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SYNTHESIS AND X-RAY STRUCTURE OF THE DINUCLEAR COBALT(0) COMPLEX $(PhC{\equiv}CPh)Co_2(CO)_4(triphos)$

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Summary

Reaction of the complex $(PhC{\equiv}CPh)Co_2(CO)_6$ with 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) under UV irradiation gave black-green crystals of $(PhC{\equiv}CPh)Co_2(CO)_4$(triphos). The structure of this complex was determined by X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$ with cell dimensions a 11.277(4), b 12.505(4), c 18.357(6) Å, α 89.15(4), β 76.19(4), γ 85.35(4)°, $Z = 2$. The structure was solved by three-dimensional Patterson and Fourier synthesis and refined by least-squares techniques to a final conventional R factor of 0.086. The structure consists of discrete dinuclear molecules where the cobalt atoms are hexacoordinated in a distorted octahedral arrangement.

Introduction

Much structural information has been collected on metal complexes derived from $(RC{\equiv}CR)Co_2(CO)_6$ by replacement of carbonyl groups with various phosphines and arsines [1—3]. Among such compounds only the structures of complexes containing monodentate or bidentate bridging phosphines and arsines have been completely elucidated by the X-ray diffraction method [2,3]. In this work we report the synthesis and the crystal structure of the complex $(PhC{\equiv}CPh)Co_2(CO)_4$(triphos) obtained by the reaction of the potentially tridentate tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane(triphos) with $(PhC{\equiv}CPh)Co_2(CO)_6$. The triphosphine behaves as a bidentate ligand, displacing only two carbonyl groups, both on the same cobalt atom, and retaining an uncoordinated phosphorus atom. The influence of the chelate ligand on the molecular structure, and especially on the metal—metal bond, is discussed.

TABLE 1

ATOMIC[a] PARAMETERS (X10^4) FOR THE STRUCTURE OF (PhC≡CPh)$Co_2(CO)_4$(triphos)

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	−5018(1)	2467(1)	2362(1)	334(10)	278(10)	311(11)	−29(8)	−94(9)	6(8)
Co(2)	−6586(2)	1914(1)	1704(1)	439(12)	443(11)	455(12)	−41(9)	−185(10)	−9(9)
P(1)	−4256(3)	2681(3)	3345(2)	382(21)	324(20)	341(21)	−58(16)	−107(18)	18(16)
P(2)	−3160(3)	2364(3)	1542(2)	346(20)	284(19)	323(20)	−24(15)	−93(17)	6(16)
P(3)	−1696(3)	5720(3)	2524(2)	463(22)	373(22)	443(23)	−63(18)	−113(19)	8(18)

F rel. scale factor = 27042

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

Experimental

Methanol, methylene chloride and petroleum ether were of reagent grade and were used without further purification. Tetrahydrofuran was purified by distillation over $LiAlH_4$. The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane and the complex $(PhC{\equiv}CPh)Co_2(CO)_6$ were prepared as previously described [4,5]. $Co_2(CO)_8$ was purchased from Strem Chemicals Inc., Dauvers, Mass. The reaction was carried out using oxygen-free solvents under nitrogen.

Preparation of the complex

To a solution of the complex $(PhC{\equiv}CPh)Co_2(CO)_6$ (1 mmol, 0.46 g) in THF (40 ml) was added the phosphine (1.2 mmol, 0.75 g) in THF (15 ml). The mixture was exposed to ultraviolet irradiation for 3 h. The solvent was removed under vacuum and the resulting residue was extracted with methylene chloride (20 ml). Addition of methanol (35 ml) and slow evaporation of the solvent gave black-green crystals, which were recrystallized from the same solvents and dried under a nitrogen stream. Anal. Found: C, 68.72; H, 4.90; Co, 11.04. $C_{59}H_{49}CO_2O_4P_3$ calcd.: C, 68.61; H, 4.78; Co, 11.41%.

Crystal data and data collection

The crystal used for data collection was a parallelepiped of dimensions 0.30 × 0.24 × 0.05 mm. The crystals are triclinic and belong to the space group $P\bar{1}$, with two $(PhC{\equiv}CPh)Co_2(CO)_4$(triphos) formulae in the unit cell which has the following dimensions: a 11.277(4), b 12.505(4), c 18.357(6) Å, α 89.15(4), β 76.19(4), γ 85.35(4)°. Intensity data were collected on an automatic computer-controlled diffractometer Philips PW 1100, equipped with a graphite monochromator, using Mo-K_α radiation. All reflections with $4° \leqslant 2\theta \leqslant 50°$ were measured using the ω—2θ scan technique with a scan speed of 0.07°/s in a range of 0.7° across the peak. Background times were taken equal to half the scan time on each side of the peak. Three standard reflections were measured every 100 minutes during data collection, but no significant variation was noticed, The intensity data were corrected for Lorentz and polarization effects; the standard deviation $\sigma(I)$ was estimated as described elsewhere [6] with an instability factor equal to 0.03. A reflection was considered unobserved if the net intensity I was $<3\sigma(I)$. From the 8817 total reflections 3786 had intensity $\geqslant 3\sigma(I)$. An absorption correction, μ(Mo-K_α) 8.00 cm^{-1}, was applied by a numerical method: transmission factors varied between 0.83 and 0.96. Atomic scattering factors were taken from the compilation of Cromer and Waber for all non-hydrogen atoms [7] and those for hydrogen atoms from Stewart et al. [8]. Corrections for anomalous dispersion effects for cobalt and phosphorus atoms were applied in the refinement stage [9].

Structure solution and refinement

The position of the cobalt and phosphorus atoms were obtained from a Patterson synthesis. The other non-hydrogen atoms were obtained from successive F_0 Fourier maps. The structure was refined by a full-matrix least-square program [10]. The minimized function is $\Sigma w(|F_0| - |F_c|)^2$, where w is the weight

TABLE 2

ATOMIC PARAMETERS ($\times 10^4$) FOR THE STRUCTURE OF (PhC CPh)$Co_2(CO)_4$(triphos)

Atom	x	y	z	U(Å^2)
O(1)	−5562(8)	4772(8)	2233(5)	642(27)
O(2)	−8506(11)	454(10)	1909(7)	1054(40)
O(3)	−7839(10)	4041(9)	1615(6)	824(33)
O(4)	−5252(11)	1287(9)	175(7)	1033(40)
C(1)	−5314(11)	3849(10)	2281(7)	440(34)
C(2)	−7749(14)	1087(12)	1784(9)	710(45)
C(3)	−7307(13)	3190(11)	1611(8)	568(40)
C(4)	−5759(14)	1519(12)	800(9)	689(45)
C(5)	−6607(11)	1958(10)	2793(7)	390(32)
C(6)	−5878(11)	1097(10)	2462(7)	386(32)
C(7)	−1101(11)	2344(10)	2685(7)	497(36)
C(8)	−1888(10)	3396(9)	2543(7)	328(30)
C(9)	−3032(11)	3615(9)	3162(7)	354(32)
C(10)	−2164(10)	3370(9)	1760(7)	372(31)
C(11)	−1030(11)	4318(9)	2562(7)	390(32)

assigned to the F_0 values according to the expression $w = 1/\sigma^2(F_0)$. The carbon atoms belonging to the phenyl groups were refined using rigid-body models for the phenyl rings. The hydrogen atoms were introduced in calculated positions (C—H distance of 0.95 Å) with an isotropic thermal factor $B_H = 1 + B_{C_{attached}}$ and were not refined. Anisotropic temperature factors were used for cobalt and phosphorus atoms; isotropic temperature factors were used for the other atoms. The final refinement gave a R value of 0.086, whereas R_w, defined as $[\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2]^{1/2}$, was 0.065. A final ΔF Fourier did not show remarkable features. The final positional and thermal parameters are reported in Tables 1—4.

Results and discussion

The complex (PhC≡CPh)$Co_2(CO)_4$(triphos) is an air-stable, black-green crystalline solid. It is diamagnetic and soluble in common organic solvents. The crystal structure consists of normal packing of such discrete molecules with no

TABLE 3

FINAL LEAST SQUARES PARAMETERS FOR THE TITLE COMPLEX GROUPS [a]

Group	x'	y'	z'	θ	φ	ψ
1	−0.8613(6)	0.2403(5)	0.3892(3)	0.806(6)	1.712(7)	1.658(4)
2	−0.5562(5)	−0.1029(5)	0.2675(4)	1.767(6)	0.183(6)	1.476(6)
3	−0.6162(5)	0.3768(5)	0.4628(4)	1.072(6)	−1.050(6)	1.443(5)
4	−0.3024(5)	0.0697(5)	0.4125(3)	1.863(7)	2.353(6)	1.646(6)
5	−0.3097(5)	0.3079(5)	−0.0071(3)	1.393(6)	1.952(5)	−1.962(5)
6	−0.1643(6)	0.0255(5)	0.3218(3)	0.221(6)	−1.849(7)	2.991(8)
7	0.0251(6)	0.7034(5)	0.2891(3)	0.261(6)	0.981(10)	−1.604(8)
8	−0.1321(6)	0.6218(4)	0.0870(4)	1.354(5)	−1.597(6)	0.284(28)

[a] x', y', z' (fractional coordinates) define the origin of the working system of the group. The Goldstein definition is used for Euler angles (radians) [13].

TABLE 4

THERMAL AND DERIVED POSITIONAL PARAMETERS ($\times 10^4$) OF GROUP ATOMS.

Atom		x	y	z	$U(\mathrm{A}^2)$
C(1)	1	−7700(8)	2208(8)	3414(4)	425(34)
C(2)	1	−8094(8)	3267(8)	3625(4)	593(41)
C(3)	1	−9160(8)	3494(8)	4182(4)	807(50)
C(4)	1	−9830(8)	2662(8)	4529(4)	792(48)
C(5)	1	−9436(8)	1603(8)	4319(4)	832(52)
C(6)	1	−8371(8)	1376(8)	3761(4)	632(43)
C(1)	2	−5738(8)	−88(5)	2584(6)	461(36)
C(2)	2	−5557(8)	−793(5)	1980(6)	579(39)
C(3)	2	−5352(8)	−1891(5)	2087(6)	717(46)
C(4)	2	−5328(8)	−2283(5)	2798(6)	737(46)
C(5)	2	−5509(8)	−1578(5)	3401(6)	712(45)
C(6)	2	−5714(8)	−480(5)	3294(6)	586(40)
C(1)	3	−5424(7)	3342(7)	4118(5)	413(33)
C(2)	3	−6027(7)	2731(7)	4711(5)	550(38)
C(3)	3	−6889(7)	3228(7)	5306(5)	699(44)
C(4)	3	−7147(7)	4336(7)	5307(5)	782(49)
C(5)	3	−6543(7)	4947(7)	4714(5)	678(44)
C(6)	3	−5682(7)	4450(7)	4120(5)	554(38)
C(1)	4	−3582(7)	1557(8)	3807(4)	451(35)
C(2)	4	−3205(7)	1705(8)	4464(4)	534(37)
C(3)	4	−2647(7)	846(8)	4782(4)	628(42)
C(4)	4	−2466(7)	−162(8)	4443(4)	703(44)
C(5)	4	−2843(7)	−310(8)	3785(4)	722(45)
C(6)	4	−3401(7)	549(8)	3467(4)	496(37)
C(1)	5	−3001(7)	2815(7)	541(3)	436(33)
C(2)	5	−3544(7)	3825(7)	430(3)	511(36)
C(3)	5	−3656(7)	4133(7)	−284(3)	643(43)
C(4)	5	−3225(7)	3430(7)	−887(3)	667(42)
C(5)	5	−2682(7)	2420(7)	−777(3)	678(43)
C(6)	5	−2570(7)	2112(7)	−63(3)	544(38)
C(1)	6	−2210(8)	1105(6)	1359(5)	391(32)
C(2)	6	−2816(8)	167(6)	1459(5)	686(43)
C(3)	6	−2154(8)	−824(6)	1295(5)	1022(58)
C(4)	6	−887(8)	−878(6)	1030(5)	871(53)
C(5)	6	−281(8)	60(6)	930(5)	672(44)
C(6)	6	−943(8)	1051(6)	1094(5)	532(38)
C(1)	7	−473(7)	6475(7)	2748(4)	448(34)
C(2)	7	−687(7)	7587(7)	2734(4)	694(44)
C(3)	7	157(7)	8239(7)	2902(4)	833(51)
C(4)	7	1215(7)	7779(7)	3082(4)	759(48)
C(5)	7	1429(7)	6668(7)	3096(4)	795(49)
C(6)	7	586(7)	6016(7)	2928(4)	665(42)
C(1)	8	−1461(9)	5987(7)	1516(4)	401(33)
C(2)	8	−2463(9)	6360(7)	1239(4)	519(37)
C(3)	8	−2300(9)	6630(7)	485(4)	676(43)
C(4)	8	−1135(9)	6527(7)	8(4)	776(47)
C(5)	8	−133(9)	6153(7)	285(4)	756(46)
C(6)	8	−295(9)	5883(7)	1039(4)	589(40)

unusual intermolecular contacts. The cobalt atoms of this dinuclear complex are both hexacoordinated in a distorted octahedral arrangement. One is bonded to carbon atoms of three carbonyl groups, the other to the carbon atom of a carbonyl group and two phosphorus atoms of the triphosphine ligand. Diphenylacetylene provides two linkages on both cobalt atoms which are, further-

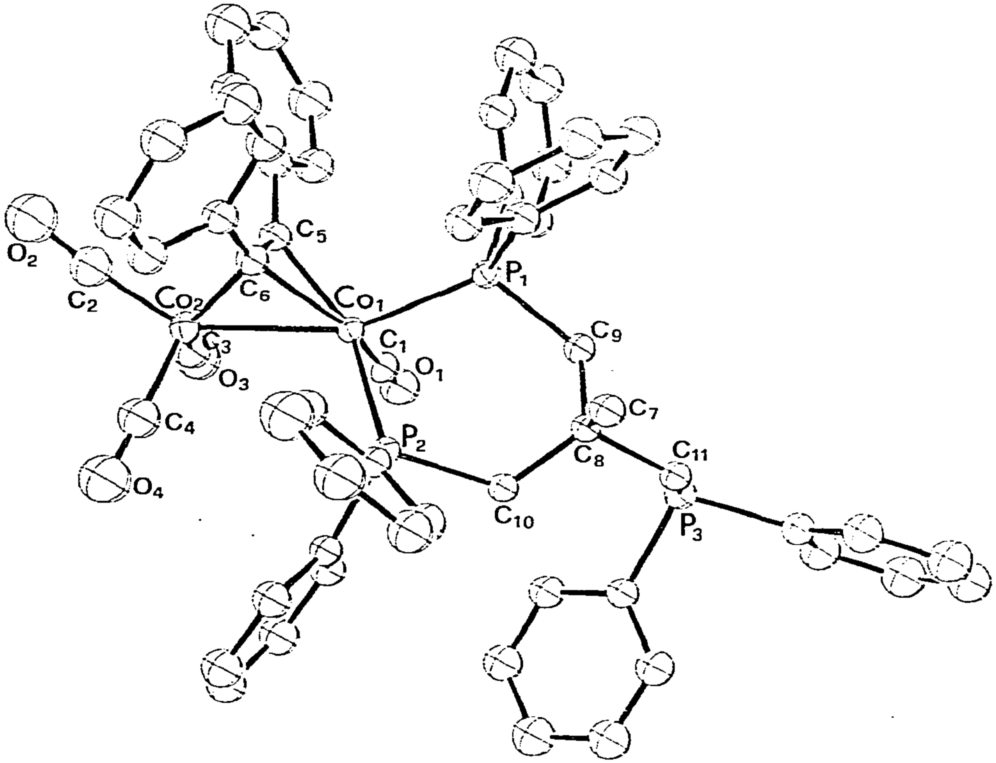

Fig. 1. Perspective view of the $(PhC{\equiv}CPh)Co_2(CO)_4$(triphos) complex.

more, linked by a metal—metal bond. Apart from the cobalt—cobalt bond, the coordination geometry of both metal atoms may be described in terms of a square pyramid with the P(1) atom of the triphos ligand and the C(2) atom of a carbonyl group at the apex of the pyramids (see Fig. 1). Both cobalt atoms are displaced from the mean basal plane toward the P(1) and C(2) atoms respectively by 0.30 and 0.26 Å. Selected bond lengths and angles are listed in Table 5. It is of interest to compare the coordination polyhedron of the present complex with that observed for other compounds which exhibit similar geometry: $(PhC{\equiv}CPh)Co_2(CO)_6$ [11], $(t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu)Co_2(CO)_6$ [12], $(HC{\equiv}CH)Co_2(CO)_4(PMe_3)_2$ [3], $(PhC{\equiv}CPh)Co_2(dpm)(CO)_4$ [2] and $(PhC{\equiv}CPh)Co_2(dam)_2(CO)_2$ * [2]. The Co(1)—Co(2) distance (2.512(3) Å) is in perfect agreement with that found in the compound $(PhC{\equiv}CPh)Co_2(dam)_2(CO)_2$, but significantly longer than in the others. In $(PhC{\equiv}CPh)Co_2(dam)_2(CO)_2$ the lengthening of the metal—metal bond is ascribed to electronic effects because of the inaccessibility of the preferred pseudoaxial sites to the bidentate bridging ligand. With the chelate ligand triphos this distance has the same value. This suggests that such lengthening may be attributable to steric hindrance due to the phenyl groups of diphenyl acetylene and triphos ligand. Similar steric hindrance is probably responsible for the broadening of the two angles P(pseudoaxial)—Co—C-

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* dpm = bis(diphenylphosphino)methane, dam = bis(diphenylarsino)methane.

TABLE 5

SELECTED BOND LENGTHS (Å) AND ANGLES (deg)

Co(1)—Co(2)	2.512(3)	C(1)—O(1)	1.17(2)
Co(1)—P(1)	2.206(4)	C(2)—O(2)	1.19(2)
Co(1)—P(2)	2.265(3)	C(3)—O(3)	1.18(2)
Co(1)—C(1)	1.74(1)	C(4)—O(4)	1.18(2)
Co(1)—C(5)	1.93(1)	C(7)—C(8)	1.58(2)
Co(1)—C(6)	2.02(1)	C(8)—C(9)	1.51(1)
Co(2)—C(2)	1.71(2)	C(8)—C(10)	1.54(2)
Co(2)—C(3)	1.76(1)	C(8)—C(11)	1.57(2)
Co(2)—C(4)	1.75(2)	P(1)—C(9)	1.85(1)
Co(2)—C(5)	2.00(1)	P(2)—C(10)	1.86(1)
Co(2)—C(6)	1.99(1)	P(3)—C(11)	1.86(1)
C(5)—C(6)	1.36(2)		

P(1)—Co(1)—P(2)	93.8(1)	C(3)—Co(2)—C(6)	138.3(6)
P(1)—Co(1)—C(1)	91.6(5)	C(4)—Co(2)—C(5)	146.6(7)
P(1)—Co(1)—C(5)	103.4(4)	C(4)—Co(2)—C(6)	109.4(6)
P(1)—Co(1)—C(6)	110.0(4)	C(5)—Co(2)—C(6)	39.8(5)
P(2)—Co(1)—C(1)	95.7(4)	Co(1)—C(1)—O(1)	177.3(12)
P(2)—Co(1)—C(5)	153.1(4)	Co(1)—C(5)—C(6)	73.4(7)
P(2)—Co(1)—C(6)	144.4(3)	Co(1)—C(6)—C(5)	66.5(7)
C(1)—Co(1)—C(5)	104.3(5)	Co(2)—C(2)—O(2)	172.0(15)
C(1)—Co(1)—C(6)	140.6(6)	Co(2)—C(3)—O(3)	174.1(12)
C(5)—Co(1)—C(6)	40.1(5)	Co(2)—C(4)—O(4)	176.2(15)
C(2)—Co(2)—C(3)	103.0(7)	Co(2)—C(5)—C(6)	70.0(8)
C(2)—Co(2)—C(4)	97.7(7)	Co(2)—C(6)—C(5)	70.2(8)
C(2)—Co(2)—C(5)	96.6(7)	C(5)—C(6)—C(1,2)	137.9(10)
C(2)—Co(2)—C(6)	93.0(7)	C(6)—C(5)—C(1,1)	139.7(10)
C(3)—Co(2)—C(5)	106.3(7)	Co(1)—C(5)—Co(2)	79.5(4)
C(3)—Co(2)—C(5)	99.5(6)	Co(1)—C(6)—Co(2)	77.5(4)

(bridging): 110.0(4) and 103.4(4)° compared to 102.2 and 96.9° in the compound $(HC{\equiv}CH)Co_2(CO)_4(PMe_3)_2$ which does not have phenyl groups on the bridging acetylene or on the phosphine. The bond distances Co—L(pseudoaxial) are considerably shorter than the corresponding Co—L(pseudoequatorial) distances (see Table 5). Such shortening is observed in all the complexes mentioned above and may be attributable to the particularly distorted octahedral configuration around cobalt atoms which does not permit a linear array of P(1)—Co(1)—Co(2) and C(2)—Co(2)—Co(1) atoms. The two bonds from Co(1) to acetylenic carbon atoms are not equal (Co(1)—C(5) = 1.93(1) Å, Co(1)—C(6) 2.02(1) Å). We are inclined to ascribe the shortening of the Co(1)—C(5) distance to the replacement of the carbonyl group opposite to the C(5) atom by a poorer π-electron acceptor such as a phosphine.

The IR spectrum, in Nujol mull, shows four bands in the ν(CO) stretching region at 2040, 1990, 1976 and 1925 cm^{-1}. The last value is consistent with the presence of a unique carbonyl group on the substituted cobalt atom, but is markedly lower than the corresponding values for complexes which, on the basis of IR and NMR data, were assumed to have a chelating bidentate phosphine ligand [1].

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