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Crystal structures of the dimeric cobalt compounds [Co(PPhMe₂)(CO)₃]₂ and [Co₂(PPhMe₂)₃(CO)₅]

Simon A. Llewellyn *, Malcolm L.H. Green, Andrew R. Cowley

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK

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Dedicated to Professor Michael Mingos, FRS, in recognition of his outstanding contributions to chemistry.

Abstract

The molecular structures of the dimeric cobalt compounds $[Co(PPhMe_2)(CO)_3]_2$ and $[Co_2(PPhMe_2)_3(CO)_5]$ have been characterised by X-ray crystallography. The compound $[Co_2(PPhMe_2)_3(CO)_5]$ contains both bridging and terminal carbonyl groups in the solid state. © 2005 Elsevier B.V. All rights reserved.

Keywords: Cobalt; Tertiary phosphine; Bridging carbonyl; Dimer

1. Introduction

The hydroformylation [1] reaction represents one of the most industrially significant applications of homogeneous catalysis. Typically, catalysts consist of Rh or Co carbonyl compounds. In the case of Co, catalysts are formed in situ from tertiary phosphine ligands and $[Co(CO)_4]_2$, to give dimeric cobalt compounds of the form [Co(L)(CO)₃]₂ (L = tertiary phosphine). These dimers are subsequently cleaved under a syngas (CO/H_2) atmosphere to give pre-catalysts of the form $[Co(L)(CO)_3(H)]$ (L = tertiary phosphine). However, the presence of excess phosphine allows for the formation of more highly substituted compounds such as $[Co(L)_2(CO)_2(H)]$ [2] and presumably $[Co_2(L)_3]$ (CO)₅]. The importance of this class of dimeric cobalt compounds in the hydroformylation of alkenes has ensured continued interest in their structural and chemical properties [2–6] Here, we report the X-ray crystal structures of two related cobalt dimers, illustrating the structural consequences of increasing the number of coordinated tertiary phosphine ligands.

2. Results and discussion

The addition of two equivalents of the tertiary phosphine PPhMe₂ to a toluene solution of $[Co(CO)_4]_2$, followed by heating, gave the compound $[Co(PPhMe_2)(CO)_3]_2$ (1), as an orange solid, in which two of the CO groups have been replaced by tertiary phosphine ligands. The compound 1 was recrystallised from dichloromethane/hexane, forming crystals that were moderately air-stable, though solutions, in wet solvents, decomposed over several hours. Compound 1 is soluble in most common organic solvents. Compound 1 has been reported previously [7], though minimal analytical data were provided, it has now been fully characterised by ¹H, ³¹P{¹H}, ¹³C{¹H} NMR and IR spectroscopies, by mass spectrometry, by microanalysis and by X-ray structure determination.

Crystals of 1, suitable for X-ray structure determination, were grown by layering a saturated dichloromethane solution of 1 with hexane. Crystal data are summarised in Table 1. A view of the solid state structure is shown in Fig. 1, while selected bond lengths (Å) and angles (°), are given in Table 2. Compound 1 has a crystallographic centre of inversion, midway along the Co–Co bond, and exhibits a staggered conformation about this bond. The molecular structure of 1 displays a dinuclear arrangement, of trigonal

^{*} Corresponding author. Tel.: +44 7787157064.

E-mail address: simon.llewellyn@chem.ox.ac.uk (S.A. Llewellyn).

Table 1	
Crystallographic data for compounds 1 and 2	2

Compound	1	2
Chemical formula	C22H22C02O6P2	C ₂₉ H ₃₃ Co ₂ O ₅ P ₃
Formula weight	562.23	672.37
<i>T</i> (K)	150	150
λ (Å)	0.71073	0.71073
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$P2_{1}2_{1}2_{1}$
<i>a</i> (Å)	7.2208(3)	9.7009(2)
b (Å)	8.5301(4)	11.0947(2)
c (Å)	11.0362(6)	28.4616(4)
α (°)	88.523(2)	90
β (°)	72.590(2)	90
γ (°)	71.824(2)	90
$V(Å^3)$	614.54(5)	3063.28(9)
Ζ	1	4
$D_{\text{calc}} (\text{Mg/m}^3)$	1.519	1.458
Absorption	1.514	1.275
coefficient (mm ⁻¹)		
<i>F</i> (000)	286	1384
Crystal size (mm)	$0.14 \times 0.22 \times 0.22$	$0.14 \times 0.20 \times 0.22$
Description of crystal	dark-red fragment	orange block
Absorption correction	semi-empirical from	semi-empirical from
	equivalent reflections	equivalent reflections
Transmission coefficients	0.72, 0.81	0.76, 0.84
(minimum, maximum)		
θ Range for	$5.0 \leqslant \theta \leqslant 27.5$	$5.0 \leqslant \theta \leqslant 27.5$
data collection (°)		
Index ranges	$-8 \leqslant h \leqslant 9$,	$-12 \leqslant h \leqslant 12$,
	$-10 \leqslant k \leqslant 10,$	$0 \leqslant k \leqslant 14,$
	$0 \leqslant l \leqslant 14$	$0 \leqslant l \leqslant 36$
Reflections measured	8528	22255
Unique reflections	2781	6797
R _{int}	0.061	0.043
Observed reflections $[I > 3\sigma(I)]$	1723	5429
Refinement method	full-matrix	full-matrix
	least-squares on F	least-squares on F
Parameters refined	145	353
Weighting scheme	Chebychev	Chebychev
	3-term polynomial	3-term polynomial
Goodness-of-fit	1.1165	1.1002
R	0.0347	0.0353
wR	0.0330	0.0359
Residual electron density (minimum, maximum) (e Å ⁻³)	-0.35, 0.27	-0.38, 0.57

 $[Co(PPhMe_2)(CO)_3]$ units, in which the two PPhMe_2 ligands are observed in *trans* positions, with respect to the Co–Co bond. The molecular structure further shows that all the carbonyl groups are terminal. This is typical for tertiary phosphine substituted dimers of this type, and contrasts with the compound $[Co(CO)_4]_2$, in which six of the carbonyl groups are found in terminal configurations, while the remaining two are in bridged configurations, in the solid state [8]. A Co–Co bond length of 2.6663(8) Å, an average Co–(CO) bond length of 1.771(4) Å, and a Co–P length of 2.1750(9) Å, are all in the range typical for this class of compound (see Table 3). The P–Co–Co' angle of 175.6(4)° is lower than has been reported for $[Co(L)(CO)_3]_2$ (L = PMe_3 and P(ⁿBu)₃), for which



Fig. 1. Molecular structure of $[Co(PPhMe_2)(CO)_3]_2$ (1). Thermal ellipsoids are drawn at 40% probability. Hydrogen atoms have been omitted for clarity.

Table 2										
Selected	bond	lengths	(Å) ar	nd ang	les (°)	in [C	Co(PPh]	Me ₂)(C	O_{2}	(1

Co(1)-Co(1)*	2.6663(8)	P(1)-C(10)	1.809(4)
Co(1) - C(1)	1.772(4)	P(1)-C(11)	1.805(4)
Co(1)–C(2)	1.782(4)	C(4)–C(5)	1.400(5)
Co(1) - C(3)	1.758(4)	C(4)–C(9)	1.401(5)
Co(1) - P(1)	2.1750(9)	C(5)–C(6)	1.389(5)
C(1)–O(1)	1.145(5)	C(6)–C(7)	1.380(6)
C(2)–O(2)	1.149(5)	C(7)–C(8)	1.379(6)
C(3)–O(3)	1.156(4)	C(8)–C(9)	1.396(5)
P(1)-C(4)	1.814(3)	P(1)-C(10)	1.809(4)
Co(1)–P(1)–C(10)	114.1(12)	Co(1)*-Co(1)-C(2)	89.1(11)
Co(1)*-Co(1)-C(1)	89.0(11)	Co(1)*-Co(1)-C(3)	83.6 (11)

P–Co–Co' bond angles of 180.0° are observed. However, P–Co–Co' angles of <180° have been reported for the compounds $[Co(L)(CO)_3]_2$ (L = P(O'Pr)_3 [9] and P(OPh)_3 [4]). NMR and IR data were consistent with the molecular structure of the crystal.

Heating a toluene solution of $[Co(CO)_4]_2$, with three equivalents of PPhMe₂, led to the formation of $[Co_2(PPh-Me_2)_3(CO)_5]$. This compound was purified by recrystallisation from dichloromethane/pentane at -20 °C, to afford the product as orange/red crystals. The synthesis of **2**, by the controlled-potential electrolysis of $[Co(PPh-Me_2)(CO)_3]_2$, has been reported [10]. However, minimal characterising and structural data were given, though IR data are shown. Compound **2** has thus been characterised by ¹H, ³¹P{¹H}, ¹³C{¹H} NMR, and IR spectroscopies, by mass spectrometry, by microanalysis, and by X-ray structure determination.

Crystals of the compound **2**, suitable for X-ray structure determination, were grown by the cooling of a saturated dichloromethane/pentane solution. Crystal data are summarised in Table 1. A view of the molecular structure of **2** in the solid state is given in Fig. 2. Selected bond lengths (Å) and angles (°), are given in Table 4. The molecular structure of **2** shows both $CO_{bridging}$ and $CO_{terminal}$ groups. The two $CO_{bridging}$ groups have Co–C bond lengths of

Table 3	
Selected bond lengths (Å) and angles (°) for compounds 1 and 2 of the form [Co(L)(CO) ₃] ₂	

Ligand	Bond lengths (Å)	Bond angles (°)		
	Со-Со	Co-(CO)	Co–P	P–Co–Co′
CO [8]	2.522(1)	1.820(1), 1.930(1)		
PMe ₃ [12]	2.669(1)	1.772(3)	2.175(1)	180.0 ^a
PPhMe ₂	2.6663(8)	1.770(4)	2.1750(9)	175.6(4)
$P(^{n}Bu)_{3}[13,14]$	2.654(1)	1.75(3)	2.178(1)	180.0 ^a
$P(O'Pr)_3$ [9]	2.6544(10)	1.769(2)	2.1350(10)	177.0(6)
$P(OPh)_3$ [4]	2.6722(4)	1.783(2)	2.1224(4)	177.3(2)
[Co ₂ (PPhMe ₂) ₃ (CO) ₅]	2.5216(6)	1.788(3)-1.978(3)	2.2320(10), 2.1952(10)	116.8(3), 119.2(3)

^a esd not given.



Fig. 2. ORTEP view of [Co₂(PPhMe₂)₃(CO)₅] (2). Thermal ellipsoids are drawn at 40% probability. Hydrogen atoms have been omitted for clarity.

Table 4 Selected bond lengths (Å) and angles (°) in [Co₂(PPhMe₂)₃(CO)₅] (**2**)

Selected Solid length	iio (i i) und ungie	$()$ in $[co_2(11)m(c_2)]$	s(co)s](=)
Co(1)-Co(2)	2.5216(6)	C(2)–O(2)	1.180(4)
Co(1)-C(1)	1.938(3)	C(3)–O(3)	1.143(4)
Co(1)–C(2)	1.987(3)	C(4)–O(4)	1.146(4)
Co(1)–C(3)	1.788(3)	C(5)–O(5)	1.145(4)
Co(1)-C(4)	1.780(4)	Co(2)–C(5)	1.785(4)
Co(1)–P(1)	2.2194(10)	Co(2)–P(2)	2.2320(10)
Co(2)-C(1)	1.908(4)	Co(2)–P(3)	2.1952(10)
Co(2)–C(2)	1.878(3)	C(1)–O(1)	1.183(4)
Co(2)–Co(1)–P(1)	116.8(3)	Co(2)-Co(1)-C(2)	47.4(10)
C(1)-Co(2)-P(2)	163.6(11)	Co(2)-Co(1)-C(3)	107.9(11)
Co(1)-Co(2)-P(3)	119.2(3)	Co(2)-Co(1)-C(4)	122.7(11)
Co(2)-Co(1)-C(1)	48.5(11)	Co(1)-Co(2)-C(5)	113.3(11)

1.938(3) and 1.987(3) Å (cf. 1.930(1) Å for $[Co(CO)_4]_2$, see Table 3). The average Co–CO_{terminal} bond length in **2** is 1.784(4) Å. This compares with a 1.770(4) Å average Co–CO_{terminal} bond length, observed for the compound $[Co(PPhMe_2)(CO)_3]_2$. The presence of $CO_{bridging}$ groups, in the solid state structure, contrasts with $[Co(L)(CO)_3]_2$.

where L = alkyl, aryl or alkoxy tertiary phosphine, in which all appended carbonyl groups are observed in terminal configurations. The Flack [11] enantiopole parameter calculated for **2** was 0.355. This value, coupled with a small esd, indicates that the crystal was a twin by inversion, containing both enantiomers. This may suggest that the two enantiomers interconvert in solution, perhaps via exchange of terminal and bridging CO groups.

The ¹H NMR and ³¹P{¹H} NMR spectra of **2** indicate two chemically distinct PPhMe₂ groups, in a ratio of 2:1. The solid state structure of **2** would suggest the presence of three chemically distinct ³¹P nuclei. That only two distinct ³¹P nuclei are observed in the ³¹P{¹H} NMR spectrum of **2** suggests that an exchange between CO_{terminal} and CO_{bridging} groups may occur in solution. The ¹³C{¹H} NMR spectrum shows a broad single resonance δ 225.9, which may be attributed to the CO_{terminal} groups. The absence of other resonances attributable to other CO_{terminal} and CO_{bridging} groups, also suggests that the CO_{terminal} and CO_{bridging} groups observed in the solid state structure of **2**, may exchange in solution. A similar situation has been reported for the compound $[Co_2(PEt_3)_3(CO)_5]$ [12]. The difference between the solid-state/solution behaviour of **2** when contrasted with that of **1**, suggests the existence of a delicate balance between the terminal and bridging carbonyl groups that is perturbed by changes in the electronic and steric properties of the metal centres.

3. Experimental

All manipulations of air- and/or moisture-sensitive compounds were carried out under an inert atmosphere of dinitrogen, in either an inert-atmosphere box or using standard Schlenk line techniques. Solvents used in the preparation of air- and/or moisture-sensitive compounds were dried by passage through an alumina column under a positive pressure of dinitrogen. Dinitrogen was passed through the dried solvents for 20 min before use. C₆D₆ was degassed using three freeze-pump-thaw cycles and was vacuum distilled from sodium. Solution NMR spectra were recorded with either a Varian UNITYplus (¹H: 500.0 MHz, ¹³C: ^{125.7} MHz, ³¹P: 202.4 MHz) or a Varian Mercury 300 (¹H: 300.2 MHz, ¹³C: 75.5 MHz, ³¹P: 121.5 MHz). The spectra were either internally referenced relative to the residual protio-solvent (¹H) and solvent (¹³C) resonances relative to trimethylsilane (¹H, ¹³C, $\delta = 0$ ppm), or were referenced externally, relative to H₃PO₄ (³¹P, $\delta = 0$ ppm). Infrared spectra were recorded on either a Perkin-Elmer 1710 FT-IR spectrometer or a Perkin-Elmer 1600 FT-IR instrument in the range 4000-400 cm⁻¹. Samples were prepared either as Nujol mulls between KBr plates, or as solutions in CH₂Cl₂. Data are quoted in wave numbers (cm^{-1}). The compound $[Co_2(CO)_8]$ was purchased from Strem, and PPhMe₂ was purchased from Aldrich. Both were used as received.

3.1. Synthesis of $[Co(PPhMe_2)(CO)_3]_2$ (1)

The compound $[Co_2(CO)_8]$ (2.00 g, 5.85 mmol) was dissolved in 20 ml of toluene to give a deep purple solution. PPhMe₂ (2.18 ml, 11.70 mmol) was then added portionwise by syringe. Effervescence was observed immediately. The resulting suspension was then heated at 60 °C until the reaction was complete as judged by IR (CH₂Cl₂). Solvents were removed under reduced pressure to give a pale brown solid, which was recrystallised from dichloromethane and pentane. The resulting red/brown crystals were isolated by filtration and dried under vacuum. Crystals suitable for single-crystal X-ray diffraction were grown by layering hexane onto a saturated dichloromethane. Yield of **1**, 2.15 g (65.4%).

¹H NMR (C₆D₆) (δ): 1.23 [d, ²J_{PH} = 8.79 Hz, 12H, PPh(CH₃)₂], 6.97 [m, 6H, ArH], 7.29 [s, 4H, ArH]; ¹³C{¹H} NMR (δ): 9.16 [d, J_{PC} = 30.65 Hz, PPh(CH₃)₂], 128.20 [s, ArC], 128.82 [m, ArC], 129.87 [m, ArC], 137.31 [d, ArC], 203.32 [t, ²J_{PC} = 9.78 Hz, Co(CO)₃]; ³¹P{¹H} NMR (δ): 35.33 [s, PPh(CH₃)₂]. IR (Nujol, KBr): 1938 s. m/z (FI) 138 (100%) [PPhMe₂]⁺. Anal. Calc. for 1: C, 47.1; H, 3.9; N, 0. Found: C, 47.0; H, 3.9; N, 0%.

3.2. Synthesis of $[Co_2(PPhMe_2)_3(CO)_5]$ (2)

The compound $[Co_2(CO)_8]$ (1.00 g, 2.93 mmol) was dissolved in 10 ml of toluene. PPhMe₂ (1.63 ml, 8.78 mmol) was then added and the resulting suspension was stirred at 60 °C for 48 h. Solvents were then removed in vacuo, and the resulting dark red/brown solid was dissolved in 20 ml of CH₂Cl₂. Addition of 10 ml of pentane led to the precipitation of an orange/red solid. The resulting suspension was concentrated to ca. 10 ml and filtered. The mother liquor was then cooled to -25 °C, which led to the precipitation of red crystals that were isolated by filtration and dried under vacuum. Crystals suitable for single-crystal X-ray diffraction were grown by cooling a saturated dichloromethane/pentane solution to -25 °C. Yield of **2**, 1.20 g (60.9%).

¹H NMR (C₆D₆) (δ): 1.22 [d, ²J_{PH} = 4.04 Hz, 12H, PPh(CH₃)₂], 1.46 [d, ²J_{PH} = 7.92 Hz, 6H, PPh(CH₃)₂], 7.15 [m, 15H, ArH]; ¹³C{¹H} NMR (δ): 14.78 [t, ¹J_{PC} = 13.28 Hz, PPh(CH₃)₂], 15.75 [d, ¹J_{PC} = 4.96 Hz, PPh(CH₃)₂], 129.79 [m, ArC], 139.45 [s, ArC], 139.92 [s, ArC], 140.95 [s, ArC], 141.20 [s, ArC], 141.45 [s, ArC], 225.9 [s, Co(CO)_{terminal}]; ³¹P{¹H} NMR (δ): 9.85 [s, PPh(CH₃)₂], 13.01 [s, PPh(CH₃)₂]. IR (CH₂Cl₂) 1744 m, 1942 s, 1994 s. *m*/*z* (FI) 335 (50%) [Co(PPh(CH₃)₂)]⁺. *Anal.* Calc. for **2**: C, 51.8; H, 4.9; N, 0. Found: C, 51.4; H, 4.8; N, 0%.

4. Crystallography

Data collections were performed by Dr. A.R. Cowley, using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package [13]. The crystal structures were solved using direct-methods program SIR-92 [14], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS [15] program suite. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Crystal structure diagrams were produced using the CRYSTALS [15] program suite. Crystal data are summarised in Table 1.

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Appendix A. Supplementary data

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 283842 and 283843. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica. 2005.11.005.

References

- [1] D.S. Breslow, R.F. Heck, Chem. Ind. (London) (1960) 467.
- [2] M.J. Chen, R.J. Klingler, J.W. Rathke, K.W. Kramarz, Organometallics 23 (2004) 2701.
- [3] R. Meijboom, M. Haumann, A. Roodt, L. Damoense, Helv. Chim. Acta 88 (2005) 676.
- [4] M. Haumann, R. Meijboom, J.R. Moss, A. Roodt, Dalton Trans. (2004) 1679.

- [5] C. Crause, L. Bennie, L. Damoense, C.L. Dwyer, C. Grove, N. Grimmer, W.J. Van Rensburg, M.M. Kirk, K.M. Mokheseng, S. Otto, P.J. Steynberg, Dalton Trans. (2003) 2036.
- [6] A. Polas, J.D.E.T. Wilton-Ely, A.M.Z. Slawin, D.F. Foster, P.J. Steynberg, M.J. Green, D.J. Cole-Hamilton, Dalton Trans. (2003) 4669.
- [7] A.R. Manning, J. Chem. Soc. A (1968) 1135.
- [8] G.G. Sumner, H.P. Klug, L.E. Alexander, Acta Crystallogr. 17 (1964) 732.
- [9] D.H. Farrar, A.J. Lough, A.J. Pöe, T.A. Stromnova, Acta Crystallogr., Sect. C 51 (1995) 2008.
- [10] P. Reeb, Y. Mugnier, C. Moise, E. Laviron, J. Organomet. Chem. 273 (1984) 247.
- [11] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.
- [12] C. Pegot, R. Poilblanc, C.R. Acad. Sci. Ser. IIc 268 (1969) 955.
- [13] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
- [14] A. Altomare, G. Carascano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343.
- [15] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, R.I. Cooper, CRYSTALS Issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.