Halogenation Reactions of Electron-rich Diphosphazane Ligand-bridged Derivatives of Dicobalt Octacarbonyl: Crystal Structures of [Co₂(μ-I)-(μ-CO)(CO)₂{μ-(MeO)₂PN(Et)P(OMe)₂}₂]BPh₄ and [Co(CO)₂{P(OMe)₃}₂-{(MeO)₂PN(Et)P(OMe)₂-xP}]BPh₄†

Neil J. Bailey, John S. Field,* Raymond J. Haines, and Lesley A. Rix
Unit of Metal Cluster Chemistry, Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg 3200, South Africa

Halogenation of $[Co_2(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) by I_2, Br$_2$, or freshly distilled CCl_4 affords the cations $[Co_2(\mu-X)(\mu-CO)(CO)_2\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^+$ (X = I, Br, or Cl respectively). A single-crystal X-ray diffraction study on $[Co_2(\mu-I)(\mu-CO)(CO)_2\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4$ confirms that these cations have A-frame structures with a neutral ligand, CO, occupying a bridging site additional to the bridging halogen atom. For R = Me (only) the cations slowly undergo a Michaelis–Arbusov type rearrangement initiated by attack of halide ions at a co-ordinated phosphorus atom, to give the neutral complexes $[Co_2(\mu-X)(\mu-CO)(CO)_2-\{\mu-(MeO)_2PN(Et)P(OMe)_2\}\{\mu-(MeO)_2PN(Et)P(O)(OMe)\}]$. The latter could not be isolated but $[Co_2(\mu-I)(\mu-CO)(CO)_2\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}\{\mu-(Pr^iO)_2PN(Et)P(O)(OPr^i)\}]$ is readily isolated from the reaction of $[Co_2(\mu-I)(\mu-CO)(CO)_2\{\mu-(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]^+$ with hydride ions. When undistilled (Analar grade) rather than freshly distilled CCl_4 is used to chlorinate $[Co_2(CO)_4-\{\mu-(MeO)_2PN(Et)P(OMe)_2\}_2]$ an unexpected product, *viz.* $[Co(CO)_2\{P(OMe)_3\}_2\{(MeO)_2-PN(Et)P(OMe)_2-\kappa P\}]^+$ is formed; this cation contains one cobalt atom bonded to two trimethyl phosphite ligands, two carbonyl ligands, and a pendant diphosphazane ligand, as confirmed X-ray crystallographically.

We are making extensive use of diphosphazane ligands of the type R₂PN(Et)PR₂ (R = aryl, alkyl, aryloxy, or alkoxy group) to bridge two metal atoms in dinuclear or polynuclear complexes, thereby stabilizing them to fragmentation to mononuclear species. For example, an extensive chemistry of the complexes $[M_2(\mu-CO)(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$ (M = Fe or Ru, R = Me or Pr^i)[1] has been developed, in which the two metal atoms are held in close proximity to each other by the bridging ligands during a reaction. Another consequence of this approach is that the presence of a bridging bidentate donor ligand leads to an increase in the electron density at the metal atom centres, with the result that complexes containing these ligands are electron-rich. For this reason the $[M_2(\mu-CO)-(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) complexes are susceptible to attack by a wide range of electrophilic reagents especially protons and halogens, leading to a host of new products, some with fascinating structures and others with potential as multicentred catalysts.[2]

Of relevance here is our use of diphosphazane ligands to synthesize tetrasubstituted derivatives of [Co₂(CO)₈], *viz.* $[Co_2(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$ (1; R = Me or Pr^i)[3] in which the two cobalt atoms are bridged by two diphosphazane ligands. The bridging ligands are expected to hold the two cobalt atoms in close proximity to each other during a reaction, in contrast to [Co₂(CO)₈] itself, where, for example, substitution of CO by Group 15 donor ligands frequently leads to fragmentation and formation of mononuclear products.[4] Moreover, complexes (1) are electron-rich and, as such, are expected to be very susceptible to attack by electrophilic reagents. Thus, the original aim of this work was to develop the chemistry of complexes (1) and, in particular, to attempt the synthesis of dicobalt dihydrido complexes of the type $[Co_2H_2(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]$, as well as the disubstituted derivatives $[Co_2H_2(CO)_6\{\mu-(RO)_2PN(Et)P(OR)_2\}]$; the latter could be

(1)   (2)
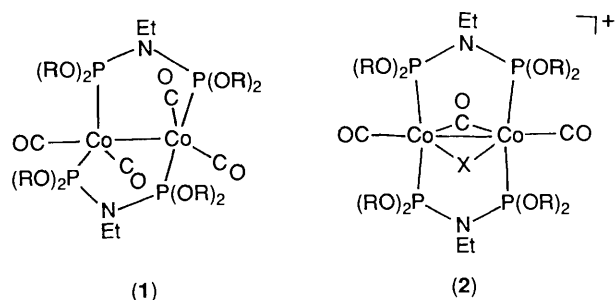
regarded as dinuclear analogues of the mononuclear, commercially useful hydroformylation catalyst $[CoH(CO)_3(PBu_3)]$.[5]

Our approach to the conversion of complexes (1) into dihydrido species has been two-fold. One has been to treat them with protons, the result being the formation of complexes of the type $[Co_2(\mu-H)(CO)_4\{\mu-(RO)_2PN(Et)P(OR)_2\}_2]^+$ (R = Me or Pr^i); unfortunately, subsequent addition of hydride ions merely served to deprotonate the cation, rather than to result in the formation of the desired dihydrido complex.[6] The other approach is represented here; complexes (1) are treated with halogenating agents with the aim of synthesizing compounds which can be used as precursors for the synthesis of dicobalt dihydrido complexes.

Table 1. Characterization data for the new complexes

Complex	Analysis^a (%)			I.r. data,^{b} v(CO)/cm^{-1}	^{31}P-$\{^1$H$\}$ N.m.r. data,^{c} δ/p.p.m.
	C	H	N		
[Co₂(μ-I)(μ-CO)(CO)₂{μ-(MeO)₂PN(Et)P-(OMe)₂}₂]BPh₄	42.1 (42.3)	5.2 (4.9)	2.1 (2.3)	1 995w(sh), 1 980s, 1 845s	145.06(s)
[Co₂(μ-I)(μ-CO)(CO)₂{μ-(Pr^{i}O)₂PN(Et)P-(OPr^i)₂}₂]BPh₄	49.4 (49.6)	6.6 (6.5)	2.2 (2.1)	1 985w(sh), 1 965s, 1 850s	135.45(s)
[Co₂(μ-Br)(μ-CO)(CO)₂{μ-(MeO)₂PN(Et)P-(OMe)₂}₂]PF₆	20.3 (20.3)	4.2 (3.8)	3.3 (3.2)	1 995w(sh), 1 982s, 1 850s	144.75(s)
[Co₂(μ-Br)(μ-CO)(CO)₂{μ-(Pr^{i}O)₂PN(Et)P-(OPr^i)₂}₂]BPh₄	51.7 (51.5)	6.9 (6.8)	1.9 (2.1)	1 982w(sh), 1 957s, 1 850s	135.92(s)
[Co₂(μ-Cl)(μ-CO)(CO)₂{μ-(MeO)₂PN(Et)P-(OMe)₂}₂]BPh₄	48.2 (48.5)	5.4 (5.6)	2.9 (2.9)	1 998w(sh), 1 982s, 1 855s	144.83(s)
[Co₂(μ-Cl)(μ-CO)(CO)₂{μ-(Pr^{i}O)₂PN(Et)P-(OPr^i)₂}₂]BPh₄	53.7 (53.3)	7.2 (6.9)	2.4 (2.3)	1 980w(sh), 1 965s, 1 857s	136.16(s)
[Co(CO)₂{P(OMe)₃}₂{(MeO)₂PN(Et)P-(OMe)₂-κP}]BPh₄	50.4 (50.1)	6.3 (6.1)	1.8 (1.5)	2 030s, 1 985s	103.97(s), 141.88(s), 143.97(s)
[Co₂(μ-I)(μ-CO)(CO)₂{μ-(Pr^{i}O)₂PN(Et)P(OPr^i)₂}{μ-(Pr^{i}O)₂PN(Et)P(O)(OPr^i)}]	34.5 (34.7)	6.1 (6.1)	2.7 (2.9)	1 967s, 1 940s, 1 827s	102.2, 147.55^{d,e}

^{a} Calculated values in parentheses. ^{b} Measured in dichloromethane. ^{c} Measured in CDCl₃ at 22 °C relative to external H₃PO₄. ^{d} At −90 °C. ^{e} Centres of complex multiplets.
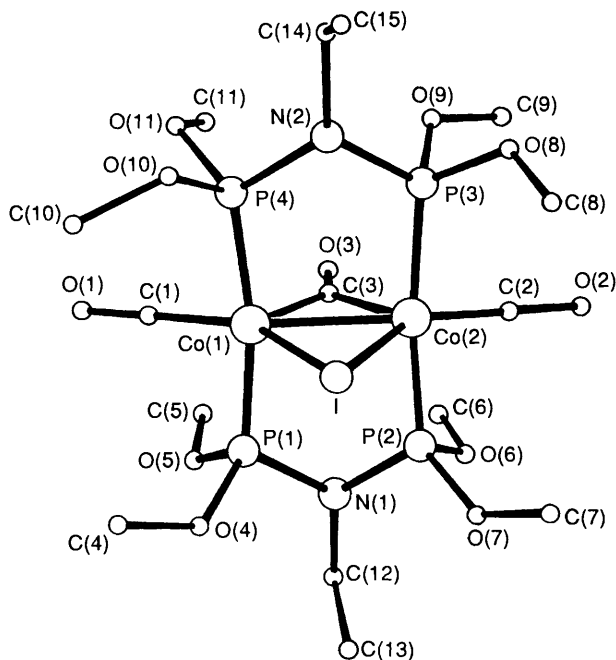

Figure 1. Perspective view of [Co₂(μ-I)(μ-CO)(CO)₂{μ-(MeO)₂PN(Et)-P(OMe)₂}₂]$^+$ showing the atom labelling scheme. There are two cations in the asymmetric unit labelled A and B

Results and Discussion

Halogenation of [Co₂(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}₂] (1) in toluene using 1 equivalent of iodine or bromine resulted in the formation of a new compound, as evidenced by the appearance of new peaks in the v(CO) region of the i.r. spectrum of the reaction mixture; in particular, a strong band in the bridging carbonyl region appeared. The product was best obtained as an orange crystalline material by carrying out the reaction in the presence of either sodium tetraphenylborate or ammonium

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* Distances and angles given in the text are averaged over both crystallographically independent, but structurally equivalent, molecules in the asymmetric unit.

hexafluorophosphate, followed by crystallization of the precipitate which separated from the toluene solution from dichloromethane–light petroleum. Analytical and spectroscopic data (Table 1) characterize the compounds as [Co₂(μ-X)(μ-CO)-(CO)₂{μ-(RO)₂PN(Et)P(OR)₂}₂]Z (2; X = Br or I, R = Me or Pr^i, Z = BPh₄ or PF₆), formulations which were confirmed by a complete X-ray crystal-structure determination on [Co₂(μ-I)-(μ-CO)(CO)₂{μ-(MeO)₂PN(Et)P(OMe)₂}₂]BPh₄ (see below). Bromination of complexes (1) could also be achieved using carbon tetrabromide as the halogenating agent. Indeed, chlorination of complexes (1) was best achieved by using excess carbon tetrachloride as the halogenating agent; the reaction was carried out in toluene in the presence of sodium tetraphenylborate, and the precipitate which separated from the toluene solution was crystallized from dichloromethane–light petroleum to give orange crystals of [Co₂(μ-Cl)(μ-CO)(CO)₂-{μ-(RO)₂PN(Et)P(OR)₂}₂]BPh₄ (R = Me or Pr^i). Table 1 gives the characterizing analytical and spectroscopic data. It should be noted that unless *freshly distilled* carbon tetrachloride is used, the reaction takes a different route (see below). Halogenation of complexes (1) therefore parallels the iodination of the stoicheiometrically equivalent,[7] but structurally different,[8] [Co₂(CO)₄{μ-Ph₂PCH₂PPh₂}₂] complex; in the latter reaction the cation [Co₂(μ-I)(μ-CO)(CO)₂{μ-Ph₂PCH₂-PPh₂}₂]$^+$ is formed; thus, in all these halogenation reactions formally a 'halogenonium ion' adds across the metal–metal bond, with loss of carbon monoxide, and formation of a bridging carbonyl group.

The band patterns in the v(CO) region of the i.r. spectra of cations (2) (Table 1) are very similar to those reported for [Rh₂(μ-X)(μ-CO)(CO)₂{μ-(RO)₂PN(Et)P(OR)₂}₂]$^+$ (X = Cl, Br, or I; R = Me or Ph),[9] [Co₂(μ-I)(μ-CO)(CO)₂(μ-Me₂-PCH₂PMe₂)(μ-Ph₂PCH₂PPh₂)]$^+$,[10] [Rh₂(μ-Cl)(μ-CO)-(CO)₂{μ-Ph₂PCH₂PPh₂}₂]$^+$,[11] and [Ir₂(μ-Cl)(μ-CO)(CO)₂-{μ-Ph₂PCH₂PPh₂}₂]$^+$.[12] X-Ray analyses of the last three complexes showed that they have A-frame structures with a neutral ligand, CO, occupying a bridging site in addition to the halogen atom.[10-12] Cations (2) are expected to have similar structures but, in order to establish this unambiguously, a single-crystal X-ray diffraction study was carried out on [Co₂(μ-I)(μ-CO)(CO)₂{μ-(MeO)₂PN(Et)P(OMe)₂}₂]BPh₄. Figure 1 gives a perspective view of the cation while Table 2 summarizes the important interatomic distances and angles.* The cation does

Table 2. Selected interatomic distances (Å) and angles (°) for $[Co_2(\mu\text{-I})(\mu\text{-CO})(CO)_2\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]BPh_4$

I(1A)–Co(1A)	2.610(2)	I(1A)–Co(2A)	2.623(2)	I(1B)–Co(1B)	2.604(2)	I(1B)–Co(2B)	2.630(2)
Co(1A)–Co(2A)	2.503(2)	Co(1A)–P(1A)	2.174(5)	Co(1B)–Co(2B)	2.498(2)	Co(1B)–P(1B)	2.171(5)
Co(1A)–P(4A)	2.173(5)	Co(1A)–C(1A)	1.72(2)	Co(1B)–P(4B)	2.179(4)	Co(1B)–C(1B)	1.72(2)
Co(1A)–C(3A)	1.93(1)	Co(2A)–P(2A)	2.174(5)	Co(1B)–C(3B)	1.92(1)	Co(2B)–P(2B)	2.181(5)
Co(2A)–P(3A)	2.177(5)	Co(2A)–C(2A)	1.77(1)	Co(2B)–P(3B)	2.181(5)	Co(2B)–C(2B)	1.74(2)
Co(2A)–C(3A)	1.93(1)			Co(2B)–C(3B)	1.92(1)		
P(1A)···P(2A)	2.837(7)	P(3A)···P(4A)	2.850(7)	P(1B)···P(2B)	2.862(7)	P(3B)···P(4B)	2.860(7)

Co(1A)–I(1A)–Co(2A)	57.1(1)	I(1A)–Co(1A)–Co(2A)	61.7(1)	Co(1B)–I(1B)–Co(2B)	57.0(1)	I(1B)–Co(1B)–Co(2B)	62.0(1)
I(1A)–Co(1A)–P(1A)	88.4(1)	I(1A)–Co(1A)–P(4A)	90.5(1)	I(1B)–Co(1B)–P(1B)	90.7(1)	I(1B)–Co(1B)–P(4B)	87.9(1)
I(1A)–Co(1A)–C(1A)	136.3(5)	I(1A)–Co(1A)–C(3A)	111.3(4)	I(1B)–Co(1B)–C(1B)	135.8(6)	I(1B)–Co(1B)–C(3B)	111.4(4)
Co(2A)–Co(1A)–P(1A)	95.2(1)	Co(2A)–Co(1A)–P(4A)	94.9(1)	Co(2B)–Co(1B)–P(1B)	95.4(1)	Co(2B)–Co(1B)–P(4B)	95.0(1)
Co(2A)–Co(1A)–C(1A)	162.0(5)	Co(2A)–Co(1A)–C(3A)	49.6(4)	Co(2B)–Co(1B)–C(1B)	162.1(6)	Co(2B)–Co(1B)–C(3B)	49.4(4)
P(1A)–Co(1A)–P(4A)	167.9(2)	P(1A)–Co(1A)–C(1A)	86.8(7)	P(1B)–Co(1B)–P(4B)	167.3(2)	P(1B)–Co(1B)–C(1B)	86.7(1)
P(1A)–Co(1A)–C(3A)	97.3(5)	P(4A)–Co(1A)–C(1A)	85.6(6)	P(1B)–Co(1B)–C(3B)	94.8(5)	P(4B)–Co(1B)–C(1B)	85.6(7)
P(4A)–Co(1A)–C(3A)	94.4(5)	C(1A)–Co(1A)–C(3A)	112.5(6)	P(4B)–Co(1B)–C(3B)	97.4(5)	C(1B)–Co(1B)–C(3B)	112.8(7)
I(1A)–Co(2A)–Co(1A)	61.2(1)	I(1A)–Co(2A)–P(2A)	91.7(1)	I(1B)–Co(2B)–Co(1B)	61.0(1)	I(1B)–Co(2B)–P(2B)	90.5(1)
I(1A)–Co(2A)–P(3A)	91.6(1)	I(1A)–Co(2A)–C(2A)	131.3(5)	I(1B)–Co(2B)–P(3B)	92.6(1)	I(1B)–Co(2B)–C(3B)	110.3(4)
I(1A)–Co(2A)–C(3A)	110.7(4)	Co(1A)–Co(2A)–P(2A)	93.5(1)	I(1B)–Co(2B)–C(3B)	110.3(4)	Co(1B)–Co(2B)–P(2B)	94.2(1)
Co(1A)–Co(2A)–P(3A)	94.2(1)	Co(1A)–Co(2A)–C(2A)	167.5(5)	Co(1B)–Co(2B)–P(3B)	94.3(1)	Co(1B)–Co(2B)–C(2B)	166.1(7)
Co(1A)–Co(2A)–C(3A)	49.5(4)	P(2A)–Co(2A)–P(3A)	172.3(2)	Co(1B)–Co(2B)–C(3B)	49.4(4)	P(2B)–Co(2B)–P(3B)	171.4(2)
P(2A)–Co(2A)–C(2A)	87.4(6)	P(2A)–Co(2A)–C(3A)	92.6(5)	P(2B)–Co(2B)–C(2B)	85.3(8)	P(2B)–Co(2B)–C(3B)	93.8(5)
P(3A)–Co(2A)–C(2A)	85.2(6)	P(3A)–Co(2A)–C(3A)	92.7(5)	P(3B)–Co(2B)–C(2B)	86.7(8)	P(3B)–Co(2B)–C(3B)	92.5(5)
C(2A)–Co(2A)–C(3A)	118.0(6)	Co(1A)–C(3A)–Co(2A)	80.9(5)	C(2B)–Co(2B)–C(3B)	116.8(8)	Co(1B)–C(3B)–Co(2B)	81.2(6)

indeed have the expected A-frame structure; in fact the symmetry of the cation approximates closely to C_{2h}. The average Co–Co–C(O) angle of 164.4° reflects a slightly more linear arrangement along the metal–metal bond than in $[Rh_2(\mu\text{-Cl})(\mu\text{-CO})(CO)_2\{\mu\text{-Ph}_2PCH_2PPh_2\}_2]^+$ and $[Ir_2(\mu\text{-Cl})(\mu\text{-CO})(CO)_2\{\mu\text{-Ph}_2PCH_2PPh_2\}_2]^+$, where the corresponding angles are 162.2(3) and 153.9(3)° respectively,[11,12] but is similar to the value of 166.4(3)° reported for the average Co–Co–C(O) angle in $[Co_2(\mu\text{-I})(\mu\text{-CO})(CO)_2(\mu\text{-Me}_2PCH_2PMe_2)(\mu\text{-Ph}_2PCH_2PPh_2)]^+$.[10] Significantly, the terminal carbonyl groups bend away from the bridging iodine atom towards the bridging carbonyl group. The Co(1)–Co(2) bond length of 2.510(2) Å is shorter than the values reported for cobalt metal[13] (2.593 Å), $[Co_2(CO)_8]^{14}$ [2.524(2) Å], $[Co_2(\eta^5\text{-C}_5H_5)(\mu\text{-PMe}_2)(CO)_4]^{15}$ [2.593(2) Å], $[Co_2(\mu\text{-I})(\mu\text{-CO})(CO)_2(\mu\text{-Me}_2PCH_2PMe_2)(\mu\text{-Ph}_2PCH_2PPh_2)]^{+10}$ [2.555(2) Å], and $[Co_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_4(\mu\text{-Ph}_2PCH_2PPh_2)]^{+16}$ [2.637(1) Å], but is consistent with a single bond; certainly electron counting predicts the presence of a single bond between the metal atoms. Interestingly, the Co–Co distance is significantly shorter than the 'bite' of the bridging diphosphazane ligands (average P···P distance 2.843 Å); in fact this is, to the best of our knowledge, the shortest reported distance between two atoms bridged by diphosphazane ligands of the type $R_2PN(R')PR_2$ (R = alkyl, aryl, alkoxy, or aryloxy group; R' = alkyl group).

The halogenation reactions of complexes (**1**) contrast their protonation reactions since, in the latter, CO loss does not occur; complexes (**1**) react with protons to form bridging hydrido species of the type $[Co_2(\mu\text{-H})(CO)_4\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]^+$ (R = Me or Pr^i).[6] Yet, it is apparent that a tetracarbonyl complex is a likely intermediate in the halogenation reactions and, for this reason, the iodination and bromination of complexes (**1**) were monitored at regular time intervals using i.r. spectroscopy. No evidence for the transient formation of a tetracarbonyl intermediate was obtained, even in the presence of added carbon monoxide, in fact the reaction is complete after ca. 2 min. Significantly, if a solution of $[Co_2(\mu\text{-X})(\mu\text{-CO})(CO)_2\{\mu\text{-(RO)}_2PN(Et)P(OR)_2\}_2]X$ (X = Cl, Br, or I; R = Me *only*) in dichloromethane is left to stand for 2—3 d a change in the i.r. spectrum is indeed

observed; the band pattern in the ν(CO) region remains similar but the peaks shift to lower wavenumbers, e.g. after standing the $[Co_2(\mu\text{-I})(\mu\text{-CO})(CO)_2\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]^+$ solution affords new peaks at 1 970(sh), 1 950s, and 1 815m cm^{-1}, measured in dichloromethane. On the basis that $[Fe_2(\mu\text{-X})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]^+$ (X = Cl, Br, or I) is attacked by halide ions forming $[Fe_2(\mu\text{-X})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}\{\mu\text{-(MeO)}_2PN(Et)P(O)(OMe)\}]$ we propose that the cation has undergone a Michaelis–Arbusov type rearrangement reaction,[17,18] involving attack of a halide ion at a co-ordinated phosphorus atom, with formation of neutral complexes of the type $[Co_2(\mu\text{-X})(\mu\text{-CO})(CO)_2\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}\{\mu\text{-(MeO)}_2PN(Et)P(O)(OMe)\}]$. Despite several attempts, including addition of excess of halide ions to facilitate the rearrangement reaction, it was not possible to isolate the rearrangement product. It was possible, however, to isolate a Michaelis–Arbusov rearrangement product from the reaction of a stronger nucleophile, viz. H^-, with $[Co_2(\mu\text{-I})(\mu\text{-CO})(CO)_2\{\mu\text{-(Pr}^i\text{O})_2PN(Et)P(OPr}^i)_2\}_2]^+$. This reaction, originally attempted with the aim of synthesizing a dihydrido complex, was carried out in dichloromethane using $NaBH_4$ as the hydride source; an i.r. spectrum of the reaction mixture showed mostly starting material but also new ν(CO) peaks at lower wavenumbers. Using column chromatography the compound $[Co_2(\mu\text{-I})(\mu\text{-CO})(CO)_2\{\mu\text{-(Pr}^i\text{O})_2PN(Et)P(OPr}^i)_2\}\{\mu\text{-(Pr}^i\text{O})_2PN(Et)P(O)(OPr}^i)\}]$ was separated and subsequently crystallized from light petroleum. Table 1 gives the characterizing data, especially significant being the $^{31}P\text{-}\{^1H\}$ n.m.r. data at -90 °C. There are two sets of resonances, one of ca. fifteen lines centred at 147.55 p.p.m. and the other of ca. eight lines centred at 102.2 p.p.m.; both are complex multiplets, the overall pattern being very similar to that for $[Fe_2(\mu\text{-X})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}\{\mu\text{-(MeO)}_2PN(Et)P(O)(OMe)\}]^2$ and typical for an ABCX system.

During the course of our studies on the chlorination of complexes (**1**) using carbon tetrachloride we observed that, when undistilled (Analar grade, BDH) rather than freshly distilled carbon tetrachloride was used (under otherwise identical conditions), ν(CO) peaks appeared in the i.r. spectrum of the reaction mixture which could not be attributed to the expected product, i.e. $[Co_2(\mu\text{-Cl})(\mu\text{-CO})(CO)_2\{\mu\text{-(RO)}_2PN(Et)\text{-}$
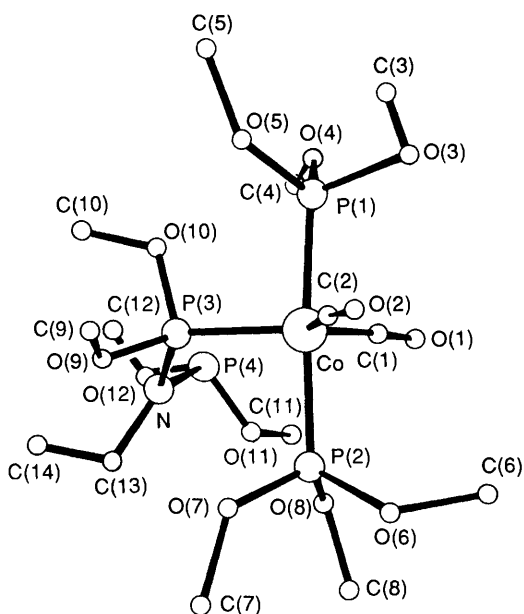
Figure 2. Perspective view of [Co(CO)₂{P(OMe)₃}₂{(MeO)₂PN(Et)-P(OMe)₂-κP}]⁺ showing the atom labelling scheme

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Table 3. Selected interatomic distances (Å) and angles (°) for [Co(CO)₂{P(OMe)₃}₂{(MeO)₂PN(Et)P(OMe)₂-κP}]BPh₄

Co–P(1)	2.166(6)	Co–P(2)	2.186(5)
Co–P(3)	2.209(6)	Co–C(1)	1.68(3)
Co–C(2)	1.75(2)	P(3)–N	1.65(2)
P(4)–N	1.72(2)	N–C(13)	1.53(3)
P(1)–Co–P(2)	172.4(3)	P(1)–Co–P(3)	94.0(2)
P(1)–Co–C(1)	85.0(10)	P(1)–Co–C(2)	89.6(7)
P(2)–Co–P(3)	92.4(2)	P(2)–Co–C(1)	88.3(10)
P(2)–Co–C(2)	91.3(7)	P(3)–Co–C(1)	119.7(10)
P(3)–Co–C(2)	115.3(7)	C(1)–Co–C(2)	124.9(13)
P(3)–N–P(4)	116.0(11)	P(3)–N–C(13)	122.7(17)
P(4)–N–C(13)	119.3(16)		

P(OR)₂}₂]Cl (R = Me or Prⁱ). Typically, these unexpected peaks were found at ca 2 030 and ca. 1 980 cm⁻¹, characteristic of some new compound which contained terminal carbonyl groups only. Unfortunately it was not possible to isolate this compound when dichloromethane was used as the solvent, but it was possible to isolate yellow crystals from the reaction of [Co₂(CO)₄{μ-(MeO)₂PN(Et)P(OMe)₂}₂] with Analar grade carbon tetrachloride in the presence of NaBPh₄ when methanol was used as the solvent. The analytical and spectroscopic data in Table 1 are consistent with the compound being [Co(CO)₂-{P(OMe)₃}₂{(MeO)₂PN(Et)P(OMe)₂-κP}]BPh₄; of note is the presence of three peaks in the ³¹P-{¹H} n.m.r. spectrum indicative of three inequivalent phosphorus atoms in the compound. However, a single-crystal X-ray diffraction study was necessary to establish fully the identity and structure of this compound. Figure 2 gives a perspective view of the cation while Table 3 summarizes some important distances and angles. The cation is, indeed, mononuclear, the geometry at the cobalt atom being trigonal bipyramidal with the axial positions occupied by P(OMe)₃ groups and the equatorial positions by two carbonyl groups and by a pendant diphosphazane ligand. Clearly some 'impurity' in the Analar grade carbon tetrachloride causes the chlorination reaction to proceed via a different route to that occurring when freshly distilled carbon tetrachloride is used. In particular, cleavage of Co–Co, Co–P, and P–N bonds must

occur to yield, eventually, a mononuclear complex with a pendant diphosphazane ligand, two carbonyl ligands, and two co-ordinated P(OMe)₂Cl groups, the latter being rapidly solvolysed to give trimethyl phosphite ligands if methanol is used as solvent. No attempt has been made to ascertain the nature of the 'impurity' in the Analar grade carbon tetrachloride but it can be noted that, on every occasion that the chlorination of complexes (1) was attempted with Analar grade carbon tetrachloride, the unexpected mononuclear product was obtained.

Experimental

Although none of the compounds reported here is particularly air-sensitive, all the manipulations (reactions, chromatography, and recrystallizations) described below were carried out under inert atmospheres of either dinitrogen or argon.

Proton and ³¹P-{¹H} n.m.r. data were obtained on a Varian FT80A instrument at 20 °C using deuteriated solvent as internal lock and reference (¹H, SiMe₄, δ = 0; ³¹P, 85% H₃PO₄ in D₂O, δ = 0; downfield positive). Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. Microanalysis for C, H, and N was performed in the Microanalytical laboratory of the Department of Chemistry, University of Natal, Pietermaritz-burg.

The compounds [Co₂(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}₂] (R = Me or Prⁱ) were prepared as described previously.[3]

Syntheses.—[Co₂(μ-X)(μ-CO)(CO)₂{μ-(RO)₂PN(Et)-P(OR)₂}₂]Z (X = Br or I, R = Me or Prⁱ, Z = BPh₄ or PF₆). An equimolar amount of NaBPh₄ (NH₄PF₆ in the case of X = Br, R = Me) dissolved in the minimum of methanol was added to a solution of [Co₂(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}₂] (0.200 g) in toluene (25 cm³). An equimolar amount of iodine (or bromine) dissolved in the minimum of toluene was added dropwise to the stirred solution over a period of ca. 10 min. The solution was stirred for a further 30 min during which time a precipitate separated. The solution was filtered and the precipitate crystallized from dichloromethane–light petroleum (b.p. 60—80 °C) to give an orange crystalline solid. Typical yield: 80%.

[Co₂(μ-Cl)(μ-CO)(CO)₂{μ-(RO)₂PN(Et)P(OR)₂}₂]BPh₄ (R = Me or Prⁱ). Equimolar amounts (ca. 0.5 mmol) of carbon tetrachloride (freshly distilled) and NaBPh₄ were dissolved in toluene (35 cm³) to which sufficient methanol had been added to ensure dissolution of the NaBPh₄. The solution was stirred and [Co₂(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}₂] (0.30 mmol) dissolved in dichloromethane (10 cm³) was added dropwise over a period of ca. 10 min. The reaction mixture was stirred for a further 2—3 h by which time a green oil had precipitated. The solvent was removed in vacuo and the oily residue recrystallized from dichloromethane–light petroleum (60—80 °C) to produce red-orange crystals of [Co₂(μ-Cl)(μ-CO)(CO)₂{μ-(RO)₂PN(Et)-P(OR)₂}₂]BPh₄ (R = Me or Prⁱ). Yield: 75%.

[Co₂(μ-I)(μ-CO)(CO)₂{μ-(PrⁱO)₂PN(Et)P(OPrⁱ)₂}{μ-(PrⁱO)₂PN(Et)P(O)(OPrⁱ)}]. A solution of [Co₂(μ-I)(μ-CO)-(CO)₂{μ-(PrⁱO)₂PN(Et)P(OPrⁱ)₂}₂]I (ca. 0.3 mmol) was prepared by addition of an equimolar amount of iodine to a stirred solution of [Co₂(CO)₄{μ-(PrⁱO)₂PN(Et)P(OPrⁱ)₂}₂] (0.31 g, 0.30 mmol) in methanol (25 cm³). The i.r. spectrum of the solution confirmed the clean formation of [Co₂(μ-I)(μ-CO)-(CO)₂{μ-(PrⁱO)₂PN(Et)P(OPrⁱ)₂}₂]⁺ [ν(CO): see Table 1]. A large excess of NaBH₄ (ca. 0.5 g) was added and the solution stirred for ca. 1 h. The solution was filtered through Celite, the solvent removed in vacuo, and the residue extracted with toluene. The volume of the toluene extract was reduced and the concentrate subjected to column chromatography on alumina (Activity III: 15 × 2 cm column) using dichloromethane–light

Table 4. Atomic co-ordinates ($\times 10^4$) for [Co$_2$(μ-I)(μ-CO)(CO)$_2${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$]BPh$_4$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
I(1A)	4 744(1)	2 745(1)	3 813(1)	C(6B)	7 716(25)	3 861(14)	679(12)
Co(1A)	3 296(2)	3 238(1)	4 736(1)	C(7B)	3 476(26)	4 462(14)	265(13)
Co(2A)	4 810(2)	2 155(1)	4 978(1)	C(8B)	3 969(17)	2 865(9)	−993(8)
P(1A)	1 842(3)	2 772(2)	4 571(2)	C(9B)	8 019(20)	2 434(11)	−1 208(10)
P(2A)	3 493(4)	1 540(2)	4 924(2)	C(10B)	4 162(14)	441(7)	1 419(7)
P(3A)	6 309(4)	2 645(2)	5 052(2)	C(11B)	8 128(17)	589(9)	534(8)
P(4A)	4 598(4)	3 877(2)	4 749(2)	C(12B)	5 236(17)	3 833(9)	2 014(8)
O(1A)	1 375(13)	4 389(7)	4 902(6)	C(13B)	3 855(23)	4 192(12)	2 140(11)
O(2A)	6 324(11)	916(6)	5 502(5)	C(14B)	5 535(13)	947(7)	−553(6)
O(3A)	3 280(10)	2 644(5)	6 037(5)	C(15B)	4 151(15)	1 019(8)	−653(7)
O(4A)	1 446(11)	2 961(6)	3 894(5)	B(A)	840(15)	9 609(8)	2 490(8)
O(5A)	486(11)	2 951(6)	4 951(5)	C(16A)	124(14)	9 044(8)	2 391(7)
O(6A)	3 978(23)	1 043(12)	4 412(10)	C(17A)	−861(18)	9 211(10)	2 003(9)
O(7A)	3 340(17)	956(9)	5 437(9)	C(18A)	−1 551(20)	8 736(11)	1 948(10)
O(8A)	7 087(19)	2 399(10)	5 575(10)	C(19A)	−1 291(20)	8 091(11)	2 290(10)
O(9A)	7 576(19)	2 474(10)	4 640(9)	C(20A)	−406(17)	7 901(9)	2 664(8)
O(10A)	4 960(10)	4 380(6)	4 147(5)	C(21A)	347(15)	8 361(8)	2 727(7)
O(11A)	4 148(10)	4 413(5)	5 202(5)	C(22A)	109(14)	9 869(8)	3 117(7)
N(1A)	2 170(12)	1 945(6)	4 669(6)	C(23A)	−1 060(16)	10 328(9)	3 095(8)
N(2A)	5 997(10)	3 468(6)	4 918(5)	C(24A)	−1 773(19)	10 523(10)	3 647(10)
C(1A)	2 150(15)	3 940(8)	4 819(7)	C(25A)	−1 321(19)	10 259(10)	4 218(9)
C(2A)	5 752(14)	1 408(8)	5 318(7)	C(26A)	−217(17)	9 811(9)	4 270(8)
C(3A)	3 612(12)	2 673(7)	5 523(6)	C(27A)	488(15)	9 633(8)	3 687(7)
C(4A)	1 156(19)	3 659(10)	3 587(9)	C(28A)	2 365(13)	9 293(7)	2 548(6)
C(5A)	279(21)	2 828(11)	5 658(10)	C(29A)	3 002(15)	8 751(8)	2 260(7)
C(6A)	4 989(36)	707(19)	4 182(16)	C(30A)	4 298(19)	8 559(10)	2 247(9)
C(7A)	2 874(22)	1 083(12)	6 094(11)	C(31A)	4 951(20)	8 864(11)	2 548(10)
C(8A)	6 579(27)	2 263(14)	6 179(14)	C(32A)	4 294(19)	9 464(10)	2 802(9)
C(9A)	8 001(28)	2 118(15)	4 192(14)	C(33A)	3 041(15)	9 637(8)	2 813(7)
C(10A)	4 161(22)	4 728(12)	3 749(11)	C(34A)	906(13)	10 211(7)	1 892(7)
C(11A)	3 794(17)	4 197(9)	5 866(8)	C(35A)	1 117(14)	10 080(8)	1 262(7)
C(12A)	1 195(18)	1 565(10)	4 627(9)	C(36A)	1 244(18)	10 610(10)	744(9)
C(13A)	1 341(21)	1 409(11)	3 922(10)	C(37A)	1 114(17)	11 240(10)	807(8)
C(14A)	6 951(19)	3 896(10)	4 976(10)	C(38A)	913(17)	11 401(10)	1 410(9)
C(15A)	7 849(21)	3 998(11)	4 450(10)	C(39A)	781(17)	10 902(10)	1 940(9)
I(1B)	3 568(1)	2 521(1)	768(1)	B(B)	−1 066(16)	5 475(8)	2 026(8)
Co(1B)	5 692(2)	1 901(1)	1 142(1)	C(16B)	−2 559(12)	5 810(7)	2 263(6)
Co(2B)	5 720(2)	2 844(1)	230(1)	C(17B)	−2 871(13)	6 350(7)	2 579(6)
P(1B)	5 414(4)	2 535(2)	1 837(2)	C(18B)	−4 099(15)	6 664(8)	2 727(7)
P(2B)	5 454(4)	3 619(2)	795(2)	C(19B)	−5 063(19)	6 459(10)	2 530(9)
P(3B)	5 949(3)	2 193(2)	−452(2)	C(20B)	−4 766(16)	5 902(9)	2 231(8)
P(4B)	5 713(3)	1 136(2)	600(2)	C(21B)	−3 524(14)	5 604(8)	2 081(7)
O(1B)	6 438(13)	795(7)	2 115(6)	C(22B)	−828(14)	4 677(8)	2 095(7)
O(2B)	6 293(14)	3 883(8)	−809(7)	C(23B)	−1 577(16)	4 257(9)	2 510(8)
O(3B)	8 127(10)	2 203(5)	591(5)	C(24B)	−1 264(20)	3 538(11)	2 637(10)
O(4B)	4 101(12)	2 592(6)	2 294(6)	C(25B)	−174(23)	3 243(12)	2 296(11)
O(5B)	6 326(13)	2 332(7)	2 342(6)	C(26B)	634(21)	3 593(12)	1 889(10)
O(6B)	6 415(12)	4 121(7)	641(6)	C(27B)	310(20)	4 331(11)	1 790(10)
O(7B)	4 245(14)	4 171(8)	748(7)	C(28B)	−168(13)	5 640(7)	2 468(7)
O(8B)	5 187(9)	2 466(5)	−1 033(5)	C(29B)	931(18)	5 887(9)	2 217(9)
O(9B)	7 325(10)	1 977(5)	−799(5)	C(30B)	1 701(21)	5 969(12)	2 637(11)
O(10B)	4 593(9)	743(5)	763(4)	C(31B)	1 398(22)	5 824(12)	3 238(11)
O(11B)	6 827(10)	504(5)	649(5)	C(32B)	357(20)	5 546(11)	3 526(10)
N(1B)	5 369(12)	3 341(7)	1 571(6)	C(33B)	−428(16)	5 486(9)	3 127(8)
N(2B)	5 623(9)	1 430(5)	−159(4)	C(34B)	−845(15)	5 868(8)	1 316(8)
C(1B)	6 168(16)	1 234(9)	1 715(8)	C(35B)	−900(17)	5 585(9)	801(9)
C(2B)	6 121(19)	3 461(11)	−389(10)	C(36B)	−794(19)	5 966(11)	167(10)
C(3B)	7 058(13)	2 275(7)	643(7)	C(37B)	−653(22)	6 612(13)	81(11)
C(4B)	3 520(19)	2 048(10)	2 611(9)	C(38B)	−669(19)	6 949(10)	557(10)
C(5B)	7 655(20)	2 160(11)	2 176(10)	C(39B)	−764(17)	6 567(9)	1 163(8)

petroleum (b.p. 60—80 °C) as eluant. The first fraction contained the starting complex, the second yielded an unidentifiable pink oil, while *in vacuo* removal of the solvent from the third fraction gave a black residue; recrystallization of the latter from light petroleum (b.p. 60—80 °C) afforded red crystals of [Co$_2$-(μ-I)(μ-CO)(CO)$_2${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}{μ-(Pr^{i}O)$_2$PN-(Et)P(O)(OPr^i)}]. Yield: 50 mg, 15% based on [Co$_2$(CO)$_4${μ-(Pr^{i}O)$_2$PN(Et)P(OPr^i)$_2$}$_2$].

[Co(CO)$_2${P(OMe)$_3$}$_2${(MeO)$_2$PN(Et)P(OMe)$_2$-κP}]BPh$_4$. Sodium tetraphenylborate (0.10 g, 0.30 mmol) was dissolved in a mixture of methanol (25 cm^3) and carbon tetrachloride (50 cm^3). (Note: The carbon tetrachloride was taken from a bottle of BDH Analar grade and used without further purification.) Solid [Co$_2$(CO)$_4${μ-(MeO)$_2$PN(Et)P(OMe)$_2$}$_2$] (0.20 g, 0.30 mmol) was added and the solution stirred for 3 h. The solvent was removed *in vacuo* and the oily residue dissolved in

Table 5. Atomic co-ordinates ($\times 10^4$) for $[Co(CO)_2\{P(OMe)_3\}_2\{(MeO)_2PN(Et)P(OMe)_2\text{-}\kappa P\}]BPh_4$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Co	1 756(2)	3 083(2)	4 232(1)	C(12)	929(37)	5 002(28)	2 542(12)
P(1)	2 013(7)	4 477(5)	4 513(2)	C(13)	−375(29)	2 641(21)	3 096(9)
P(2)	1 547(4)	1 595(3)	4 027(2)	C(14)	−1 527(34)	3 043(26)	2 944(11)
P(3)	304(5)	3 614(3)	3 798(2)	B	−1 602(21)	1 944(16)	8 728(7)
P(4)	1 825(7)	3 838(5)	3 085(2)	C(15)	−926(12)	2 342(11)	9 145(4)
O(1)	854(22)	2 503(19)	5 003(9)	C(16)	−1 492(12)	3 082(11)	9 367(4)
O(2)	4 476(19)	3 134(14)	3 969(6)	C(17)	−823(12)	3 484(11)	9 690(4)
O(3)	2 752(21)	5 301(15)	4 315(7)	C(18)	411(12)	3 145(11)	9 790(4)
O(4)	2 647(39)	4 337(25)	4 933(11)	C(19)	976(12)	2 404(11)	9 568(4)
O(5)	661(22)	4 927(16)	4 663(7)	C(20)	308(12)	2 003(11)	9 245(4)
O(6)	1 877(17)	812(11)	4 345(5)	C(21)	−851(13)	2 574(10)	8 356(5)
O(7)	2 357(16)	1 349(11)	3 649(5)	C(22)	−1 314(13)	3 496(10)	8 269(5)
O(8)	76(15)	1 350(10)	3 977(5)	C(23)	−585(13)	4 114(10)	8 028(5)
O(9)	−1 125(15)	3 304(11)	3 844(5)	C(24)	607(13)	3 811(10)	7 874(5)
O(10)	249(15)	4 756(10)	3 813(5)	C(25)	1 070(13)	2 889(10)	7 961(5)
O(11)	2 587(19)	2 874(14)	2 993(6)	C(26)	341(13)	2 271(10)	8 202(5)
O(12)	1 343(21)	4 029(16)	2 652(6)	C(27)	−3 213(9)	2 057(9)	8 704(4)
N	442(18)	3 399(13)	3 313(6)	C(28)	−3 807(9)	2 129(9)	8 330(4)
C(1)	1 272(29)	2 718(21)	4 688(10)	C(29)	−5 159(9)	2 153(9)	8 301(4)
C(2)	3 372(21)	3 120(16)	4 069(7)	C(30)	−5 917(9)	2 104(9)	8 647(4)
C(3)	3 188(37)	5 569(25)	3 914(11)	C(31)	−5 323(9)	2 031(9)	9 021(4)
C(4)	3 678(50)	4 215(32)	5 004(13)	C(32)	−3 971(9)	2 008(9)	9 050(4)
C(5)	391(34)	5 919(26)	4 770(11)	C(33)	1 372(13)	5 724(6)	6 327(4)
C(6)	3 201(30)	677(19)	4 545(8)	C(34)	1 400(13)	5 306(6)	6 706(4)
C(7)	2 750(21)	310(15)	3 508(7)	C(35)	1 356(13)	4 306(6)	6 746(4)
C(8)	−377(24)	388(17)	3 811(8)	C(36)	1 285(13)	3 724(6)	6 406(4)
C(9)	−1 784(27)	3 277(19)	4 233(9)	C(37)	1 256(13)	4 142(6)	6 027(4)
C(10)	−525(33)	5 371(23)	3 570(10)	C(38)	1 300(13)	5 142(6)	5 987(4)
C(11)	3 738(31)	2 888(22)	2 781(10)				

methanol. Cooling to −10 °C resulted in the formation of yellow crystals of $[Co(CO)_2\{P(OMe)_3\}_2\{(MeO)_2PN(Et)P(OMe)_2\text{-}\kappa P\}]BPh_4$ over a period of 2—3 d. Yield: 0.16 g, 60%.

X-Ray Structural Analysis of $[Co_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4$.—Orange crystals were obtained by allowing light petroleum (40—60 °C) vapour to diffuse slowly into a dichloromethane solution of the compound.

Crystal data. $C_{39}H_{54}BCo_2IN_2O_{11}P_4$, $M = 1\ 106.35$, triclinic, space group $P\bar{1}$, $a = 11.088(3)$, $b = 20.701(5)$, $c = 22.226(8)$ Å, $\alpha = 77.70(1)$, $\beta = 79.69(1)$, $\gamma = 77.10(1)°$, $U = 4\ 812.3$ Å^3, $Z = 4$, $D_c = 1.527$ g cm^{-3}, $F(000) = 2\ 248$, $\lambda = 0.710\ 69$ Å, $\mu(Mo\text{-}K_\alpha) = 15.6$ cm^{-1}, crystal size $0.35 \times 0.27 \times 0.46$ mm. The crystal quality was poor, as evidenced by broad, ill defined reflection peaks but, despite many attempts, it was not possible to grow an improved crystal.

Data collection. Unit-cell parameters and intensity data were obtained by previously detailed procedures,[19] using a CAD4 diffractometer operating in the ω—2θ scan mode, with graphite-monochromatized Mo-K_α radiation. A total of 17 162 reflections were collected in the range $2 \leqslant \theta \leqslant 23°$; of these 9 833 with $I > 4\sigma(I)$ were used in the solution and refinement of the structure. The reflection intensities were corrected for absorption using the ψ-scan (empirical) method.[20] No significant decay occurred during the data collection.

Structure solution and refinement. Direct methods (I and Co atoms) followed by Fourier-difference syntheses. Full-matrix least-squares refinement with I, Co, and P anisotropic, O, N, C, and B isotropic; H atoms not located. The weighting scheme $w = 1.497/[\sigma^2(F) + 0.006F^2]$ gave satisfactory agreement analyses. Final R and R' values are 0.090 and 0.103. Maximum shift/e.s.d. in last least-squares cycle = 0.204. Final Fourier difference map featureless with maximum peak height = 1.5 e Å^{-3}. All computations made with the programs SHELX 76[21] and SHELX 86.[22] Final atomic co-ordinates are listed in Table 4.

X-Ray Structural Analysis of $[Co(CO)_2\{P(OMe)_3\}_2\{(MeO)_2PN(Et)P(OMe)_2\text{-}\kappa P\}]BPh_4$.—Yellow crystals were obtained by cooling a methanol solution of the compound to −10 °C.

Crystal data. $C_{38}H_{55}BCoNO_{12}P_4$, $M = 911.06$, orthorhombic, space group $P2_12_12_1$, $a = 10.291(2)$, $b = 13.875(3)$, $c = 33.415(8)$ Å, $U = 4\ 770.9$ Å^3, $Z = 4$, $D_c = 1.268$ g cm^{-3}, $F(000) = 1\ 912$, $\lambda = 0.710\ 69$ Å, $\mu(Mo\text{-}K_\alpha) = 5.66$ cm^{-1}, crystal size $0.46 \times 0.58 \times 0.89$ mm. The crystal quality was poor, as evidenced by broad, ill defined reflection peaks but, despite many attempts, it was not possible to obtain a smaller, better-defined crystal.

Data collection. Unit-cell parameters and intensity data were obtained by previously detailed procedures,[19] using a CAD4 diffractometer operating in the ω—2θ scan mode, with graphite-monochromatized Mo-K_α radiation. A total of 3 927 reflections were collected in the range $2 \leqslant \theta \leqslant 23°$; of these 2 270 with $I > 4\sigma(I)$ were used in the solution and refinement of the structure. The reflection intensities were corrected for absorption using the ψ-scan (empirical) method.[20] No significant decay occurred during the data collection.

Structure solution and refinement. Patterson function (Co and P atoms) followed by Fourier-difference syntheses. Full-matrix least-squares refinement with Co and P anisotropic, O, N, and C isotropic. Phenyl rings refined as rigid groups; H atoms not located. The weighting scheme $w = 1.000/[\sigma^2(F) + 0.001F^2]$ gave satisfactory agreement analyses. Final R and R' values are 0.111 and 0.117. Inversion of the atom co-ordinates followed by a complete refinement resulted in an insignificant increase in R'. Maximum shift/e.s.d. in last least-squares cycle = 0.11. Final Fourier difference map featureless with maximum peak height = 2.0 e Å^{-3}. All computations made with the programs SHELX 76[21] and SHELX 86.[22] Final atomic co-ordinates are listed in Table 5.

Additional material available from the Cambridge Crystal-

lographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

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