

PARAMAGNETIC CARBONYL COBALT(II) COMPLEXES. MOLECULAR STRUCTURE OF BROMOCARBONYL-1,1,1-TRIS(DIPHENYLPHOSPHINOMETHYL)ETHANECOBALT(II) TETRAPHENYLBORATE

C.A. GHILARDI, S. MIDOLLINI and L. SACCONI *

Istituto di Chimica Generale ed Inorganica, Università, Laboratorio CNR, Firenze, Via J. Nardi, 39 (Italy)

(Received August 2nd, 1979)

Summary

Carbon monoxide or cyclohexyl isonitrile (L) react with the dinuclear five-coordinated derivatives of 1,1,1-tris(diphenylphosphinomethyl)ethane, (triphos), [(triphos)Co(μ -X)₂Co(triphos)](BPh₄)₂ (X = halide) to give complexes of formula [(triphos)Co(L)X]BPh₄. The latter are rare examples of paramagnetic cobalt(II) carbonyl complexes. The molecular structure of [(triphos)Co(CO)Br]BPh₄ has been determined from counter diffraction data. The crystals are monoclinic, space group *P*2₁/*a* with cell dimensions *a* 20.225(8), *b* 20.664(9), *c* 13.301(5); β 97.24(5)°, *D*_c = 1.338 g cm⁻³ for *Z* = 4. Full-matrix least squares refinement led to the conventional *R* factor of 0.057 for 3648 observed reflections. The molecular structure consists of five-coordinate [(triphos)Co(CO)Br]⁺ cations of intermediate geometry and BPh₄⁻ anions.

Introduction

The tripodal tri(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, forms with 3*d* metals the stable carbonyl derivatives [(triphos)-Mn(CO)₃]BPh₄ [1], [(triphos)Fe(CO)₂] [2], [(triphos)Co(CO)₂]BPh₄ [3] and [(triphos)Ni(CO)] [4]. All these complexes are diamagnetic with the metal atom attaining the 18-outer-electron configuration.

We have now found that paramagnetic cobalt(II) carbonyl derivatives, having formulae [(triphos)Co(CO)X]BPh₄ (X = Cl, Br) are easily formed by reaction of carbon monoxide with the dimeric dihalo complexes [(triphos)Co(μ -X)₂Co(triphos)](BPh₄)₂ [5]. The analogous cyclohexyl isonitrile derivatives [(triphos)Co(CNCy)X]BPh₄ have also been prepared.

With the exception of the carbon monoxide adduct of halide bis(triethyl-

phosphine) cobalt(II) [6] no paramagnetic cobalt(II) complexes of CO have previously been isolated and structurally characterized. Some other low spin cobalt(II) carbonyl adducts has been detected in solution by spectroscopic techniques [7,8].

The title complexes have been characterized and their physical properties studied by the usual methods, and a complete X-ray structure determination of the complex [(triphos)Co(CO)Br]BPh₄ has been carried out.

Experimental

The ligand triphos [9] and the complexes [(triphos)Co(μ -X)₂Co(triphos)]-(BPh₄)₂, X = Cl, Br, [5] were prepared by the methods previously described. All other chemicals were reagent grade and were used without further purification. All the reactions were carried out under dry nitrogen, using deoxygenated solvents, and the complexes were dried in a stream of dry nitrogen.

Preparation of [(triphos)Co(CO)X]BPh₄, X = Cl, Br

Carbon monoxide was bubbled at 0°C through a solution of the complex [(triphos)Co(μ -Cl)₂Co(triphos)](BPh₄)₂ (1 mmol) or the analogous bromo derivative in 50 ml of CH₂Cl₂. Butanol (20 ml) was added to the resulting green solution and a fast stream of nitrogen was passed through the solution until crystallization began. The crystalline green product was filtered off and washed with ethanol and light petroleum ether. $\nu(\text{CO}) = 2060 \text{ cm}^{-1}$ for both complexes.

Preparations of [(triphos)Co(CO)I]BPh₄

Cobalt(II) iodide (1 mmol) in 10 ml of ethanol was added to a solution of the ligand triphos (1 mmol) in 30 ml of CH₂Cl₂. Carbon monoxide was bubbled at 0°C through the solution, which suddenly turned green. After addition of 1 mmol of NaBPh₄ and evaporation of the solvent in a stream of nitrogen green crystals separated. Samples of this compound obtained from several preparations were always a mixture of [(triphos)Co(CO)I]BPh₄ and [(triphos)Co(CO)₂]BPh₄, as shown by elemental analysis, magnetic measurements, and by the infrared spectrum, which shows, besides the band at 2050 cm⁻¹ attributable to the CO stretching frequency of the complex [(triphos)Co(CO)I]BPh₄ (see below), two bands at 2030 and 1972 cm⁻¹ of the two CO stretching frequencies of the cobalt(I) complex [(triphos)Co(CO)₂]BPh₄ [3].

Preparation of [(triphos)Co(CNCy)X]BPh₄C₆H₆, X = Cl, Br

The complexes were prepared by a method analogous to that used for the above compounds, by using CNCy in place of CO. The green complexes were recrystallized from methylene chloride, benzene and ethanol. $\nu(\text{CN}) = 2195 \text{ cm}^{-1}$ for both complexes.

Physical measurements

Infrared and electronic spectra, conductivity and magnetic susceptibility measurements were recorded as previously described [11]. The analytical and magnetic data of the complexes are reported in Table 1. Table 2 lists the electronic spectral data.

TABLE 1
ANALYTICAL AND MAGNETIC DATA FOR THE COMPLEXES

Compound	Found (calcd.) (%)					μ_{eff} (293 K) μ_{B}
	C	H	Co	Cl	N	
[(triphos)Co(CO)Cl]BPh ₄	73.79 (74.34)	5.76 (5.58)	5.45 (5.53)	3.70 (3.32)		1.86
[(triphos)Co(CO)Br]BPh ₄	71.09 (71.37)	5.47 (5.35)	5.05 (5.30)			2.00
[(triphos)Co(CNCy)Cl]BPh ₄ · C ₆ H ₆	77.20 (76.44)	6.36 (6.25)	4.73 (4.80)	2.92 (2.89)	1.06 (1.14)	1.82
[(triphos)Co(CNCy)Br]BPh ₄ · C ₆ H ₆	73.97 (73.76)	6.11 (6.03)	4.43 (4.64)		1.16 (1.10)	1.97

Collection and reduction of X-ray intensity data

The crystal used, very irregularly shaped, had dimensions 0.34 × 0.25 × 0.22 mm. The crystals belong to monoclinic system with extinctions (*h*0*l* with *h* odd and 0*k*0 with *k* odd) characteristic of the space group *P*2₁/*a*. Unit cell parameters were determined from a least-squares refinement of the setting angles of 24 reflections carefully centered on a Philips PW 1100 automatic diffractometer. The unit cell dimensions are *a* 20.255(8), *b* 20.664(9), *c* 13.301(5) Å; β 97.24(5)°. The observed density of 1.33 g cm⁻³, measured by flotation, agrees with the value of 1.338 g cm⁻³ calculated for four formula units [(triphos)Co(CO)Br]BPh₄ per cell.

Data collection was carried out using Mo-*K*_α (λ 0.7107 Å) radiation monochromatized by a graphite crystal at a take off angle of 3.5°. Reflections within 2θ ≤ 45° were collected using the ω - 2θ scan technique. The scan range was calculated according to the formula of Alexander and Smith [11], scan range = A + B tanθ with A = 0.8 and B = 0.69. The scan speed was 0.08° per second, stationary background measurements were taken before and after each scan for a time equal to half the scan time. The intensities of three standard reflections

(Continued on p. 284)

TABLE 2
MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA OF THE COMPLEXES

Compound		Absorption Max ^a cm ⁻¹ (ϵ_{M} for solutions)
[(triphos)Co(CO)Cl]BPh ₄	A	8350, 15,150, 25,000 sh
	B	8450(200), 15,400(969)
[(triphos)Co(CO)Br]BPh ₄	A	8050, 14,900, 26,000 sh
	B	8350(145), 15,250(810), 27,000 sh
[(triphos)Co(CO)I]BPh ₄	A	7800, 14,700, 25,000 sh
	B	8050, 15,150
[(triphos)Co(CNCy)Cl]BPh ₄	A	8500, 14,700, 25,000 sh
	B	8450(168), 14,700(918)
[(triphos)Co(CNCy)Br]BPh ₄	A	8300, 14,500, 25,000 sh
	B	8300(174), 14,500(964), 25,000 sh

^a Key: A, solid; B, 1,2-dichloroethane solution.

TABLE 3
POSITIONAL AND THERMAL PARAMETERS FOR [(triphos)Co(CO)Br]BPh₄

Atom	x	y	z	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.31009(5)	0.12696(5)	0.50517(9)	0.0605(7)	0.0419(6)	0.0912(9)	-0.0050(6)	-0.0072(7)	-0.0030(7)
Co	0.29943(5)	0.01345(6)	0.48309(9)	0.0304(7)	0.0389(7)	0.0423(6)	-0.0054(6)	0.0000(6)	-0.0004(7)
P(1)	0.3148(1)	-0.0650(1)	0.3725(2)	0.032(1)	0.039(1)	0.040(2)	-0.001(1)	0.003(1)	0.000(1)
P(2)	0.2583(1)	-0.0552(1)	0.5963(2)	0.037(1)	0.042(2)	0.034(1)	0.000(1)	0.001(1)	0.000(1)
P(3)	0.1937(3)	0.0265(1)	0.4043(2)	0.033(1)	0.040(1)	0.042(2)	0.002(1)	0.003(2)	0.000(1)
O	0.4386(3)	0.0160(3)	0.5708(6)	0.043(4)	0.075(5)	0.113(6)	-0.001(4)	-0.017(5)	-0.006(5)
C	0.3841(5)	0.0122(4)	0.5385(7)	0.045(7)	0.047(6)	0.058(7)	-0.005(6)	-0.001(6)	-0.002(6)
C(1)	0.1364(4)	-0.1706(4)	0.3837(7)	0.048(2)					
C(2)	0.1862(4)	-0.1139(4)	0.4154(7)	0.040(2)					
C(3)	0.2538(4)	-0.1301(4)	0.3793(6)	0.038(2)					
C(4)	0.1916(4)	-0.1089(4)	0.5327(6)	0.039(2)					
C(5)	0.1544(4)	-0.0515(4)	0.3657(7)	0.040(2)					
B	0.3951(5)	0.2556(5)	-0.0151(8)	0.045(3)					

^a The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^2 + U_{22}h^2b^2 + U_{33}l^2c^2 + 2U_{12}hka^*b^* + \dots)]$.

TABLE 4

THERMAL AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS

Atom	x	y	z	U (Å ²)
C(6)	0.3098(3)	-0.0357(2)	0.2440(5)	0.037(2)
C(7)	0.2675(3)	-0.0623(2)	0.1637(6)	0.056(3)
C(8)	0.2701(3)	-0.0404(2)	0.0650(5)	0.072(3)
C(9)	0.3151(3)	0.0081(2)	0.0467(5)	0.074(3)
C(10)	0.3574(3)	0.0347(2)	0.1271(5)	0.062(3)
C(11)	0.3548(3)	0.0128(2)	0.2257(5)	0.053(3)
C(12)	0.3942(3)	-0.1097(3)	0.3855(3)	0.040(2)
C(13)	0.4230(3)	-0.1266(3)	0.2992(3)	0.052(3)
C(14)	0.4822(3)	-0.1620(3)	0.3087(3)	0.060(3)
C(15)	0.5126(3)	-0.1805(3)	0.4044(3)	0.053(3)
C(16)	0.4838(3)	-0.1636(3)	0.4906(3)	0.059(3)
C(17)	0.4246(3)	-0.1282(3)	0.4812(3)	0.052(3)
C(18)	0.2212(3)	-0.0189(2)	0.6996(5)	0.040(2)
C(19)	0.1803(3)	-0.0559(2)	0.7541(5)	0.052(3)
C(20)	0.1523(3)	-0.0284(2)	0.8347(5)	0.059(3)
C(21)	0.1653(3)	0.0362(2)	0.8608(5)	0.059(3)
C(22)	0.2062(3)	0.0732(2)	0.8064(5)	0.061(3)
C(23)	0.2342(3)	0.0457(2)	0.7258(5)	0.052(3)
C(24)	0.3194(3)	-0.1107(3)	0.6650(4)	0.041(2)
C(25)	0.3183(3)	-0.1779(3)	0.6538(4)	0.059(3)
C(26)	0.3702(3)	-0.2153(3)	0.7024(4)	0.074(3)
C(27)	0.4232(3)	-0.1855(3)	0.7622(4)	0.072(3)
C(28)	0.4244(4)	-0.1184(3)	0.7734(4)	0.073(3)
C(29)	0.3725(3)	-0.0810(3)	0.7248(4)	0.057(3)
C(30)	0.1367(3)	0.0686(3)	0.4797(4)	0.042(2)
C(31)	0.1410(3)	0.1360(3)	0.4828(4)	0.059(3)
C(32)	0.1008(3)	0.1713(3)	0.5410(4)	0.071(3)
C(33)	0.0565(3)	0.1392(3)	0.5960(4)	0.073(3)
C(34)	0.0522(3)	0.0718(3)	0.5929(4)	0.067(3)
C(35)	0.0923(3)	0.0365(3)	0.5347(4)	0.056(3)
C(36)	0.1796(2)	0.0735(3)	0.2876(5)	0.037(2)
C(37)	0.1153(2)	0.0720(3)	0.2355(5)	0.056(3)
C(38)	0.1006(2)	0.1064(3)	0.1452(5)	0.063(3)
C(39)	0.1502(2)	0.1422(3)	0.1069(5)	0.066(3)
C(40)	0.2146(2)	0.1437(3)	0.1589(5)	0.073(3)
C(41)	0.2293(2)	0.1093(3)	0.2493(5)	0.058(3)
C(42)	0.4287(3)	0.3179(2)	-0.0694(4)	0.042(2)
C(43)	0.4871(3)	0.3139(2)	-0.1146(4)	0.051(3)
C(44)	0.5165(3)	0.3700(2)	-0.1471(4)	0.062(3)
C(45)	0.4873(3)	0.4301(2)	-0.1343(4)	0.063(3)
C(46)	0.4289(3)	0.4342(2)	-0.0890(4)	0.061(3)
C(47)	0.3996(3)	0.3781(2)	-0.0565(4)	0.051(3)
C(48)	0.4084(3)	0.2620(3)	0.1115(5)	0.042(2)
C(49)	0.4412(3)	0.3154(3)	0.1585(5)	0.060(3)
C(50)	0.4488(3)	0.3208(3)	0.2639(5)	0.078(3)
C(51)	0.4236(3)	0.2728(3)	0.3223(5)	0.073(3)
C(52)	0.3909(3)	0.2194(3)	0.2752(5)	0.077(3)
C(53)	0.3833(3)	0.2139(3)	0.1699(5)	0.064(3)
C(54)	0.3115(4)	0.2608(3)	-0.0550(5)	0.063(3)
C(55)	0.2870(4)	0.2470(3)	-0.1554(5)	0.090(4)
C(56)	0.2189(4)	0.2515(3)	-0.1878(5)	0.097(4)
C(57)	0.1752(4)	0.2697(3)	-0.1197(5)	0.097(4)
C(58)	0.1996(4)	0.2834(3)	-0.0192(5)	0.113(5)
C(59)	0.2678(4)	0.2790(3)	0.0132(5)	0.082(3)
C(60)	0.4283(2)	0.1847(3)	-0.0446(5)	0.048(3)
C(61)	0.3905(2)	0.1357(3)	-0.0961(5)	0.071(3)
C(62)	0.4207(2)	0.0774(3)	-0.1174(5)	0.093(4)
C(63)	0.4886(2)	0.0682(3)	-0.0873(5)	0.086(4)
C(64)	0.5264(2)	0.1172(3)	-0.0357(5)	0.077(3)
C(65)	0.4962(2)	0.1754(3)	-0.0144(5)	0.061(3)

measured every 90 minutes showed no systematic trend.

After correction for background the intensities were assigned standard deviations calculated as described elsewhere [12] using the value of 0.05 for the instability factor K . 3648 reflections having $I \geq 3\sigma(I)$ were considered observed and included in the following calculations. The data were corrected for Lorentz-polarization effects but no absorption correction was applied, the linear absorption coefficient μ being 11.3 cm^{-1} .

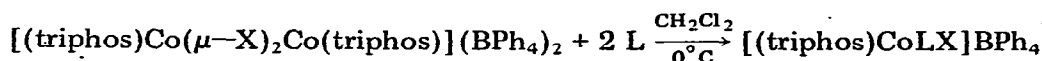
Solution and refinement of the structure

Calculations were carried out on a CII 10070 computer using the SHELX-76 programs [13]. Scattering factors were taken from ref. 14. The structure was solved by the heavy atom technique. The position of the bromine and the cobalt atoms were derived from the Patterson function. All the other non-hydrogen atoms were located from successive Fourier maps. Full-matrix least-squares refinements were carried out, the function minimized being $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $1/\sigma^2(F_o)$. The agreement factors R and R_w are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. Anisotropic thermal parameters were used only for the atoms within the coordination sphere. The carbon atoms of the phenyl ring were treated as rigid groups of D_{6h} symmetry with C—C 1.395 Å and individual thermal parameters. A few cycles of refinement lowered the R factor to 0.068. At this point the hydrogen atoms were introduced in calculated positions with C—H invariant at 1.08 Å. Two final cycles lowered the R and R_w factors to 0.057 and 0.059 respectively. Final positional and thermal parameters are listed in Tables 3 and 4.

Results and discussion

Paramagnetic carbonyl complexes of cobalt(II) are very rare: the only paramagnetic complexes of this type so far isolated are the carbonyl complexes of cobalt(II) with halides and triethylphosphine the five-coordinated stereochemistry of which was deduced from indirect evidence [6].

Our results show that carbon monoxide reacts readily at 0°C and 1 atmosphere with the dimeric complexes $[(\text{triphos})\text{Co}(\mu\text{-X})_2\text{Co}(\text{triphos})](\text{BPh}_4)_2$, X = Cl, Br, giving crystalline compounds of formula $[(\text{triphos})\text{Co}(\text{CO})\text{X}]\text{BPh}_4$. The



analogous cyclohexyl isonitrole derivatives were prepared using cyclohexyl isonitrile, CNCy, in place of carbon monoxide. The iodo-derivative $[(\text{triphos})\text{Co}(\text{CO})\text{I}]\text{BPh}_4$ was prepared by treatment of CoI_2 and triphos with carbon monoxide and NaBPh_4 *. However the samples of this complex obtained from several preparations always contained the cobalt(I) complex $[(\text{triphos})\text{Co}(\text{CO})_2](\text{BPh}_4)$ in variable amounts [3]. The formation of small amounts of this cobalt(I) carbonyl derivative also takes place when carbon monoxide is bubbled through solutions of the bromo and chloro derivative for a long time (>2 h) at

* The dimeric iodo complex $[(\text{triphos})\text{Co}(\mu\text{-I}_2)\text{Co}(\text{triphos})](\text{BPh}_4)_2$ could not be prepared.

a temperature $>40^{\circ}\text{C}$. The amounts were larger for the chloro derivative, showing that reduction of the cobalt(II) is favoured by the presence of easily oxidable anions ($\text{I} \gg \text{Br} > \text{Cl}$). Similar behaviour has been previously observed in other reactions [7,15].

All the complexes are soluble in methylene chloride, 1,2-dichloroethane and acetone, and the isonitrile derivatives are also soluble in benzene.

The $[(\text{triphos})\text{Co}(\text{CO})\text{X}]\text{BPh}_4$ complexes slowly decompose in air, both in the solid state and in solution. If nitrogen is passed through the deoxygenated solution of such complexes above 40°C , carbon monoxide is slowly displaced from the complexes and the compounds $[(\text{triphos})\text{CoX}]$ [15] are formed. The cyclohexyl isonitrile derivatives are air stable.

All the complexes are paramagnetic with μ_{eff} , at room temperature, in the range $1.82\text{--}2.00 \mu_{\text{B}}$ indicative of a doublet ground state. The complexes are 1 : 1 electrolytes in 1,2-dichloroethane.

The IR spectra, both in the solid state (Nujol mulls) and in methylene chloride solution, show a strong $\nu(\text{CO})$ band at $2050\text{--}2060 \text{ cm}^{-1}$ for the carbonyl derivatives and a strong $\nu(\text{CN})$ band at 2195 cm^{-1} for the cyclohexyl derivatives.

The electronic spectra of the compounds are summarized in Table 2. The reflectance spectra are closely similar to the corresponding absorption spectra in 1,2-dichloroethane. A bathochromic shift is observed on going from the chloro to iodo derivative. Replacement of carbon monoxide by cyclohexyl isonitrile does not produce significant changes in the spectra. The spectra are fully comparable with those of other five-coordinated low spin d^7 complexes with intermediate geometry [16].

The molecular structure of the complex $[(\text{triphos})\text{Co}(\text{CO})\text{Br}]\text{BPh}_4$ consists of discrete $[(\text{triphos})\text{Co}(\text{CO})\text{Br}]^+$ cations and BPh_4^- anions. Figure 1 shows a perspective view of the cation. Bond distances and angles with their estimated

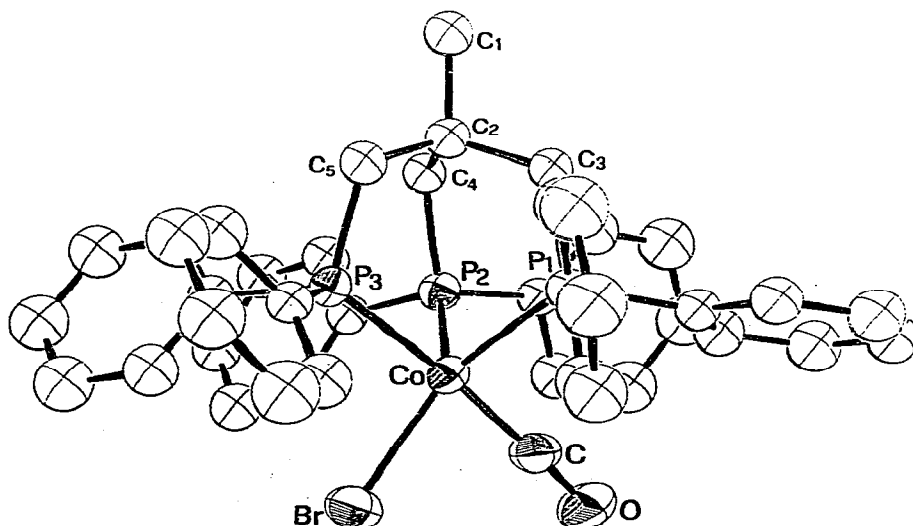


Fig. 1. Perspective view of the $[(\text{triphos})\text{Co}(\text{CO})\text{Br}]^+$ cation.

standard deviations are given in Table 5. The metal atom is coordinated by the three phosphorus atoms of the triphos ligand, by the bromine atom, and by the CO group. The coordination geometry may be regarded either as a distorted trigonal bipyramid with P(3) and CO at the axial positions (P(3)—Co—CO angle $173.0(1)^\circ$) or as a distorted square pyramid with P(2) in the apical position. On the latter view the metal atom lies 0.44 Å above the basal plane while the apical Co—P bond distance is longer than the basal bonds. This lengthening is a common feature of low spin square pyramidal cobalt(II) and nickel(II) complexes and may be simply attributed to the steric properties of the *d* electrons [17]. The values of the Co—P bond distances, ranging from 2.241(2) to 2.290(3) Å

TABLE 5
SELECTED BOND LENGTHS (Å) AND ANGLES (deg)

About the metal atom			
Co—Br	2.372(1)	Co—P(3)	2.259(2)
Co—P(1)	2.241(2)	Co—C	1.795(9)
Co—P(2)	2.290(3)	C—O	1.134(9)
P(1)—Co—P(2)	94.4(1)	P(2)—Co—C	97.2(3)
P(1)—Co—P(3)	89.4(1)	P(3)—Co—Br	90.7(1)
P(2)—Co—P(3)	89.4(1)	P(3)—Co—C	173.0(3)
P(1)—Co—Br	140.9(1)	Br—Co—C	83.5(3)
P(1)—Co—C	92.5(3)	Co—C—O	174.8(8)
P(2)—Co—Br	124.7(1)		
In the rest of the cation			
P(1)—C(3)	1.836(7)	P(3)—C(30)	1.839(6)
P(1)—C(6)	1.804(6)	P(3)—C(36)	1.823(6)
P(1)—C(12)	1.842(6)	C(1)—C(2)	1.57(1)
P(2)—C(4)	1.861(7)	C(2)—C(3)	1.54(1)
P(2)—C(18)	1.810(6)	C(2)—C(4)	1.55(1)
P(2)—C(24)	1.842(6)	C(2)—C(5)	1.55(1)
P(3)—C(5)	1.841(7)		
Co—P(1)—C(3)	109.9(3)	Co—P(3)—C(36)	119.7(2)
Co—P(1)—C(6)	112.6(2)	C(5)—P(3)—C(30)	106.8(3)
Co—P(1)—C(12)	120.1(2)	C(5)—P(3)—C(36)	102.3(2)
C(3)—P(1)—C(6)	109.5(3)	C(30)—P(3)—C(36)	99.9(2)
C(3)—P(1)—C(12)	102.2(3)	C(1)—C(2)—C(3)	108.6(6)
C(6)—P(1)—C(12)	101.7(2)	C(1)—C(2)—C(4)	106.5(7)
Co—P(2)—C(4)	111.5(3)	C(1)—C(2)—C(5)	106.8(6)
Co—P(2)—C(18)	117.2(2)	C(3)—C(2)—C(4)	111.8(6)
Co—P(2)—C(24)	116.1(2)	C(3)—C(2)—C(5)	112.6(7)
C(4)—P(2)—C(18)	104.3(3)	C(4)—C(2)—C(5)	110.3(7)
C(4)—P(2)—C(24)	104.8(3)	P(1)—C(3)—C(2)	119.0(5)
C(18)—P(2)—C(24)	101.4(3)	P(2)—C(4)—C(2)	117.0(5)
Co—P(3)—C(5)	111.8(3)	P(3)—C(5)—C(2)	117.9(5)
Co—P(3)—C(30)	114.8(2)		
In the anion			
B—C(42)	1.66(1)	B—C(54)	1.71(1)
B—C(48)	1.68(1)	B—C(60)	1.58(1)
C(42)—B—C(48)	110.6(6)	C(48)—B—C(54)	109.5(6)
C(42)—B—C(54)	105.0(6)	C(48)—B—C(60)	106.6(6)
C(42)—B—C(60)	111.2(6)	C(54)—B—C(60)	113.1(6)

are comparable with those reported for other five-coordinate cobalt(II) complexes where the triphos ligand is involved [5,18]. For the Co—CO bond distance of 1.795(9) Å there are no other cobalt(II) carbonyl complexes for comparison; however it appears rather long compared with the values of 1.73(1) and 1.63(2) Å reported for the five-coordinate cobalt(I) carbonyl complexes $[\text{Co}(3\text{-}3\text{-P}_3)(\text{P}(\text{OMe})_3)\text{CO}]^+$ and $[\text{Co}(\text{np}_3)\text{CO}]^+$, where 3-3-P₃ and np₃ are PhP-(CH₂-CH₂-CH₂-PPh₂)₂ and N(CH₂-CH₂-PPh₂)₃, respectively [19,20]. This fact together with the value of the C—O bond distance of 1.134(9) Å is indicative of a weak metal—carbonyl bond. The C—O bond distance however, has not been corrected for possible librational shortening. Indirect evidence for the weakness of the metal—carbonyl interaction is provided by the very high value of the stretching frequency of 2060 cm⁻¹ compared with values of 1935 and 1930 cm⁻¹ reported for the two cobalt(I) complexes mentioned above [19,20].

The lability of the Co—CO bond in these complexes, which may be compared with that in the copper(I) carbon monoxide adducts [21], makes these molecules potentially suitable for carbon monoxide activation in catalytic processes.

Acknowledgements

The authors thank Mr. F. Cecconi for technical assistance, and Mr. G. Vignozzi and Mr. F. Nuzzi for microanalyses.

References

- 1 J. Ellerman and H.A. Lindner, *Z. Naturforsch.*, **31b** (1976) 1350.
- 2 H. Behrens, H.D. Feilner and E. Lindner, *Z. Anorg. Allg. Chem.*, **385** (1971) 321.
- 3 P. Dapporto, S. Midollini and L. Sacconi, *Inorg. Chem.*, **14** (1975) 1643.
- 4 J. Chatt and F.A. Hart, *J. Chem. Soc.*, (1965) 812.
- 5 C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chem.*, **14** (1975) 2513.
- 6 G. Booth and J. Chatt, *J. Chem. Soc.*, (1962) 2099.
- 7 M. Bressan, B. Corain, P. Rigo and A. Turco, *Inorg. Chem.*, **9** (1970) 1733.
- 8 B.B. Wayland, M.E. Abd-Elmageed and L.F. Mehne, *Inorg. Chem.*, **14** (1975) 1456 and references therein.
- 9 W. Hewertson and M.R. Watson, *J. Chem. Soc.*, (1962) 1490.
- 10 L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, **6** (1967) 262.
- 11 L.E. Alexander and G.S. Smith, *Acta Crystallogr.*, **17** (1964) 1195.
- 12 P.W.R. Corfield, R.J. Doedens and J.A. Ibers, *Inorg. Chem.*, **6** (1976) 197.
- 13 "Shelx-76" System of Programs, G.M. Sheldrick, (1976).
- 14 "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, 1974.
- 15 L. Sacconi and S. Midollini, *J. Chem. Soc. Dalton*, (1972) 1213.
- 16 M. Di Vaira, *J. Chem. Soc. Dalton*, (1975) 2360; M. Di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, **16** (1977) 1518.
- 17 P.L. Orioli, *Coord. Chem. Rev.*, **6** (1971) 285.
- 18 C. Benelli, M. Di Vaira, G. Noccioli and L. Sacconi, *Inorg. Chem.*, **16** (1977) 182.
- 19 R. Mason, G.R. Scollary, D.L. Dubois and D.W. Meek, *J. Organometal. Chem.*, **114** (1976) C30.
- 20 C.A. Ghilardi, A. Sabatini and L. Sacconi, *Inorg. Chem.*, **15** (1976) 2763.
- 21 M.R. Churchill, B.G. De Boer, F.J. Rotella, O.M. Abu Salah and M.I. Bruce, *Inorg. Chem.*, **14** (1975) 2051; R.R. Gagné, J.L. Allison, R.S. Gall and C.A. Koval, *J. Amer. Chem. Soc.*, **99** (1977) 7170; M. Pasquali, C. Floriani and A. Gaetani Manfredotti, *J. Chem. Soc. Chem. Commun.*, (1978) 921.