Synthesis, Characterization, and Crystal Structure of the Dimeric, Paramagnetic Cobalt(0) Complex $\{[MeC(CH_2PPh_2)_3Co]_2(\mu\text{-}N_2)\}$

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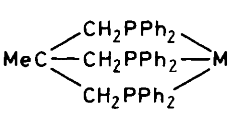
The first example of a paramagnetic, dimeric cobalt(0) complex, containing a bridging dinitrogen ligand, $\{[MeC(CH_2PPh_2)_3Co]_2(\mu\text{-}N_2)\}$, has been prepared and its molecular structure established by *X*-ray crystallography.

The tripod-like terdentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, tppme, plays an important role in co-ordination and organometallic chemistry, owing to its special geometry, which allows only *facial* cordination to the metal. Indeed the (tppme)M fragments (M = Co, Ni, Rh, Pd, Ir, Pt) can activate a large variety of small molecules or stabilize groups of atoms, which cannot exist by themselves.[1] Thus the synthesis of (tppme)M complexes, containing at most some weakly co-ordinating ligands, is of interest in activation and reactivity studies.

Here we report the preparation and structure of a cobalt complex, $\{[(tppme)Co]_2(\mu\text{-}N_2)\}$, (**1**), containing a bridging dinitrogen ligand, which is, to our knowledge, the first example of a fully characterized, paramagnetic, dimeric cobalt(0) complex. A previously reported, formally analogous, compound $\{[(PPh_3)_3Co]_2(\mu\text{-}N_2)\}$ has been formulated only on the basis of elemental and gas analyses and i.r. spectroscopic measurements.[2]

Compound (**1**) was isolated by reducing equimolar solutions of $CoCl_2$ and tppme in tetrahydrofuran (THF) with an excess of 1.5% sodium amalgam (molar ratio Co:Na 1:4). The reaction was performed under nitrogen at 40 °C. Large deep-brown crystals of (**1**) were obtained by addition of n-butanol to the reduced THF solution (20% yield).



(tppme)M

The solid compound was extremely oxygen and moisture sensitive and dissolved in benzene and THF, while it reacted with halogenated solvents. It was paramagnetic with a $\mu_{eff.}$ for the dimer, at room temperature, of 4.36 μ_B,† which slowly decreased to 3.80 μ_B, at 92 K.

Powder e.s.r. spectra recorded at liquid helium temperature showed two resonances at $g = 2.13$ and 4.62, the latter being very weak. The i.r. spectrum (Nujol mull under nitrogen) did not show any absorption band above 1600 cm^{-1}, thus indicating the symmetrical position of the N_2 molecule (see below) and the absence of any bands due to N–H stretching vibrations.

Crystal data: $C_{41}H_{39}CoNP_3$, $a = 18.101(14)$, $b = 15.364(10)$, $c = 12.921(9)$ Å, $\beta = 93.33(5)°$, $U = 3587.5$ Å^3, monoclinic, space group $P2_1/n$, $Z = 4$, $D_c = 1.291$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 6.36$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å. The crystal was coated in paraffin and the intensities were rescaled to take account of a 25% decay in standard reflections. Intensity data

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† This value is the average of the results of three magnetic measurements (4.30, 4.38, 4.41 μ_B) performed on three different samples of (**1**) under nitrogen using the Gouy method.

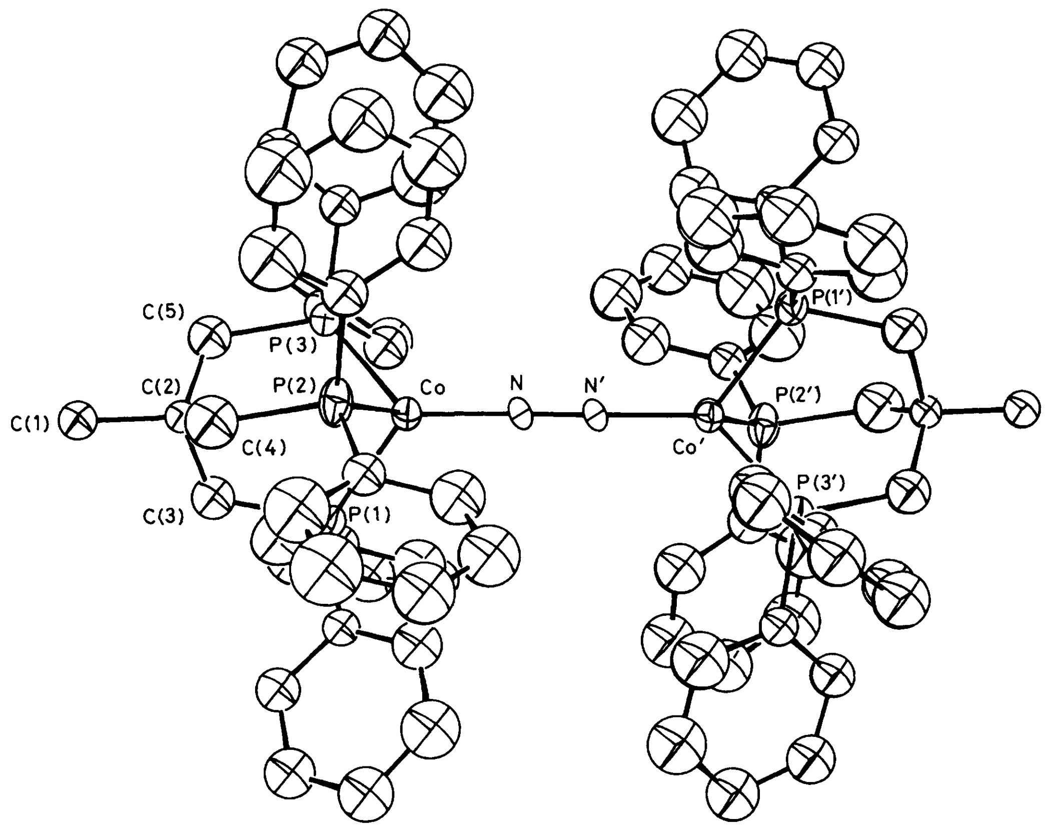

Figure 1. The molecular structure of {[(tppme)Co]$_2$(μ-N$_2$)}, (**1**). Ortep drawing with 30% probability ellipsoids. Selected bond distances and angles Co–P(1) 2.168(6), Co–P(2) 2.164(7), Co–P(3) 2.160(6), Co–N 1.76(1), N–N' 1.18(2) Å, Co–N–N' 170.6(15)°.

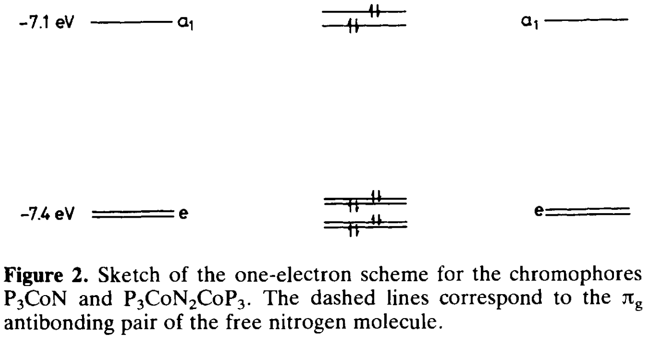

Figure 2. Sketch of the one-electron scheme for the chromophores P$_3$CoN and P$_3$CoN$_2$CoP$_3$. The dashed lines correspond to the π_g antibonding pair of the free nitrogen molecule.

were collected on a Philips PW 1100 automatic diffractometer, using the ω–2θ scan technique and graphite monochromated Mo-K_α radiation. The structure was solved by the heavy atom method and refined by full-matrix least-squares techniques. During the refinement the phenyl rings were treated as rigid bodies. The present R and R_w factors are 0.092 and 0.087 respectively, for 1377 observed reflections ($2\theta \leq 40°$) having $I \geq 3\sigma(I)$.‡

The binuclear molecule (see Figure 1) consists of two (tppme)Co entities held together by an end-on bridging dinitrogen ligand. The two halves of the molecule are related by a crystallographic centre of symmetry. Each cobalt atom displays a distorted tetrahedral geometry, being co-ordinated to the three phosphorus atoms of one tppme ligand and to one nitrogen atom of the bridging N$_2$ group. The distortion of the tetrahedron can be seen from the values of the P–Co–P angles (av. 93.3°), which are significantly smaller than the P–Co–N values (av. 122.7°).

The most interesting feature of the structure is the linear Co–N–N–Co array, the Co–N–N' angle being 170.6(15)°. The N–N bond distance [1.18(2) Å] corresponds well with the values found in other binuclear metal complexes containing a bridging dinitrogen ligand.[3] The value of 1.18(2) Å, compared with 1.095 Å reported for the free molecule[4] (triple bond) and with 1.23 Å found in azoethane[4] (double bond), clearly suggests a reduction of the bond order. The lengthening of the N–N distance is accompanied by a shortening of the Co–N bond [1.76(1) Å]. The latter value is significantly shorter than the sum of covalent radii and than the values reported in literature.[5] Comparable Co–N and N–N bond distances, 1.72 and 1.18 Å respectively, have been found for a heteronuclear

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

cobalt complex, containing bridging dinitrogen and phosphines as ligands.[6]

A qualitative description of the electronic structure of the title compound can be attempted using ligand field theory in its angular overlap version.[7] Assuming a C_{3v} symmetry for the chromophore P_3CoN and the mean values of the bond distances and angles resulting from the crystal structure, we have obtained the energy level scheme shown in Figure 2 for the 3d orbitals of the metal. The energies were roughly evaluated starting from the wave-functions and energies of the neutral atoms by using the Wolfsberg–Helmoltz approximation. The mixing between the two P_3CoN fragments and the introduction of the π_g ($D_{\infty h}$ notation) antibonding pair of the nitrogen molecule yield an electronic configuration (see Figure 2) with two unpaired electrons. The antibonding π_g pair of the nitrogen was set at about -7 eV, that is the value for the free molecule,[8] but slightly different values are possible, owing to the interaction with the metal orbitals. This fact could explain the lengthening of the N–N distance up to values expected for a double bond.

The above electronic structure provides a spin-triplet ground state, however a thermally accessible spin-quintet could also be possible, owing to the closeness of the low-lying excited levels. Indeed at the present stage of the investigation a triplet–quintet spin equilibrium seems more suitable to account for the magnetic moment[9] and its variation with temperature.

Reactivity experiments of (**1**) with small molecules such as CO, CO_2, SO_2, P_4, *etc.*, are in progress.

Received, 29th January 1985; Com. 138

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