

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

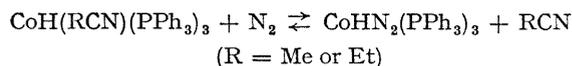
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For the complex $\text{CoHN}_2(\text{PPh}_3)_3$,¹ X-ray analysis² indicates that the Co-N≡N linkage is nearly linear. This linkage is analogous to the M-N≡C-R linkage in organonitrile complexes in which the organo-nitrile is bonded to the metal through 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 cm^{-1} assignable to the C≡N stretching vibration, which is about 45 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 π -antibonding C≡N ligand. Benzonitrile complexes of ruthenium(II) also show a lowering of ν_{CN} resulting from coordination of monodentate organo-nitriles to a metal cation.³ 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° to give acetonitrile and

benzene. Its reaction with carbon monoxide yields carbonyl complexes, $\text{CoH}(\text{CO})(\text{PPh}_3)_4$ ³ and $[\text{Co}(\text{CO})_3\text{PPh}_3]_2$.⁵ 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 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.

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⁵ W. Hieber and W. Freyer, *Chem. Ber.*, 1958, **91**, 1230.