Synthesis, Molecular Structure, and Dynamic Behaviour in Solution of Octakis(t-butyl isocyanide)dicobalt

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Reduction of $[Co(CNBu^t)_5][PF_6]$ with potassium amalgam in tetrahydrofuran affords red air-sensitive crystals of octakis(t-butyl isocyanide)dicobalt. Crystals of $[Co_2(CNBu^t)_8]$ are orthorhombic, space group $P2_12_12$, with two molecules in a cell of dimensions a = 18.017(4), b = 12.149(4), and c = 11.382(5) Å. The structure has been solved by conventional techniques and refined by least squares to R 0.085 for 2 376 reflection intensities recorded on a four-circle diffractometer. The molecular geometry resembles that of $[Co_2(CO)_8]$, but is substantially distorted, especially with respect to one of the basal isocyanide functions. Non-bonded contacts calculated for an idealized molecular geometry strongly suggest the importance of intermolecular contacts in the adopted distortions. The cobalt–cobalt distance is 2.4567(20) Å. The ^{13}C n.m.r. spectrum of an enriched (10%) sample of $[Co_2(\textit{C}NBu^t)_8]$ shows one resonance at ambient temperature collapsing (coalescence temperature −60 °C) to three resonances (1 : 1 : 2) at −90 °C. Evidence is presented for an intramolecular exchange process. Reaction of $[Co_2(CNBu^t)_8]$ with CO, NO, and diphenylacetylene affords respectively $[Co(CNBu^t)_5][Co(CO)_4]$, $[Co(CNBu^t)_3(NO)]$, and $[Co_2\{\mu\text{-}(\eta^2\text{-}PhC_2Ph)\}(CNBu^t)_6]$.

In the one crystalline form of octacarbonyldicobalt known the molecule has a bridged carbonyl structure,[1] whereas, in order to interpret the variations in the solution i.r. spectrum of $[Co_2(CO)_8]$ with temperature, it has been postulated [2,3] that a non-bridged isomer is in equilibrium with the bridged isomer. It is thought likely that in solution the two tautomers interconvert rapidly. However, this has not been established with certainty, and variable-temperature ^{13}C n.m.r. measurements down to −90 °C show [4] only one signal. Substituted derivatives of $[Co_2(CO)_8]$ generally retain the structural type set by the octacarbonyl, but there are some exceptions; [5-7] $[Co_2(CO)_6(PBu_3)_2]$ adopts the D_{3h} structure, and other $[Co_2(CO)_6(PR_3)_2]$ structures are known which do not have bridging carbonyls. In view of these observations, attempts to prepare octakis(isocyanide)dicobalt complexes, and elucidate their structures, would be of interest. In addition, such an investigation would have considerable synthetic potential. Previous studies [8-10] have focused on the stepwise replacement of carbon monoxide from the octacarbonyl. In our approach to the problem, some aspects of which have been mentioned in a preliminary communication,[11] the direct reduction of cobalt(I) isocyanide complexes has been examined.

RESULTS AND DISCUSSION

Treatment (12 h) of pentakis(t-butyl isocyanide)cobalt hexafluorophosphate [12] with potassium amalgam† in tetrahydrofuran (thf) solution at room temperature (r.t.) led to the formation of an orange-brown solution. Removal of the solvent and extraction with hexane, gave, on cooling (−78 °C), orange-red air-sensitive crystals of octakis(t-butyl isocyanide)cobalt. Examination of the i.r. spectrum showed the presence of both bridging and terminal isocyanide stretching frequencies; however, the terminal bands were rather featureless envelopes, of little value in establishing structural identity. The n.m.r. spectra (^1H and normal-abundance ^{13}C) did not establish the structure in the liquid phase, although the temperature dependence of the ^1H spectrum suggested the possible occurrence of a dynamic process in solution. Attempts to obtain satisfactory molecular-weight measurements in solution or to observe a parent ion in the mass spectrum were unsuccessful. However, a suitable crystal for X-ray diffraction studies was obtained, and therefore such a study was undertaken. The molecular geometry of the complex is given in Figure 1, viewed along the crystallographic two-fold axis which bisects the metal–metal bond. Terminal methyl groups have been omitted from this Figure for the sake of clarity, but are included in the packing diagram (Figure 2), which is drawn in the same direction. Internuclear distances (uncorrected for thermal effects) and interbond angles are listed in Table 1 and 2 respectively.

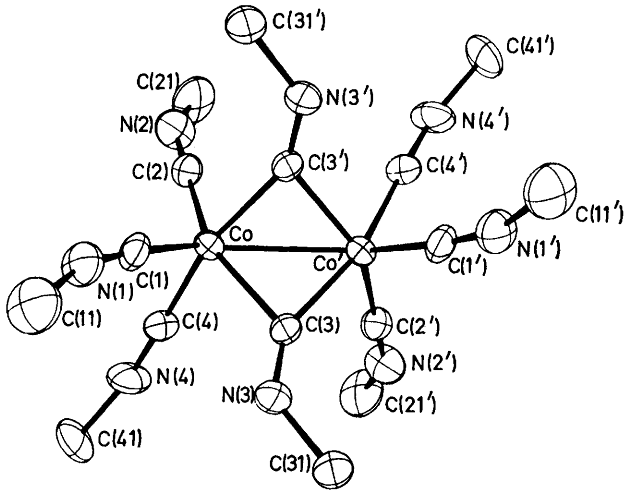

FIGURE 1 Geometry and numbering for the central portion of the complex $[Co_2(CNBu^t)_8]$. Thermal ellipsoids are constructed at the 30% electron-probability level

The central framework of the complex is isoelectronic and essentially isostructural [1] with octacarbonyldicobalt.

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† Reduction with sodium amalgam or C_8K also gives $[Co_2(CNBu^t)_8]$, but in less satisfactory yield. The presence of an excess of t-butyl isocyanide suppressed reduction.

The cobalt geometry (ignoring, for the moment, the metal–metal bond) may be described as square-based pyramidal with the basal plane comprising two bridging, C(3) and C(3′), and two terminal, C(2) and C(4), isocyanide functions, the remaining (axial) ligand, C(1)-NBu^t, lying effectively perpendicular to this plane. The two metal co-ordination spheres are linked across the C(3)–C(3′) edge, with a dihedral angle between their basal planes of *ca.* 96°.

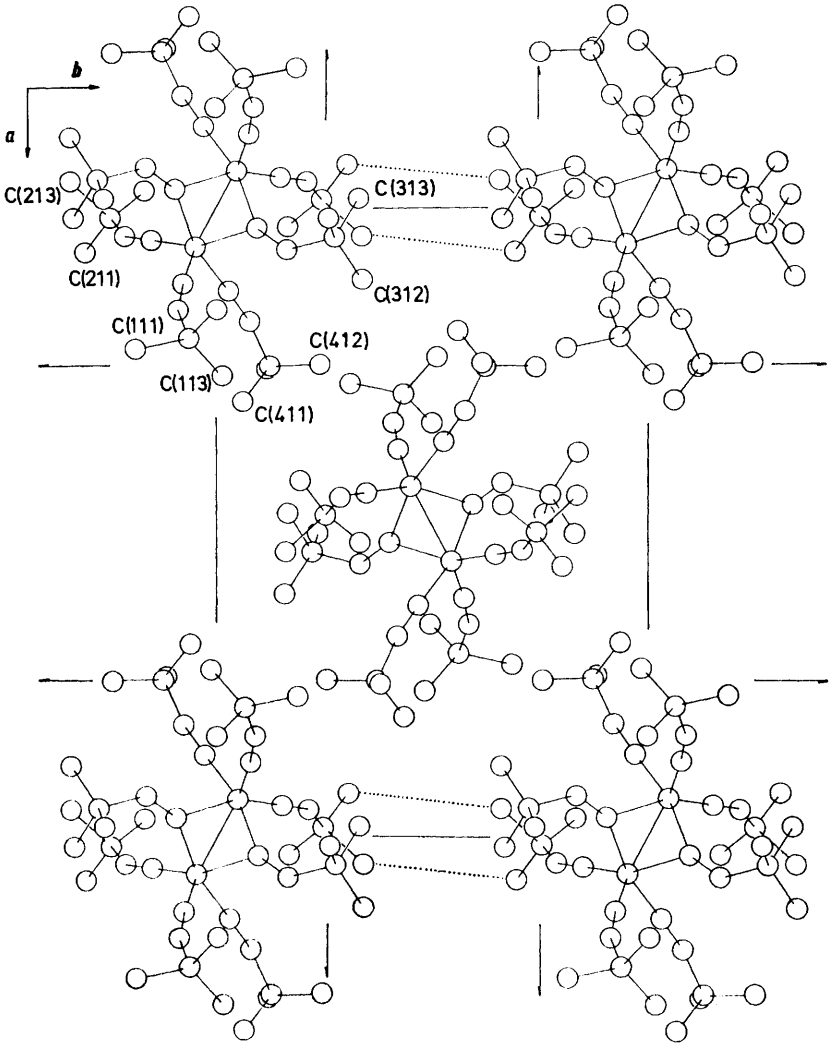


FIGURE 2 Molecular packing diagram for [$Co_2(CNBu^t)_8$] projected onto the *ab* plane. Only the minimum symmetry elements required to define the array completely are shown

In [$Co_2(CNBu^t)_8$] the basal ' plane ' is, in fact, distinctly buckled. A least-squares fit of the atomic coordinates of atoms C(3), C(3′), C(2), and C(4) produces a plane, defined by the equation $11.130x - 4.936y + 7.663z = 1.328$ Å, from which these atoms deviate by −0.13, +0.13, −0.12, and +0.12 Å respectively. We will subsequently produce evidence to suggest that a deviation of C(2) from the ' true ' basal plane is responsible for this distortion, and accordingly the term ' basal plane ' hereafter refers only to the three-atom sequence C(3)–C(3′)–C(4). With respect to this new standard, C(2) is *ca.* 0.50 Å below, and Co *ca.* 0.24 Å above, the plane, where ' above ' defines the position of the axial ligand C(1)NBu^t.

Cobalt–carbon (terminal) distances are 1.842 (14), 1.856 (14), and 1.813 (15) Å, to C(2), C(4), and C(1) respectively. In general these are typical of values previously recorded [13] for Co–CNR linkages, in which substantial multiple-bond character (through metal→ligand back bonding) is postulated. In the complexes [$Co(CNC_6H_5)_5$]$^+$ and [$Co(CNC_6H_5)_5$]$^{2+}$,[13] the square-based pyramidal geometry of the present molecule is also found, but an important difference between these cations and [$Co_2(CNBu^t)_8$] is the relative lengths of basal and axial Co–C bonds; in [$Co(CNC_6H_5)_5$]$^+$ and [$Co(CNC_6H_5)_5$]$^{2+}$ the axial is longer than the basal mean by *ca.* 0.05 and 0.11 Å respectively, but in [$Co_2(CNBu^t)_8$] the reverse is true, the average difference here being 0.036 Å, although the high associated errors (±0.010 Å on the equatorial lengths and ±0.014 Å on the axial length) render this difference barely significant.

TABLE 1

Interatomic distances (Å) with estimated standard deviations in parentheses

Co–Co′	2.456 7(20)	C(3)–N(3)	1.209(16)
Co–C(1)	1.813(15)	N(3)–C(31)	1.465(18)
Co–C(2)	1.842(14)	C(31)–C(311)	1.48(4)
Co–C(3)	1.975(11)	C(31)–C(312)	1.52(3)
Co–C(4)	1.856(14)	C(31)–C(313)	1.55(3)
Co–C(3′)	1.930(11)		
		C(4)–N(4)	1.153(19)
C(1)–N(1)	1.153(20)	N(4)–C(41)	1.449(22)
N(1)–C(11)	1.436(26)	C(41)–C(411)	1.47(3)
C(11)–C(111)	1.59(6)	C(41)–C(412)	1.45(4)
C(11)–C(112)	1.58(6)	C(41)–C(413)	1.57(4)
C(11)–C(113)	1.51(7)		
C(2)–N(2)	1.169(20)		
N(2)–C(21)	1.433(27)		
C(21)–C(211)	1.45(5)		
C(21)–C(212)	1.45(4)		
C(21)–C(213)	1.60(5)		

The shortest distance between metal atoms in $[Co_2(CNBu^t)_8]$ is 2.456 7(20) Å, not untypical of the lengths usually found in cobalt cluster compounds,[14] but considerably (*ca.* 0.3 Å) shorter than the (non-bridged) distances observed in $[Co_2(CNMe)_{10}]^{4+}$ (ref. 13) and $[Co_2(CN)_{10}]^{6-}$ (ref. 15). In $[Co_2(CNBu^t)_8]$ the Co–Co linkage is also *ca.* 0.07 Å shorter than that in $[Co_2(CO)_8]$, 2.524(2) Å. Table 3 compares average bond lengths and molecular geometries for these two complexes, and demonstrates that reduction in the Co–Co bond length from $[Co_2(CO)_8]$ to $[Co_2(CNBu^t)_8]$ is accompanied by an increase in Co–ligand distances. These trends may be readily attributed to the relative π-acceptor properties of carbonyl and isocyanide ligands,[16,17] the former being the better π acceptor and the latter the better σ donor. Naturally, an increased participation in $Co \rightarrow \pi^*(L)$ back donation leads to a reduction in the strength of the metal–metal bond for the change L = CNBu^t to L = CO.

The major differences in molecular geometry (Table 3) observed in going from the carbonyl to the isocyanide complex may be summarised as (*i*) an increased folding of the basal planes, (*ii*) an increase in the dihedral angle between bridge planes, and (*iii*) a decrease in the dihedral angle between bridge plane and axial vector. All these trends are mutually compatible, and are probably a simple consequence of a shortening of the metal–metal distance.

TABLE 2

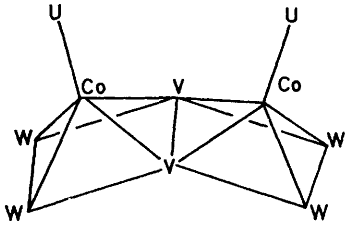
Bond angles (°)

Co′–Co–C(1)	128.9(5)	Co–C(2)–N(2)	176.5(13)
Co′–Co–C(2)	102.9(4)	C(2)–N(2)–C(21)	154.6(17)
Co′–Co–C(3)	50.2(3)	N(2)–C(21)–C(211)	109.4(23)
Co′–Co–C(4)	112.1(4)	N(2)–C(21)–C(212)	113.1(22)
Co′–Co–C(3′)	51.8(3)	N(2)–C(21)–C(213)	102.9(22)
C(1)–Co–C(2)	118.9(6)	C(211)–C(21)–C(212)	121.9(27)
C(1)–Co–C(3)	91.8(5)	C(211)–C(21)–C(213)	101.1(27)
C(1)–Co–C(4)	95.4(6)	C(212)–C(21)–C(213)	105.9(27)
C(1)–Co–C(3′)	98.3(6)		
C(2)–Co–C(3)	149.2(5)	Co–C(3)–Co′	78.0(4)
C(2)–Co–C(4)	91.8(6)	Co–C(3)–N(3)	132.1(9)
C(2)–Co–C(3′)	89.3(5)	Co′–C(3)–N(3)	150.0(10)
C(3)–Co–C(4)	87.1(5)	C(3)–N(3)–C(31)	131.2(12)
C(3)–Co–C(3′)	83.7(5)	N(3)–C(31)–C(311)	106.7(17)
C(4)–Co–C(3′)	163.6(5)	N(3)–C(31)–C(312)	107.2(15)
		N(3)–C(31)–C(313)	114.1(16)
Co–C(1)–N(1)	175.2(13)	C(311)–C(31)–C(312)	102.9(20)
C(1)–N(1)–C(11)	160.5(16)	C(311)–C(31)–C(313)	108.5(19)
N(1)–C(11)–C(111)	104.5(23)	C(312)–C(31)–C(313)	116.5(18)
N(1)–C(11)–C(112)	107.6(23)		
N(1)–C(11)–C(113)	110.2(29)	Co–C(4)–N(4)	174.5(14)
C(111)–C(11)–C(112)	110.6(29)	C(4)–N(4)–C(41)	164.1(17)
C(111)–C(11)–C(113)	118.8(33)	N(4)–C(41)–C(411)	110.8(18)
C(112)–C(11)–C(113)	104.8(33)	N(4)–C(41)–C(412)	108.8(18)
		N(4)–C(41)–C(413)	104.6(18)
		C(411)–C(41)–C(412)	116.3(21)
		C(411)–C(41)–C(413)	107.9(20)
		C(412)–C(41)–C(413)	107.7(22)

The distances from cobalt to the bridge atom in $[Co_2(CNBu^t)_8]$ differ by 0.045 Å (*ca.* 4σ) with the longer bond lying *anti* to the alkyl group. This is in direct contrast to the corresponding distortions noted by Cotton and co-workers[18] for $[(\eta\text{-}C_5H_5)Ni(\mu\text{-}CNMe)_2Ni(\eta\text{-}C_5H_5)]$, a complex with a relevance to the present one since $Ni(\eta\text{-}C_5H_5)$ and $Co(CNR)_3$ fragments are almost certainly isolobal,[19] and for $[(\eta\text{-}C_5H_5)(OC)Fe(\mu\text{-}CNMe)_2Fe(CO)(\eta\text{-}C_5H_5)]$,[20] although in $[Pt_3(CNBu^t)_6]$[21] the bridging isocyanide ligands are more symmetrically bonded. In the CNMe complexes the observed asymmetries are probably a result of intramolecular steric congestion; indeed, it has been noted[20] that replacement of Me by Bu^t in a model of the iron complex severely increases intramolecular contacts. For $[Co_2(CNBu^t)_8]$ it is tempting to assume that a similar feature occurs, since Figure 1 would tend to suggest crowding between the methyl of C(31′), C(11), and C(21). This

TABLE 3

Comparison of average molecular geometries and average bond lengths (Å) for $[Co_2(CNBu^t)_8]$ and $[Co_2(CO)_8]$



	$[Co_2(CNBu^t)_8]$ [a]	$[Co_2(CO)_8]$ [b]
Co–W	1.849	1.804
Co–U	1.813	1.783
Co–V	1.953	1.921
Co–Co	2.457	2.524
σ Basal plane [c,d] (Å)	*e*	0.07
Co displacement from basal plane (Å)	0.24	0.32
Basal plane–basal plane angle (°)	96.3	100.2
Basal plane–axial vector angle [f] (°)	84.6	83.9
Bridge plane	Co–Co–CNBu^t	Co–Co–CO
σ Bridge plane [c] (Å)	0.02	0.01
Basal plane–bridge plane angle (°)	60.0	46.7
Axial vector–bridge plane angle (°)	37.7	42.0
Bridge plane–bridge plane angle (°)	119.8	127.5

[a] Precise C_2 symmetry about the Co–Co bond. [b] Average of two independent molecules per asymmetric unit. Each has required C_s symmetry, perpendicular to the Co–Co vector, although the overall geometry is close to C_{2v}. [c] The σ of a plane refers to the estimated standard deviation of the defining atoms from that plane. [d] Basal plane is VVWW. [e] Three-atom sequence C(3)C(3′)C(4) see text. [f] Axial vector Co–U.

assumption is apparently reinforced by the observation that the Co–C(3′)–N(3′) angle, 150.0 (10)°, is considerably wider than Co′–C(3′)–N(3′), 132.1(9)°. However, the asymmetry of the Co–C(3) and Co–C(3′) bonds is in the ' wrong ' direction, and, perhaps more to the point, no short intramolecular contacts between these methyl groups actually occur. Furthermore, one might have expected the C(3)–N(3)–C(31) angle to widen under such conditions, but at 131.2 (12)° it lies well within the range now established for bridging isocyanides.[18–22]

The question of interligand contacts in [Co$_2$(CNBu^t)$_8$] is also an important one with respect to the non-linearity of the terminal isocyanide chains. Although the three independent Co–C–N angles are all reasonably close to 180°, angles at nitrogen range from 164.1 to 154.6°, the most severe distortion occurring at N(2). We recall here that atom C(2) was omitted from our definition of the ' true ' basal plane. Our reason derives from examination of the C(1)–Co–C angles (Table 2). For C(3), C(3′), and C(4) these range from 91.8 (5) to 98.3 (6)°, but for C(2) the value is 118.9 (6)°, suggesting a somewhat special environment for the C(2)NBu^t ligand.*

Bending at the nitrogen atom in terminally bound isocyanides can either be attributed to steric factors or to an unequal population of the π^* C≡N levels, degenerate in the free ligand, this latter feature appearing to dominate in the equatorial functions of the complex [Ru(CNBu^t)$_4$(PPh$_3$)].[11,23]

In an attempt to determine the relative importance of steric and electronic factors in [Co$_2$(CNBu^t)$_8$] we have calculated the interligand contacts for an idealized molecule in the same crystal environment. These values, and a comparison of the important Bu^t · · · Bu^t contacts in both distorted and undistorted molecular models, are contained in Supplementary Publication No. SUP 22634 (21 pp.).† A complete analysis of these data will be given elsewhere; the important conclusion is that the substantial bendings at nitrogen observed in the terminal isocyanide functions of [Co$_2$(CNBu^t)$_8$] may be accounted for by steric factors alone. t-Butyl isocyanide is recognised as a bulky intramolecular ligand. Our analysis highlights that, in fact, *inter*molecular contacts are almost certainly the more important for this particular crystalline arrangement.

With the establishment of the solid-state structure of [Co$_2$(CNBu^t)$_8$] it was possible to examine further the question of structure in solution. As previously mentioned the natural-abundance ^{13}C n.m.r. spectrum at ambient temperature shows only two signals at 54.85 and 31.5 p.p.m. which are assigned to the quaternary and methyl carbons of the t-butyl groups respectively. On cooling to −90 °C in [^{2}H$_8$]toluene both signals broaden somewhat, but could not be separately resolved. A sample enriched with ^{13}C in the isocyanide groups (*C*NBu^t) (*ca.* 10%) ‡ was therefore prepared and showed a strong signal at 191.4 p.p.m., which at −90 °C ([^{2}H$_8$]-toluene) was split into three signals (intensity ratio *ca.* 1 : 1 : 2) at 229.0, 182.0, and 177.7 p.p.m. (average 191.6 p.p.m.). This is in agreement with the structure of [Co$_2$(CNBu^t)$_8$] in solution being the same as established in the solid state (bridging isocyanides), there being three distinct isocyanide environments. The signal at 229.0 p.p.m. corresponds to the bridging environment, *i.e.* C(3) and C(3′) in Figure 1, that at 182.0 p.p.m. to terminally bonded C(1) and C(1′), and that at 177.7 p.p.m. to C(2), C(2′), C(4), and C(4′). The apparent equivalence of the terminally bonded isocyanide carbon environments C(2), C(2′), C(4), and C(4′) suggests that rapid inversion at the nitrogen § atoms of the bridging isocyanides occurs, resulting in the averaging of the pairs C(2) and C(4′), and C(2′) and C(4). A similar inversion process was observed [21] with the platinum system [Pt$_3$(CNBu^t)$_6$].

In order to throw light on the exchange process a small amount of unlabelled, free, t-butyl isocyanide was added to the ^{13}C n.m.r. sample, and the spectrum rerun at ambient temperature. This showed separate signals for the complexed exchanging isocyanide (at 191.4 p.p.m.), and for unco-ordinated t-butyl isocyanide (at 156.4 p.p.m.). The intensity of the latter signal showed that some free, labelled, t-butyl isocyanide was present, having been formed by a slow intermolecular exchange with complexed ligand, but the observation of the two separate signals indicates that this process is slow on the n.m.r. time scale, so that the process responsible for the observed exchange between the three different CNBu^t sites must be intramolecular. From the estimated coalescence temperature for this exchange process (−60 °C, [^{2}H$_8$]toluene), an approximate value for the activation energy of 40.2 kJ mol^{-1} can be calculated.

It is interesting that within the limitations of the ^{13}C n.m.r. experiment there is no evidence for the presence in solution of the tautomer without bridging isocyanide ligands. This is in striking contrast to the [Co$_2$(CO)$_8$] system.[2,3] However, such a species could be traversed in the exchange process. Studies by Adams and Cotton [24] have shown that isocyanide ligands can pass rapidly between terminal and bridging positions and, in this way, from one metal atom to another. Thus the most plausible mechanism for the exchange process, illustrated in Scheme 1, would involve a two-for-two synchronous bridge opening and closing. Clearly, in addition, rotation about a Co–Co bond, and pairwise exchange of axial and equatorial sites in the presumed metal–metal bonded trigonal-bipyramidal structures are also possible. However, since this intermediate is

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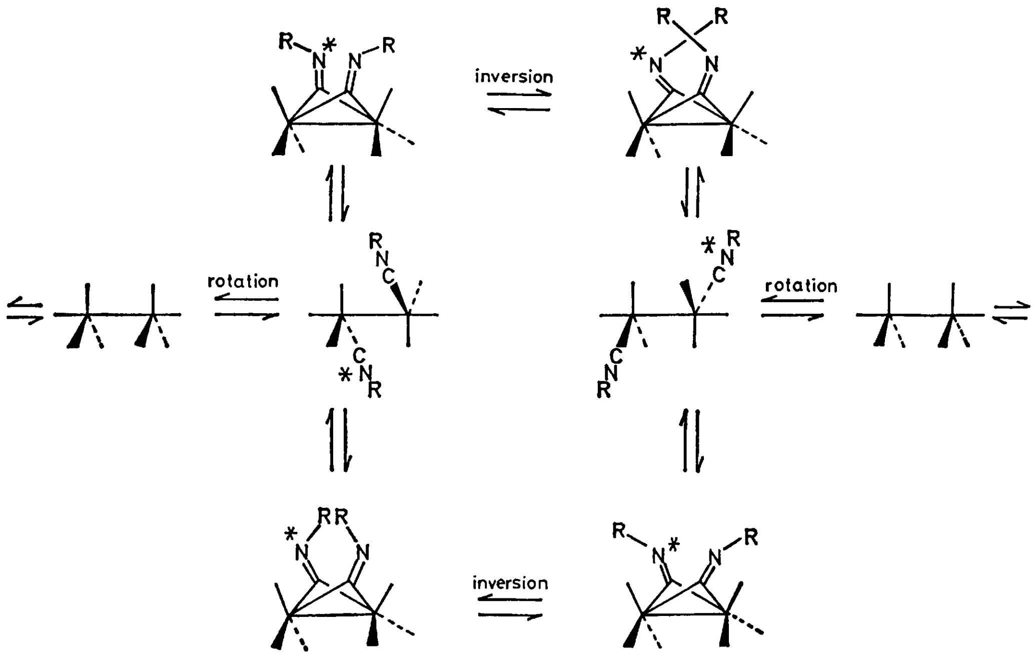
* We recognise that the lack of good overall planarity of the C(2)–C(3)–C(3′)–C(4) group could equally be described in terms of any of the latter three atoms residing ' out-of-plane.' In such a situation additional distortion of the apical [C(1)] ligand would be necessary to render the C(1)–Co–C(3,3′,4) angles effectively equivalent; however, our analysis of intra- and intermolecular contacts provides no indication that this may be the case.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

‡ Prepared by reduction (potassium amalgam) of enriched [Co(CNBu^t)$_5$][PF$_6$].

§ There was no evidence for the formation of the presumably less stable *syn* isomer.



SCHEME 1 Ligands and cobalt atoms omitted for clarity

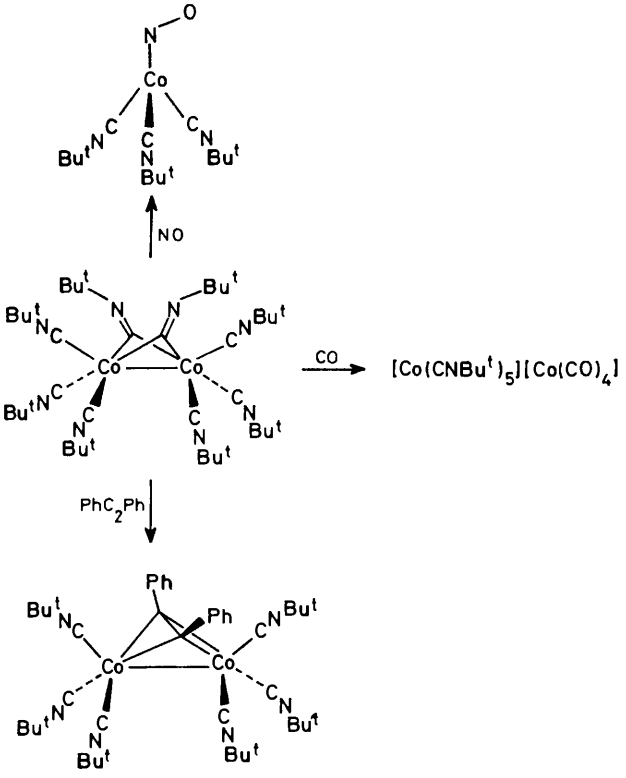
of higher energy than the bridged tautomer, and was not observed, this aspect of the exchange manifold can only be surmised. It is also not possible to say, on the basis of the data available, which conformer of the non-bridged species is the immediate precursor of the bridged tautomers.

Finally, a brief preliminary study has been made of the chemical reactions of octakis(t-butyl isocyanide)dicobalt with carbon monoxide, nitric oxide (NO), and diphenylacetylene. As illustrated in Scheme 2, reactions similar to those observed with the octacarbonyl compound occur. Carbon monoxide rapidly reacts leading to a disproportionation reaction, and the formation of the ionic complex pentakis(t-butyl isocyanide)cobalt tetracarbonylcobaltate, characterized by elemental analysis and by the occurrence in the i.r. spectrum of bands typical of a cobalt(I) isocyanide complex and of the anionic species $[Co(CO)_4]^-$. Nitric oxide forms the air-stable red crystalline nitrosyltris(t-butyl isocyanide)-cobalt, and diphenylacetylene rapidly reacts to form the black crystalline complex μ-(η^2-diphenylacetylene)-hexakis(t-butyl isocyanide)dicobalt, presumably isostructural with the hexacarbonyl analogue. Further aspects of the chemistry of these and related complexes will be reported in a subsequent paper.

EXPERIMENTAL

Hydrogen-1 and ^{13}C n.m.r. spectra were recorded using JEOL PS-100 and PFT-100 spectrometers, respectively. Carbon chemical shifts are relative to tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 457 spectrophotometer. Mass spectra were recorded on an A.E.I. MS902 spectrometer operating at 70 eV.* Reactions were carried out in Schlenk tubes under a dry oxygen-free nitrogen atmosphere.

Synthesis of Octakis(t-butyl isocyanide)dicobalt.—A solution of pentakis(t-butyl isocyanide)cobalt hexafluorophosphate (2.00 g, 3.2 mmol) in dry peroxide-free thf (100 cm^3) was stirred (r.t.) with an excess of potassium



SCHEME 2

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[*] Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J; 1 mmHg ≈ 13.6 × 9.8 Pa; 1 atm = 101 325 Pa.

amalgam (5%) for 12 h. The orange-brown solution was decanted and evaporated to dryness *in vacuo*, then extracted with n-hexane (150 cm^3). The volume of the solvent was reduced to 50 cm^3, and on cooling (−78 °C) orange-red prisms slowly formed. These were recrystallized (−78 °C) from the minimum volume of n-pentane to give orange-red *needles* $[Co_2(CNBu^t)_8]$ (0.61 g, 49%), m.p. 140 °C (Found: C, 61.5; H, 9.0; N, 13.8. $C_{40}H_{72}Co_2N_8$ requires C, 61.4; H, 9.3; N, 14.3%), $\nu_{max.}$ (Nujol) at 2 100s (sh), 2 010s (br), 1 680m (sh), and 1 668s cm^{-1}. N.m.r.: ^1H ($[^2H_8]$toluene, r.t.), τ 8.59(s); $[^2H_8]$toluene, −90 °C), overlapping signals at τ 8.3, 8.6, and 9.0 (1 : 2 : 1); ^{13}C ($[^2H_8]$toluene, r.t.), 31.45 (CNC*Me*$_3$) and 54.85 p.p.m. (CNCMe$_3$), slight broadening at −90 °C.

Reactions of Octakis(t-butyl isocyanide)dicobalt.—(a) *With carbon monoxide.* A solution of $[Co_2(CNBu^t)_8]$ (0.50 g, 0.64 mmol) in hexane (20 cm^3) was stirred (r.t.) under an excess (1 atm) of carbon monoxide for 1 h. The resulting yellow precipitate was collected and recrystallized (−78 °C) from a mixture of diethyl ether and hexane to give yellow air-stable *crystals* of $[Co(CNBu^t)_5][Co(CO)_4]$ (70%)(Found: C, 52.8; H, 6.7; N, 9.9. $C_{29}H_{45}Co_2N_5O_4$ requires C, 53.2; H, 6.9; N, 10.2%), $\nu_{max.}$ (Nujol) at 2 059m, 2 018m (NC), and 1 873s (CO) cm^{-1}.

(b) *With nitric oxide.* A solution of $[Co_2(CNBu^t)_8]$ (0.50 g, 0.64 mmol) in thf (30 cm^3) was stirred under an atmosphere of nitric oxide (200 mmHg) for 10 min at room temperature. Volatile material was removed *in vacuo*, and the residue dissolved in hexane (20 cm^3). The resulting solution was filtered and cooled (−78 °C) to give red air-stable *crystals* of $[Co(CNBu^t)_3(NO)]$ (0.21 g, 49%), m.p. (decomp.) 107 °C (Found: C, 53.5; H, 8.0; N, 16.3. $C_{15}H_{27}CoN_4O$ requires C, 53.2; H, 8.1; N, 16.5%), $\nu_{max.}$ (hexane) at 2 137m, 2 101m, 2 054s (NC), and 1 704s (NO) cm^{-1}. N.m.r.: ^1H (C_6D_6, r.t.), τ 8.85.

(c) *With diphenylacetylene.* A solution of $[Co_2(CNBu^t)_8]$ (0.42 g, 0.54 mmol) in hexane (50 cm^3) was cooled (−30 °C) and diphenylacetylene (0.14 g, 0.79 mmol) added. The reaction mixture was stirred (15 min) and allowed to warm to room temperature. The resulting solution was filtered and cooled (−78 °C) to give crystalline material, which was recrystallized (−78 °C) from pentane to give black *prisms* of $[Co_2\{\mu\text{-}(\eta^2\text{-}PhC_2Ph)\}(CNBu^t)_6]$ (0.14 g, 33%), m.p. 155 °C (decomp.) (Found: C, 66.5; H, 8.4; N, 10.1. $C_{44}H_{64}Co_2N_6$ requires C, 66.5; H, 8.2; N, 10.6%), $\nu_{max.}$ (Nujol) at 2 100(sh), 2 021s (sh) (NC) and 1 599m (C≡C). N.m.r.: ^1H (C_6D_6, r.t.), τ 2.0—3.2 (m, 10 H, C_6H_5) and 9.08 (s, 54 H, Bu^t).

Crystal-structure Determination.—Crystals of octakis(t-butyl isocyanide)dicobalt, prepared as above, are obtained as small, well formed needles elongated along |001|. A single crystal, *ca.* 0.03 (*c*) × 0.01 (*a*) × 0.01 cm (*b*) was mounted in a 0.5 mm Lindemann capillary under an atmosphere of dry nitrogen and used throughout this experiment. Weissenberg and precession photographs (Cu-K_α *X*-radiation) yielded approximate cell dimensions, and unambiguously defined the non-centrosymmetric orthorhombic space group $P2_12_12$.

On transference to a Syntex $P2_1$ four-circle autodiffractometer [25] 15 reflections, $13 < 2\theta < 22°$ (Mo-K_α), were taken from a 30 min rotation photograph and were accurately centred in 2θ, ω, and χ. The unit cell was chosen by inspection of the real-space vectors generated thereafter. Using graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha1}$ 0.709 26, $\lambda_{\alpha2}$ 0.713 54 Å) one octant of the diffraction sphere between θ 1.45 and 30.0° was collected at 298 ± 1 K. Peaks were scanned (θ—2θ in 96 steps) from 1.0 below $K_{\alpha1}$ to 1.0 above $K_{\alpha2}$ at rates between 0.033 7 and 0.483 3 °s^{-1}, the precise speed determined by an initial 2 s peak count in which 150 and 1 500 counts were used as minimum and maximum thresholds respectively. Regular remeasurement of the beams diffracted by the (9 1 0), $(4\;3\;\bar{2})$, and (0 4 2) planes subsequently revealed [26] that no significant crystal decomposition or movement, or machine variance, had occurred over the *ca.* 131 h *X*-ray exposure. Of a total of 4 079 reflections measured, 2 732 (*ca.* 67%) were retained ($I > 1.0\sigma$) for structure solution and refinement. No correction for *X*-ray absorption was made.

Crystal data. $C_{40}H_{72}Co_2N_8$, M = 782.94, Orthorhombic, a = 18.017(4), b = 12.149(4), c = 11.382(5) Å, U = 2 491.4(17) Å^3, D_m not measured, Z = 2 (C_2 symmetry imposed), D_c = 1.044 g cm^{-3}, $F(000)$ = 844, μ(Mo-K_α) = 7.3 cm^{-1}, space group $P2_12_12$ (D_2^3, no. 18) from systematic absences.

TABLE 4

Final positional parameters (fractional co-ordinates; ×10^5 Co; ×10^4 C, N)

Atom	*x*	*y*	*z*
Co	6 053(8)	−4 654(12)	10 478(14)
C(1)	1 213(8)	−764(10)	2 276(13)
N(1)	1 621(8)	−880(11)	3 047(13)
C(11)	2 047(12)	−652(18)	4 086(20)
C(111)	2 220(27)	−1 833(42)	4 630(44)
C(112)	1 541(28)	39(43)	4 941(46)
C(113)	2 689(35)	102(53)	3 794(57)
C(2)	500(7)	−1 502(11)	−121(12)
N(2)	434(7)	−2 115(12)	−905(12)
C(21)	155(13)	−2 466(19)	−2 023(21)
C(211)	716(24)	−3 113(32)	−2 619(36)
C(212)	−265(20)	−1 622(30)	−2 622(33)
C(213)	−433(27)	−3 403(38)	−1 674(41)
C(3)	315(6)	965(9)	1 733(11)
N(3)	661(7)	1 650(8)	2 273(10)
C(31)	446(8)	2 738(12)	2 713(15)
C(311)	175(17)	2 576(28)	3 928(34)
C(312)	1 157(17)	3 395(24)	2 889(26)
C(313)	−175(16)	3 302(24)	1 990(26)
C(4)	1 310(7)	301(11)	185(13)
N(4)	1 786(7)	767(11)	−275(14)
C(41)	2 498(9)	1 247(16)	−572(21)
C(411)	3 108(14)	621(22)	−31(23)
C(412)	2 474(18)	2 419(27)	−315(28)
C(413)	2 560(19)	1 111(28)	−1 944(30)

Retained data were corrected for Lorentz and polarization effects. Inspection of the Patterson map quickly yielded the position (4 *c* 1) of the single cobalt atom per asymmetric unit. Thereafter, all non-hydrogen atoms were located from a difference electron-density synthesis computed with the (isotropically refined) cobalt contribution. F_o moduli were weighted such that $w = (xy)^{-1}$ with $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta > b$, and $y = F_o/a$ if $F_o > a$, $y = 1$ if $F_o < a$, in which a and b took values of 29.0 and 0.29 respectively.

Metal atoms and atoms of the inner C–N–C spines of the ligands were each allowed anisotropic thermal motion. The criterion by which a reflection was deemed ' observed ' was then slightly modified so as to include all data (1 858) for which $I > 2.5\sigma$, together with those (518) relections for which $1.0\sigma < I < 2.5\sigma$ and $|F_c| > F_o$. Full-matrix least-squares refinement (166 variables including *F* scale factor, 2 376 contributing reflections) converged at *R* 0.085, *R'* 0.112. A final Δ*F* synthesis revealed no residue significantly above the relatively high background noise that is the consequence of a low $I:\sigma$ ratio. Attempts to locate the methyl hydrogens [using a $(\sin\theta)/\lambda$ maximum of 0.5] failed (or were, at best, ambiguous), presumably as a result of the comparatively large thermal amplitudes adopted by the terminal carbon atoms.

A parallel refinement with all atomic co-ordinates reflected in the *xy* plane yielded significantly higher *R* values and increased atomic standard deviations. Thus, the absolute configuration *of the particular crystal used in the analysis* is defined, and corresponds to the atomic co-ordinates of Table 4. Thermal parameters and the structure factors are given in SUP 22634. Atomic scattering factors were taken from ref. 27 for cobalt and ref. 28 for carbon and nitrogen, all sets being appropriately corrected [29] for the effects of anomalous dispersion. Except for preliminary data treatment, all calculations employed programs of the '*X*-Ray '72' crystallographic package,[30] implemented on the University of London Computer Centre CDC 7600 machine. Figure 1 was constructed using Johnson's ORTEP.[31]

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