Dinitrogen Complexes of Cobalt(0) and Cobalt(−I)

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Summary Reaction of $CoClP_3$ ($P = Et_2PhP$, Ph_3P) with sodium metal in tetrahydrofuran or toluene under nitrogen gives bridged dinitrogen complexes, $P_3Co(N_2)CoP_3$ of cobalt(0) and dinitrogen complexes $Na[Co(N_2)P_3]$ of cobalt(−I).

As an extension of our studies on the fixation of molecular nitrogen under mild conditions,[1] we report the preparation of new dinitrogen complexes of cobalt(0), of formula $P_3Co(N_2)CoP_3$, and of cobalt(−I), of formula $Na[Co(N_2)P_3]$ ($P = Et_2PhP$, Ph_3P).

The reaction between $CoCl_2(PEt_2Ph)_2$, PEt_2Ph, and powdered sodium metal in the molar ratio 1 : 1 : 2 in tetrahydrofuran (THF) under nitrogen at room temperature and atmospheric pressure leads, *via* $CoCl(PEt_2Ph)_3$,[2] to a bridged binuclear dinitrogen complex (I) of cobalt(0), [equations (1) and (2)].

$$CoCl_2(PEt_2Ph)_2 + PEt_2Ph + Na \rightarrow CoCl(PEt_2Ph)_3 + NaCl \qquad (1)$$

$$2CoCl(PEt_2Ph)_3 + 2Na + N_2 \rightarrow \underset{(I)}{(PEt_2Ph)_3Co(N_2)Co(PEt_2Ph)_3} + 2NaCl \qquad (2)$$

(I) is obtained as dark brown crystals, unstable in air and soluble in non-polar solvents. It liberates 0·50 mol of N_2 per cobalt atom on thermal decomposition at 100—120 °C and on treatment with iodine at 60 °C. The i.r. spectra of (I) in Nujol mull and in benzene solution under nitrogen do not show absorption bands assigned to N–N stretching. By analogy with the structure of the ion $\{[(NH_3)_5Ru]_2(N_2)\}^{4+}$,[3] we suggest, for compound (I), a symmetric dinitrogen bridged structure.

The reaction between $CoCl_2(PEt_2Ph)_2$, PEt_2Ph, and powdered sodium metal in the molar ratio 1 : 1 : 3 in THF under nitrogen at room temperature and atmospheric pressure gives $Na[Co(N_2)(PEt_2Ph)_3]$ (II) [see equation (3)]

$$CoCl_2(PEt_2Ph)_2 + PEt_2Ph + 3Na + N_2 \rightarrow \underset{(II)}{Na[Co(N_2)(PEt_2Ph)_3]} + 2NaCl \qquad (3)$$

(II) is obtained in the form of black, diamagnetic crystals, unstable in air and soluble in THF and acetonitrile. 1 Mol of N_2 per cobalt atom is liberated on thermal decomposition at 100—120 °C and on treatment with iodine at 50 °C. I.r. spectra in Nujol mull show a very strong absorption band at 1840 cm^{-1} (at 1875 cm^{-1} in THF solution), assignable to co-ordinated N–N stretching. On treatment with water, (II) immediately gives a known compound $CoH(N_2)(PEt_2Ph)_3$,[4] and a strongly alkaline solution. (II) reacts with carbon monoxide at −60 °C, to give isomorphous black crystals of $Na[Co(CO)(PEt_2Ph_3]$ [$\nu(CO) = 1700\ cm^{-1}$], which give $CoH(CO)(PEt_2Ph)_3$ [$\nu(Co\text{–}H) = 1910\ cm^{-1}$; $\nu(CO) = 1880\ cm^{-1}$] on treatment with water.

An asymmetric binuclear bridged dinitrogen complex of cobalt(0), (III), has been obtained from an equimolar mixture of $Na[Co(N_2)(PEt_2Ph)_3]$ and $CoCl(PPh_3)_3$ in THF under argon [equation (4)].

$$Na[Co(N_2)(PEt_2Ph)_3] + CoCl(PPh_3)_3 \rightarrow \underset{(III)}{(PEt_2Ph)_3Co(N_2)Co(PPh_3)_3} + NaCl \qquad (4)$$

Compound (III), recrystallized from benzene–n-pentane under argon, liberates 0·50 mol of N_2 per cobalt atom on thermal decomposition at 100—120 °C and on reaction with iodine at 60 °C, but its i.r. spectra in Nujol mull and in benzene solution under nitrogen do not show absorption bands assignable to N–N stretching.

The corresponding complexes of formula $[(PPh_3)_3Co]_2(N_2)$ and $Na[Co(N_2)(PPh_3)_3]$ [$\nu(N_2) = 1845\ cm^{-1}$] were obtained as dark red crystals from $CoCl(PPh_3)_3$ and sodium metal in toluene under nitrogen in a molar ratio Co : Na of 1 : 1 and 1 : 2, respectively. In contrast with the behaviour of the binuclear dinitrogen complexes of ruthenium(II)[5] and of nickel(0),[6] which are in equilibrium with the corresponding mononuclear dinitrogen complexes, the binuclear dinitrogen complexes of cobalt(0) do not show any tendency to dissociate in solution. Though the existence of a mononuclear dinitrogen complex of cobalt(0) of formula $Co(N_2)(PPh_3)_3$ [$\nu(N_2) = 2092{\cdot}8\ cm^{-1}$] has been reported,[7] the i.r. spectra of $[(PPh_3)_3Co]_2(N_2)$, in Nujol mull and in benzene solution under nitrogen, do not show absorption bands assignable to N–N stretching.

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