benzonitrile to a toluene solution of  $\text{CoHN}_2(\text{PPh}_3)_3$  did not react with nitrogen.

(Received, January 9th, 1969; Com. 034.)

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<sup>2</sup> J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Comm.*, 1968, 96.

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<sup>5</sup> W. Hieber and W. Freyer, *Chem. Ber.*, 1958, **91**, 1230.