Binuclear Rhodium Carbonyl Halide Complexes Containing the 1,1-Bis(diphenylphosphino)ethene Ligand, and the Crystal Structure of $[Rh_2Cl_2(\mu\text{-}CO)\{Ph_2PC(=CH_2)PPh_2\}_2]$

RICHARD H. DAWSON, MARJORIE M. HARDING, STEPHEN MAGINN and ANTHONY K. SMITH*

Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, U.K.

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Abstract

Treatment of $[RhCl(CO)_2]_2$ with 1,1-bis(diphenylphosphino)ethene (dppee) yields the cationic binuclear rhodium complex $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(dppee)_2]^+$ which may be isolated as the $[RhCl_2(CO)_2]^-$ salt at low temperature (230 K) but which readily forms the Cl^- salt on allowing the solution to warm to room temperature. On bubbling nitrogen through a solution of this cationic complex at room temperature, the monocarbonyl species, $[Rh_2Cl_2(\mu\text{-}CO)(dppee)_2]$ is obtained. The crystal structure of this complex has been determined. The crystals are orthorhombic, space group *Pnca*, $a = 29.98(3)$, $b = 23.70(2)$, $c = 14.78(3)$ Å, $Z = 8$. Using 3019 unique reflections the structure was refined to $R = 0.091$. The rhodium–rhodium distance is 2.650(14) Å. Direct rhodium NMR data are reported for these complexes.

Introduction

In the course of our investigations into the synthesis of mixed-metal complexes containing the bridging ligand 1,1-bis(diphenylphosphino)ethene (dppee) [1, 2], we observed that binuclear rhodium complexes of dppee were a common decomposition or side-product of the reactions when $[RhCl(CO)_2]_2$ was used as a rhodium source. Since the behaviour of the rhodium complexes containing dppee did not appear to parallel that of the extensively studied dppm–dirhodium complexes [dppm = bis(diphenylphosphino)methane] [3–9], it was of interest to investigate the reaction of $[RhCl(CO)_2]_2$ with dppee, and the results of these studies are reported herein.

Experimental

All reactions were carried out under nitrogen unless otherwise stated. Infrared spectra were recorded on a Perkin-Elmer 681 instrument. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WM 250 spectrometer, and direct ^{103}Rh NMR spectra were obtained using a Bruker WH360 spectrometer. Spectroscopic data are reported in Table I.

Mass spectra (Fast Atom Bombardment) were recorded on a VG 7070E mass spectrometer using 3-NOBA suspensions of the samples. Microanalyses were carried out in our own microanalytical laboratories (University of Liverpool).

Preparation of $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(dppee)_2]^+X^-$ (1) (a, $X = [RhCl_2(CO)_2]$; b, $X = Cl$; c, $X = PF_6$) and $[Rh_2(\mu\text{-}Cl)(CO)_2(dppee)_2][PF_6]$ (3)

A solution of $[RhCl(CO)_2]_2$ (0.22 g, 0.57 mmol) and dppee (0.45 g, 1.13 mmol) in dichloromethane

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*Author to whom correspondence should be addressed.

TABLE I. Spectroscopic Data

Complex	$\nu(CO)$ $(cm^{-1})^a$	^{31}P NMR (ppm)^b	^{103}Rh NMR (ppm)^c
$[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dppee)_2][RhCl_2(CO)_2]$ (1a)	2064m, 1989vs 1870m	37.5m	$-143.9m^d$
$[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dppee)_2]Cl$ (1b)	1989vs, 1870m	38.2m	$-144.1m^d$
$[Rh_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(dppee)_2][PF_6]$ (1c)	1987vs, 1870m	37.6m	
$[Rh_2Cl_2(\mu\text{-}CO)(dppee)_2]$ (2)	1760(s)	31.5m	$+216.8m^e$
$[Rh_2(\mu\text{-}Cl)(CO)_2(dppee)_2][PF_6]$ (3)	2004sh, 1989s	33.1m	

^{a}Infrared spectra run in CH_2Cl_2 solution $^{b31}P\{^1H\}$ NMR chemical shifts relative to 85% H_3PO_4 (downfield positive); m = multiplet. ^{c103}Rh NMR chemical shifts relative to 3.16 MHz = 0 ppm. ^{d}Temperature 218 K. ^{e}Temperature 298 K.

0020-1693/88/$3.50

TABLE II. Fractional Coordinates of Atoms[a]

Atom	x	y	z	U_{eq}
Rh(1)	0.1105(4)	0.1162(4)	0.2588(8)	0.0935(68)
Rh(2)	0.1314(4)	0.0433(4)	0.3881(7)	0.1014(72)
P(1)	0.1388(15)	0.1164(13)	0.4915(25)	0.0978(133)
P(2)	0.1122(15)	0.1917(15)	0.3440(27)	0.0984(156)
P(3)	0.0888(12)	0.0466(15)	0.1599(22)	0.1018(127)
P(4)	0.1186(14)	−0.0343(14)	0.2986(23)	0.1008(143)
Cl(1)	0.1241(13)	0.1787(11)	0.1387(19)	0.1086(233)
Cl(2)	0.1717(11)	−0.0134(11)	0.4849(21)	0.1061(225)
C(1)	0.0774(39)	−0.0260(47)	0.2153(84)	0.1307(598)
C(2)	0.0381(38)	−0.0474(46)	0.1848(78)	0.1205(453)
C(3)	0.1015(41)	0.1768(48)	0.4616(88)	0.1307(507)
C(4)	0.0831(41)	0.2024(47)	0.5352(83)	0.1235(521)
C(5)	0.0831(32)	0.0747(33)	0.3401(64)	0.0202(323)
O(5)	0.0446(31)	0.0746(34)	0.3598(63)	0.1326(430)
C(12)	0.1355(19)	0.0998(22)	0.6732(75)	0.0873(349)
C(13)	0.1256(19)	0.0804(22)	0.7600(75)	0.1455(471)
C(14)	0.0884(19)	0.0461(22)	0.7743(75)	0.1317(433)
C(15)	0.0611(19)	0.0314(22)	0.7018(75)	0.1214(483)
C(16)	0.0709(19)	0.0508(22)	0.6149(75)	0.1115(429)
C(11)	0.1081(19)	0.0850(22)	0.6006(75)	0.0608(316)
C(22)	0.2077(25)	0.2009(36)	0.5639(48)	0.0356(337)
C(23)	0.2506(25)	0.2220(36)	0.5769(48)	0.0466(336)
C(24)	0.2874(25)	0.1919(36)	0.5452(48)	0.2070(741)
C(25)	0.2813(25)	0.1406(36)	0.5005(48)	0.3728(999)
C(26)	0.2383(25)	0.1195(36)	0.4875(48)	0.1678(513)
C(21)	0.2015(25)	0.1496(36)	0.5192(48)	0.0857(441)
C(32)	0.1937(39)	0.2288(26)	0.3073(49)	0.1732(539)
C(33)	0.2327(39)	0.2607(26)	0.3125(49)	0.1513(471)
C(34)	0.2343(39)	0.3085(26)	0.3675(49)	0.1034(469)
C(35)	0.1968(39)	0.3244(26)	0.4173(49)	0.1183(484)
C(36)	0.1578(39)	0.2925(26)	0.4122(49)	0.1268(523)
C(31)	0.1562(39)	0.2447(26)	0.3572(49)	0.1116(467)
C(42)	0.0312(37)	0.2107(26)	0.3369(52)	0.2319(892)
C(43)	−0.0093(37)	0.2333(26)	0.3078(52)	0.0923(375)
C(44)	−0.0102(37)	0.2858(26)	0.2651(52)	0.1333(540)
C(45)	0.0293(37)	0.3156(26)	0.2514(52)	0.0785(397)
C(46)	0.0698(37)	0.2930(26)	0.2806(52)	0.0975(406)
C(41)	0.0708(37)	0.2405(26)	0.3233(52)	0.0948(433)
C(52)	0.0044(34)	0.0791(27)	0.1546(37)	0.0992(443)
C(53)	−0.0332(34)	0.1111(27)	0.1326(37)	0.1744(613)
C(54)	−0.0357(34)	0.1382(27)	0.0490(37)	0.0788(456)
C(55)	−0.0007(34)	0.1334(27)	−0.0126(37)	0.0323(274)
C(56)	0.0369(34)	0.1014(27)	0.0093(37)	0.0983(446)
C(51)	0.0394(34)	0.0743(27)	0.0929(37)	0.0659(340)
C(62)	0.1094(25)	−0.0228(34)	−0.0011(73)	0.1966(544)
C(63)	0.1408(25)	−0.0340(34)	−0.0684(73)	0.1267(463)
C(64)	0.1815(25)	−0.0054(34)	−0.0688(73)	0.0770(337)
C(65)	0.1907(25)	0.0345(34)	−0.0020(73)	0.1873(521)
C(66)	0.1593(25)	0.0457(34)	0.0653(73)	0.0326(323)
C(61)	0.1187(25)	0.0171(34)	0.0658(73)	0.2222(689)
C(72)	0.1174(18)	−0.1466(34)	0.3701(41)	0.0948(339)
C(73)	0.1002(18)	−0.1891(34)	0.4253(41)	0.0557(400)
C(74)	0.0627(18)	−0.1787(34)	0.4785(41)	0.1264(486)
C(75)	0.0423(18)	−0.1258(34)	0.4765(41)	0.0820(403)
C(76)	0.0595(18)	−0.0833(34)	0.4213(41)	0.1000(422)
C(71)	0.0970(18)	−0.0937(34)	0.3681(41)	0.0545(282)
C(82)	0.1577(22)	−0.0984(33)	0.1732(67)	0.1583(605)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	U_{eq}
C(83)	0.1912(22)	−0.1273(33)	0.1268(67)	0.0461(321)
C(84)	0.2355(22)	−0.1224(33)	0.1544(67)	0.0673(372)
C(85)	0.2464(22)	−0.0886(33)	0.2285(67)	0.0173(305)
C(86)	0.2129(22)	−0.0597(33)	0.2749(67)	0.0940(407)
C(81)	0.1686(22)	−0.0646(33)	0.2472(67)	0.1073(464)

[a] e.s.d.s given in parentheses.

(40 cm^3) was stirred under an atmosphere of CO for 10 min at 230 K, to give an orange-yellow solution of (**1a**). On allowing the solution to warm to room temperature whilst bubbling nitrogen through the solution (10 min), an orange solution of **1b** was obtained. Addition of an excess of KPF_6 to a dichloromethane solution of **1b** gave **1c** which, on purging with nitrogen for 10 h, gave $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-dppee})_2][PF_6]$ (**3**) in quantitative yield. *Anal.* Found (calc.): C, 52.5 (52.5); H, 3.8 (3.6); Cl, 3.3 (2.9).

Preparation of $[Rh_2Cl_2(\mu\text{-CO})(dppee)_2]$ (2)

Bubbling nitrogen through a solution of **1b** for 48 h at room temperature gave a dark red solution. This solution was evaporated to dryness under reduced pressure to give a red solid which was recrystallised from dichloromethane/heptane to give dark red crystals of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-dppee})_2]$ (**2**) (0.49 g, 78%). *Anal.* Found (calc.): C, 58.0 (58.0); H, 4.2 (4.0); P, 11.0 (11.3); Cl, 6.7 (6.5); M^+ 1097.

X-ray Crystallography

Dark red crystals of **2** were grown from an acetone/ethanol solution. Difficulty was experienced in obtaining a crystal of suitable quality. The crystal selected had approximate dimensions 0.5 × 0.2 × 0.1 mm. The crystal data and collection parameters are as follows: formula = $C_{53}H_{44}Cl_2OP_4Rh_2$; formula weight = 1097; space group = *Pnca*; $a = 29.98(3)$, $b = 23.70(2)$, $c = 14.78(3)$ Å; $V = 10502$ Å^3; $D_{calc} = 1.40$ g cm^{-3}; $D_{meas} = 1.44$ g cm^{-3}; $Z = 8$; μ(Mo Kα) = 8.63 mm^{-1}; data collection instrument: Stoe Stadi-2, using Mo Kα radiation, $\lambda = 0.71069$ Å.

The rhodium atoms were located with the use of a Patterson map, and all other non-H atoms were found in successive Fourier syntheses, using the Shelx-76 program [10] on 8388 unique reflections with $|F| > 6\sigma(F)$. This data proved to be of insufficient quality to refine the structure, so refinement was performed using 3019 reflections (up to $l = 8$), with $|F| > 8\sigma(F)$. Least-squares refinement of positional and thermal parameters (with all atoms isotropic except Rh and Cl atoms) and with the phenyl rings constrained to regular hexagons with the hydrogen atoms riding on them, led to convergence at $R = 9.1\%$. Atomic coordinates are given in Table II, and selected bond lengths and angles in Table III.

TABLE III. Selected Bond Lengths (Å) and Angles (°) for $[Rh_2Cl_2(\mu\text{-CO})(dppee)_2]$ (**2**)

Rh(1)–Rh(2)	2.650(14)	P(2)–Rh(1)–Rh(2)	96.4(1.1)
Rh(1)–P(2)	2.19(4)	P(2)–Rh(1)–P(3)	163.6(1.5)
Rh(1)–P(3)	2.30(4)	P(3)–Rh(1)–Rh(2)	93.3(0.9)
Rh(2)–P(1)	2.32(4)	Cl(1)–Rh(1)–Rh(2)	156.2(1.1)
Rh(2)–P(4)	2.30(4)	Cl(1)–Rh(1)–P(2)	85.1(1.2)
Rh(1)–Cl(1)	2.35(3)	Cl(1)–Rh(1)–P(3)	91.3(1.2)
Rh(2)–Cl(2)	2.31(3)	P(1)–Rh(2)–Rh(1)	90.6(0.9)
Rh(1)–C(5)	1.76(9)	P(1)–Rh(2)–P(4)	173.0(1.4)
Rh(2)–C(5)	1.77(9)	P(4)–Rh(2)–Rh(1)	93.9(1.0)
		Cl(2)–Rh(2)–Rh(1)	162.0(1.0)
		Cl(2)–Rh(2)–P(1)	88.6(1.2)
		Cl(2)–Rh(2)–P(4)	88.7(1.2)

Results and Discussion

The reaction of $[RhCl(CO)_2]_2$ with dppee in dichloromethane yields the cationic complex $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(dppee)_2]^+$ (**1**) which exists as the $[RhCl_2(CO)_2]^-$ salt (**1a**) at 230 K (spectroscopic evidence, see Table I), but which forms the Cl^- salt (**1b**) when a solution of **1a** is allowed to warm to room temperature. The mass spectrum of **1b** shows a weak molecular ion peak centred at $M^+ = 1117$ and the major peak centred at $M^+ = 1089$, corresponding to loss of CO from the molecular cation, and confirming the formulation of **1** as $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(dppee)_2]^+$. On bubbling nitrogen through a dichloromethane solution of **1b**, CO loss occurs to give the complex $[Rh_2Cl_2(\mu\text{-CO})(dppee)_2]$ (**2**). However, if **1b** is converted to the PF_6^- salt (**1c**) by the addition of KPF_6, and then a solution of **1c** is purged with nitrogen, the dirhodium dicarbonyl complex, $[Rh_2(\mu\text{-Cl})(CO)_2(dppee)_2][PF_6]$ (**3**) is formed. The behaviour of **1c** is analogous to that of the dppm complex $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(dppm)_2][BPh_4]$ which readily loses one CO ligand to form $[Rh_2(\mu\text{-Cl})(CO)_2(dppm)_2][BPh_4]$ [5]. However,

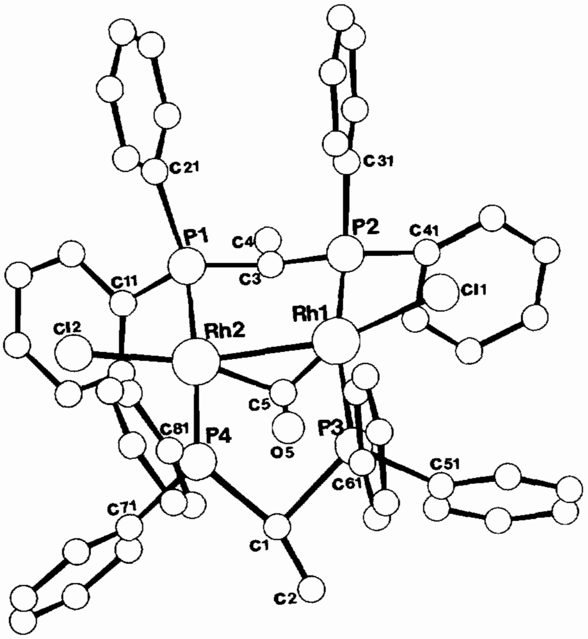

Fig. 1. The molecular structure of $[Rh_2Cl_2(\mu\text{-}CO)(dppee)_2]$ (2) with H atoms omitted.

when nitrogen is bubbled through a solution of the corresponding chloride salt, $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(dppm)_2]Cl$, the neutral complex *cis*-$[Rh_2Cl_2(CO)_2(dppm)_2]$ is formed [6]. In order to obtain the dppm analogue of 2, the complex *trans*-$[Rh_2Cl_2(CO)_2(dppm)_2]$ has to be refluxed in toluene for 2 h [7]. Thus, as has been observed previously [7], the chemistry of these complexes is dependent on both the nature of the bridging diphosphine ligands, and on the counter anion. In order to look more closely at the structural effects of changing the bridging diphosphine ligand from dppm to dppee, we undertook a crystal structure determination of 2. Unfortunately it proved impossible to obtain a good quality crystal, and so the crystal structure could only be refined down to an R factor of 9.1%. The atom parameters are given in Table II and selected bond lengths and angles in Table III. The structure of 2 is shown in Fig. 1; it consists of two rhodium atoms 2.65(1) Å apart bridged by the two dppee ligands and the carbonyl ligand. The structure is thus similar to that of $[Rh_2Br_2(\mu\text{-}CO)(dppm)_2]$ [8]. The large standard deviations associated with the bond lengths and angles of all the atoms other than rhodium preclude a full comparison of these two structures; however, it is noteworthy that the Rh–Rh bond length in the dppee complex [2.650(14) Å] is significantly shorter than that in the dppm complex [2.7566(9) Å].

Supplementary Material

Full tables of bond lengths and angles, thermal parameters, and a listing of observed and calculated structure factors are available from author A.K.S.

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References

1 R. H. Dawson and A. K. Smith, *J. Organomet. Chem., 309,* C56 (1986).
2 R. H. Dawson and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, 826 (1987).
3 J. T. Mague and J. P. Mitchener, *Inorg. Chem., 8,* 119 (1969).
4 J. T. Mague, *Inorg. Chem., 8,* 1975 (1969).
5 J. T. Mague and A. R. Sanger, *Inorg. Chem., 18,* 2060 (1979).
6 M. Cowie and S. K. Dwight, *Inorg. Chem., 19,* 209 (1980).
7 M. Cowie and S. K. Dwight, *Inorg. Chem., 19,* 2500 (1980).
8 M. Cowie and S. K. Dwight, *Inorg. Chem., 19,* 2508 (1980).
9 M. Cowie and S. K. Dwight, *Inorg. Chem., 20,* 1534 (1981).
10 G. M. Sheldrick, 'SHELX-76', University of Cambridge, 1976.