Hetero-bimetallic Dinitrogen Activation: *X*-Ray Structure of the $(Me_3P)_3CoN_2AlMe_2$ Dimer

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Dinitrogen forms a push–pull stabilized double bond [125.2(6) pm] when one end is bound to an electron-rich cobalt complex and the other end is part of an N_2Al_2 ring in the $(Me_3P)_3CoN_2AlMe_2$ dimer, the structure of which has been found by *X*-ray crystallography.

When bridging two transition-metal atoms in a complex the dinitrogen ligand may have an elongated interatomic distance depending on the electronic properties of the two metal centres.[1,2] If these differ greatly in oxidation state as in $(PMe_2Ph)_4ClReN_2MoCl_4(OMe)$[3] electrons are shifted (from Re to Mo) in such a way as to shorten both of the metal to nitrogen bonds (Re–N 182, Mo–N 190 pm) and to lengthen the N–N bond (N–N 118 pm). A similar push-pull strain can be exerted on the dinitrogen molecule if it bridges an electron-rich transition-metal centre and an acceptor-type main-group substituent.

We have synthesized a novel dimeric bimetallic diazenido-(2−) complex in which both of the nitrogen atoms are bound to metal atoms only. The salt $KN_2Co(PMe_3)_3$[4] reacted in ether at −78 °C with a diorganoaluminium halide according to equation (1). From pentane solutions in the cold, dark brown crystals of (**1**) and (**2**) were obtained in 65 and 82% yields, respectively, whereas (**3**) remained as an oil.† All three compounds are diamagnetic and slowly decompose with loss of dinitrogen at 20 °C under argon. They are very sensitive to oxygen and moisture but otherwise fairly unreactive. At room

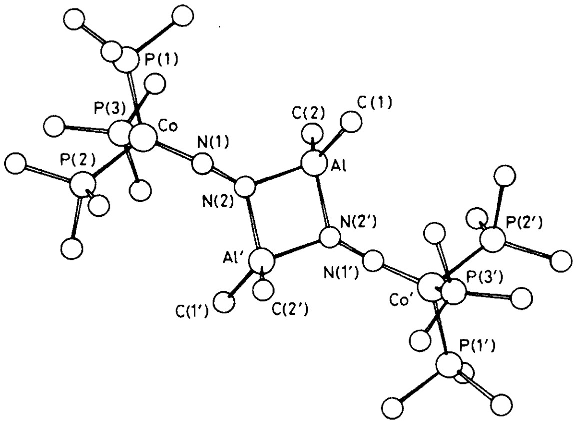

Figure 1. The crystal structure of (**1**). Some important dimensions: N(1)–N(2) 125.2(6); Al–N(2) 193.1(4) and 191.5(5); Co–N(1) 164.2(4); Co–P(av.) 216.9 pm; Co–N(1)–N(2) 171.5(4); N(1)–N(2)–Al 130.6(4) and 130.3(4); Al–N(2)–Al′ 98.3(2); N(2)–Al–N(2′) 81.7(2)°.

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† There are strong bands in the i.r. spectra (Nujol) which are probably due to N–N stretching vibrations at 1530, 1573, and 1553 cm^{-1} for (**1**), (**2**), and (**3**), respectively.

temperature (**1**) was neither carbonylated nor hydrogenated (1 bar CO or H_2 respectively) and there was no reaction with cyclopentadiene which would have been expected both for the cobalt centre and for the active dimethylaluminium group. The crystal structure of (**1**) was determined by *X*-ray diffraction (Figure 1).‡

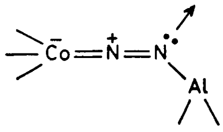
$$2\,(Me_3P)_3CoN_2K + 2\,ClAlR_2 \rightarrow [(Me_3P)_3CoN_2AlR_2]_2 + 2\,KCl \quad (1)$$

(**1**); R = Me
(**2**); R = Et
(**3**); R = CH_2Pr^i

Crystal data: $C_{22}H_{66}Al_2Co_2N_4P_6$, $M = 744.5$, orthorhombic, space group *Pbca*, $a = 1245.7(2)$, $b = 1949.4(2)$, $c = 1748.3(3)$ pm, $U = 4246 \times 10^6\ pm^3$, $Z = 8$, $D_c = 1.16\ g\ cm^{-3}$; graphite-monochromated Mo-K_α radiation, $\lambda = 71.069$ pm, μ (Mo-K_α) = 10.9 cm^{-1}. 3604 Independent reflections ($2 \leqslant 2\theta \leqslant 48°$) were measured of which 2264 with $F_o \geqslant 3.92\sigma(F_o)$ were used in the structure determination. Solution by the Patterson method and refinement of the structure gave *R* 0.052 and R_w 0.045.

The unit cell of (**1**) contains eight asymmetric units corresponding to four molecules $\{[(Me_3P)_3CoN_2AlMe_2]_2\}$. There is a centre of symmetry at the centre of the Al_2N_2 ring. The ring is almost square [Al–N 193.1(4) and 191.5(5) pm].

The cobalt centres are attached to this ring by dinitrogen bridges lying in the Al_2N_2 plane. There is only slight out-of-plane bending [the angle between the vector Co–N(2) and the Al_2N_2 plane is 14°] which suggests the bonding can be described by the simple valence bond formula (A).



(A)

Structure (A) is also consistent with a short cobalt to nitrogen bond [Co–N 164.2(4) pm] compared with that in $KN_2Co(PMe_3)_3$ (Co–N 170 pm)[4] and a formal N–N bond order of two [N–N 125.2(6) pm] which means that (**1**) is the first structurally characterized diazenido-bridged organoaluminium compound.[5] The strain in the Al_2N_2 ring in (**1**) (which contains sp^2 nitrogen atoms in its simple valence bond representation) must exceed that in the ring of $(Me_2AlNMe_2)_2$[6] (sp^3 nitrogen atoms) because it has very similar ring dimensions.

We thank the Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft for financial support of this work and Mr. J. Riede for help in collecting the *X*-ray data.

Received, 25th April 1983; Com. 501

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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 Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.