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HEXACARBONYLBIS(TRICYCLOPENTYLPHOSPHINE)DIRHODIUM AND HEXACARBONYLBIS(TRIISOPROPYLPHOSPHINE)DIRHODIUM FROM A CATALYTIC SYSTEM FOR SYNGAS CONVERSION TO ETHYLENE GLYCOL

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Summary

Two dimeric rhodium compounds, $[Rh(CO)_3P(c\text{-}C_5H_9)_3]_2$ (**1**) and $[Rh(CO)_3P(i\text{-}Pr)_3]_2$ (**2**) have been isolated from the catalytic reaction mixtures of syngas conversion to ethylene glycol, and their molecular structures without a bridging carbonyl were determined by single crystal X-ray diffraction studies.

Introduction

We have reported a novel and highly effective rhodium-trialkylphosphine catalyst system for hydrogenation of carbon monoxide to ethylene glycol [1,2]. The catalytic solution, was found to have an intense IR absorption at 1950–1960 cm^{-1} after cooling. During the course of our study to determine the exact nature of the catalyst, we isolated orange crystals of rhodium complexes, each having an unbridged dimeric rhodium(0) structure, with an IR band at 1950 cm^{-1} (Nujol mull).

Results and discussion

When a mixture of $Rh(CO)_2(acac)$ (0.6 mmol) and tricyclopentylphosphine (0.6 mmol) in 1,3-dimethyl-2-imidazolidinone (DMI) (4.0 mmol) was treated under 47.0 MPa syngas ($H_2/CO = 1/1$) at 230°C for 45 min, a dark orange-yellow solution resulted. Diamagnetic orange crystals of $[Rh(CO)_3P(c\text{-}C_5H_9)_3]_2$ (**1**) precipitated when the solution was cooled to room temperature and left stand for two days. They were separated from the solvent (DMI) by decantation, washed with an n-hexane/toluene (1 : 1) mixture, and finally dried in a stream of carbon monoxide.

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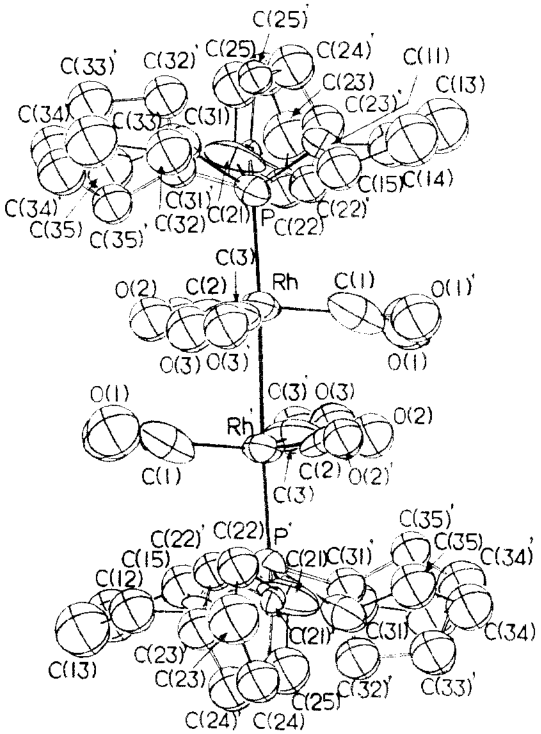

Fig. 1. A perspective view of $[Rh(CO)_3P(c\text{-}C_5H_9)_3]_2$ (1) and atom numbering.

Although the complex is unstable under nitrogen or in a vacuum, it is fairly stable under carbon monoxide at room temperature *.

We have determined the structure of **1** by a single crystal X-ray diffraction study. The overall molecular geometry and the atomic labelling scheme are illustrated in Fig. 1. Interatomic distances and angles are collected in Tables 1 and 2. The structure of the orange complex **1** consists of a binuclear rhodium core with a center of inversion at the midpoint of the Rh–Rh bond, without a bridging carbonyl, in which two axial sites are occupied by two phosphine ligands. The absence of the bridging carbonyl is consistent with the IR spectra (Nujol mull), as no absorption bands are present between 1780–1950 cm^{-1}, except at 1950 cm^{-1}. The structure P–Rh–Rh′–P′ is almost linear. The Rh-to-Rh′ distance of 2.827 Å, is somewhat longer than that of the dimeric rhodium complexes with a bridging carbonyl structure [4]. Each rhodium atom is penta-coordinate and has a trigonal-bipyramid arrangement. Interestingly, there are slight distortions of the rhodium atoms from the trigonal planes, as if the bulky phosphine ligands have pushed the three carbonyls away, so that the rhodium atoms are located 0.178 Å out of each trigonal plane.

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* Yoshida et al. reported the preparation of the orange-yellow $[Rh(CO)_3P(i\text{-}Pr)_3]_n$, identified as the unbridged dimer, via a reaction of $HRh[P(i\text{-}Pr)_3]_3$ with atmospheric carbon monoxide at ambient temperature [3].

TABLE 1

BOND DISTANCES (Å) FOR $[Rh(CO)_3P(c\text{-}C_5H_9)_3]_2$ (**1**)

Rh–Rh	2.827(1)	C(22)–C(21)	1.613(31)
P–Rh	2.318(2)	C(25)–C(21)	1.500(32)
C(1)–Rh	1.911(13)	C(23)–C(22)	1.499(28)
C(2)–Rh	1.907(10)	C(24)–C(23)	1.430(27)
C(3)–Rh	1.895(10)	C(25)–C(24)	1.510(28)
C(11)–P	1.845(9)	C(22)′–C(21)′	1.580(33)
C(21)–P	1.847(30)	C(25)′–C(21)′	1.542(30)
C(21)′–P	1.876(19)	C(23)′–C(22)′	1.518(30)
C(31)–P	1.864(26)	C(24)′–C(23)′	1.410(31)
C(31)′–P	1.845(30)	C(25)′–C(24)′	1.518(31)
O(1)–C(1)	1.227(24)	C(32)–C(31)	1.532(29)
O(1)′–C(1)	1.201(22)	C(35)–C(31)	1.601(29)
O(2)–C(2)	1.175(16)	C(33)–C(32)	1.552(26)
O(2)′–C(2)	1.171(21)	C(34)–C(33)	1.625(29)
O(3)–C(3)	1.237(23)	C(35)–C(34)	1.531(24)
O(3)′–C(3)	1.176(16)	C(32)′–C(31)′	1.466(34)
C(12)–C(11)	1.553(15)	C(35)′–C(31)′	1.529(34)
C(15)–C(11)	1.543(13)	C(33)′–C(32)′	1.582(32)
C(13)–C(12)	1.515(18)	C(34)′–C(33)′	1.517(34)
C(14)–C(13)	1.456(19)	C(35)′–C(34)′	1.494(31)
C(15)–C(14)	1.537(17)		

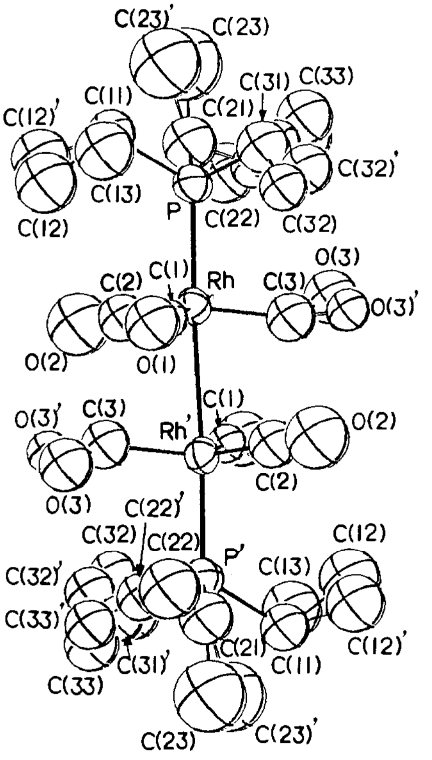

Fig. 2. A perspective view of $[Rh(CO)_3P(i\text{-}Pr_3)_3]_2$ (**2**) and atom numbering.

TABLE 2

BOND ANGLES (°) FOR [Rh(CO)$_3$P(c-C$_5$H$_9$)$_3$]$_2$ (**1**)

C(1)–Rh–P	97.1(0.4)	C(15)–C(11)–C(12)	105.7(0.8)
C(2)–Rh–P	92.8(0.3)	C(13)–C(12)–C(11)	101.5(1.0)
C(2)–Rh–C(1)	118.6(0.8)	C(14)–C(13)–C(12)	110.0(1.3)
C(3)–Rh–P	96.4(0.3)	C(15)–C(14)–C(13)	108.7(1.2)
C(3)–Rh–C(1)	116.3(0.7)	C(14)–C(15)–C(11)	101.7(1.0)
C(3)–Rh–C(2)	122.4(0.7)	C(22)–C(21)–P	114.0(2.1)
C(11)–P–Rh	117.7(0.3)	C(25)–C(21)–P	121.4(2.3)
C(21)–P–Rh	111.1(1.0)	C(25)–C(21)–C(22)	101.5(2.3)
C(21)–P–C(11)	112.1(1.3)	C(23)–C(22)–C(21)	107.0(1.9)
C(21)′–P–Rh	112.6(0.9)	C(24)–C(23)–C(22)	108.3(2.1)
C(21)′–P–C(11)	104.0(1.1)	C(25)–C(24)–C(23)	109.6(2.1)
C(21)′–P–C(21)	9.5(2.1)	C(25)′–C(21)′–P	114.5(1.7)
C(31)–P–Rh	124.1(0.7)	C(22)′–C(21)′–P	111.5(1.6)
C(31)–P–C(11)	98.0(0.9)	C(25)′–C(21)′–C(22)′	107.4(2.3)
C(31)–P–C(21)	90.5(1.3)	C(23)′–C(22)′–C(21)′	101.8(1.9)
C(31)–P–C(21)′	96.8(1.2)	C(24)′–C(23)′–C(22)′	111.1(2.2)
C(31)′–P–Rh	106.8(1.2)	C(25)′–C(24)′–C(23)′	111.6(2.4)
C(31)′–P–C(11)	102.8(1.2)	C(24)′–C(25)′–C(21)′	102.0(2.0)
C(31)′–P–C(21)	104.9(2.0)	C(32)–C(31)–P	113.5(1.7)
C(31)′–P–C(21)′	112.5(1.9)	C(35)–C(31)–P	109.5(1.6)
C(31)′–P–C(31)	18.7(1.6)	C(35)–C(31)–C(32)	103.9(1.7)
O(1)–C(1)–Rh	158.8(2.0)	C(33)–C(32)–C(31)	106.2(1.8)
O(1)′–C(1)–Rh	159.7(2.0)	C(34)–C(33)–C(32)	106.6(1.8)
O(1)′–C(1)–O(1)	40.9(1.2)	C(35)–C(34)–C(33)	104.9(1.7)
O(2)–C(2)–Rh	166.1(1.7)	C(34)–C(35)–C(31)	105.2(1.7)
O(2)′–C(2)–Rh	160.3(2.0)	C(32)′–C(31)′–P	117.7(2.4)
O(2)′–C(2)–O(2)	33.5(1.0)	C(35)′–C(31)′–P	113.6(2.2)
O(3)–C(3)–Rh	156.3(1.9)	C(35)′–C(31)′–C(32)′	113.1(2.9)
O(3)′–C(3)–Rh	166.9(1.7)	C(33)′–C(32)′–C(31)′	97.2(2.2)
O(3)′–C(3)–O(3)	36.6(1.0)	C(34)′–C(33)′–C(32)′	110.4(2.4)
O(1)′–O(1)–C(1)	67.9(2.3)	C(35)′–C(34)′–C(33)′	106.4(2.5)
C(12)–C(11)–P	113.9(0.7)	C(34)′–C(35)′–C(31)′	100.2(2.2)
C(15)–C(11)–P	114.6(0.7)		

An essentially similar result has been obtained for triisopropylphosphine. Using the same technique, we have isolated an orange complex [Rh(CO)$_3$P(i-Pr)$_3$]$_2$ (**2**) which has a structure analogous to that of **1** (Fig. 2 and Tables 3 and 4).

The unbridged dimeric structure is not unique to trialkylphosphines, but appears to be general for the other phosphines. The earlier study by Whyman described the synthesis of yellow-brown Rh$_2$(CO)$_6$(PPh$_3$)$_2$ (**3**) via the reaction of Rh$_4$(CO)$_{12}$ and triphenylphosphine under carbon monoxide pressure [5]. He assumed an unbridged dimeric structure for **3**, based on the IR spectra.

It is noteworthy that the IR spectra of **1** and **2** in DMI again show the 1950 cm^{-1} band, reproducing the spectra of their mother catalytic solutions. Heating the solution to 200°C under 20.0 MPa syngas, a broad band, from 1920 to 1980 cm^{-1}, prevails. The visible spectra indicate that the yellow colour persists even at 200°C under 20.0 MPa, thus excluding the participation of the rhodium carbonyl anion cluster complex [6].

The reaction of syngas, in the presence of **1** (0.05 mmol), in DMI (10 ml) under 47.0 MPa at 230°C, produces ethylene glycol and methanol, in turnover frequencies

TABLE 3

BOND DISTANCES (Å) FOR $[Rh(CO)_3P(i\text{-}Pr)_3]_2$ (**2**)

Rh–Rh	2.817(3)	O(3)′–C(3)	1.100(29)
P–Rh	2.321(5)	C(12)–C(11)	1.557(25)
C(1)–Rh	1.898(17)	C(13)–C(11)	1.576(19)
C(2)–Rh	1.859(24)	C(12)′–C(11)	1.530(20)
C(3)–Rh	1.919(23)	C(22)–C(21)	1.539(21)
C(11)–P	1.949(24)	C(23)–C(21)	1.551(27)
C(21)–P	1.959(28)	C(22)′–C(21)	1.524(19)
C(31)–P	1.839(41)	C(23)′–C(21)	1.571(32)
C(31)′–P	1.838(38)	C(32)–C(31)	1.567(25)
O(1)–C(1)	1.118(21)	C(33)–C(31)	1.542(21)
O(2)–C(2)	1.118(28)	C(32)′–C(31)′	1.607(40)
O(3)–C(3)	1.217(33)	C(33)′–C(31)′	1.546(20)

of 7.1 and 32.1 mol(g-atom Rh)$^{-1}$ h^{-1}, respectively. The catalytic performance is almost comparable to that of the mixture, $Rh(CO)_2(acac)$ (0.1 mmol), tricyclopentylphosphine (0.1 mmol) and DMI (10 ml), which produces ethylene glycol and methanol, at 7.5 and 36.0 mol (g-atom Rh)$^{-1}$ h^{-1}, respectively. The reaction with **2**, in place of **1**, gives rise to a similar result [2,7]. The use of (**3**), however, produces neither ethylene glycol nor methanol.

Treatment of the dimer **1** with hydrogen, under ambient conditions exclusively produces a new species, (ν(CO): 1945 cm^{-1}; ^{1}H NMR: δ −10.1 ppm (s); ^{31}P

TABLE 4

BOND ANGLES (°) FOR $[Rh(CO)_3P(i\text{-}Pr)_3]_2$ (**2**)

C(1)–Rh–P	96.8(0.6)	C(13)–C(11)–P	109.3(2.0)
C(2)–Rh–P	96.5(0.9)	C(13)–C(11)–C(12)	87.8(4.0)
C(2)–Rh–C(1)	117.6(1.0)	C(12)′–C(11)–P	112.7(3.1)
C(3)–Rh–P	96.6(0.9)	C(12)′–C(11)–C(12)	22.6(3.5)
C(3)–Rh–C(1)	120.6(1.0)	C(12)′–C(11)–C(13)	104.8(3.8)
C(3)–Rh–C(2)	117.8(1.1)	C(22)–C(21)–P	126.8(3.2)
C(11)–P–Rh	119.6(0.9)	C(23)–C(21)–P	128.8(6.9)
C(21)–P–Rh	113.2(1.0)	C(23)–C(21)–C(22)	98.5(7.0)
C(21)–P–C(11)	97.7(1.1)	C(22)′–C(21)–P	110.9(2.8)
C(31)–P–Rh	112.2(1.7)	C(22)′–C(21)–C(22)	27.7(3.2)
C(31)–P–C(11)	99.3(2.3)	C(22)′–C(21)–C(23)	98.6(6.7)
C(31)–P–C(21)	113.4(2.1)	C(23)′–C(21)–P	110.4(6.0)
C(31)′–P–Rh	114.8(1.6)	C(23)′–C(21)–C(22)	120.4(6.7)
C(31)′–P–C(11)	111.0(1.7)	C(23)′–C(21)–C(23)	22.6(10.6)
C(31)′–P–C(21)	96.8(1.9)	C(23)′–C(21)–C(22)′	120.4(6.6)
C(31)′–P–C(31)	18.6(2.0)	C(32)–C(31)–P	118.0(4.1)
O(1)–C(1)–Rh	177.4(1.8)	C(33)–C(31)–P	93.4(4.5)
O(2)–C(2)–Rh	178.5(2.8)	C(33)–C(31)–C(32)	135.4(5.9)
O(3)–C(3)–Rh	140.0(3.0)	C(32)′–C(31)′–P	114.8(6.7)
O(3)′–C(3)–Rh	163.9(2.7)	C(33)′–C(31)′–P	94.4(3.1)
O(3)′–C(3)–O(3)	40.7(2.3)	C(33)′–C(31)′–C(32)′	136.2(6.3)
C(12)–C(11)–P	105.8(3.7)		

NMR: δ 70.9 ppm (d), J(Rh–P) 135.6 Hz) which is identified as the monomeric hydride (**4**), produced in the reaction (1):

$$\underset{(\mathbf{1})}{[\mathrm{Rh(CO)_3PR_3}]_2} + \mathrm{H_2} \rightleftharpoons 2\ \underset{(\mathbf{4})}{\mathrm{HRh(CO)}_x\mathrm{PR_3}} + (3 - x)\ \mathrm{CO} \qquad (1)$$

It was believed that species of the type $\mathrm{HRh(CO)_2(PR_3)_2}$ or $\mathrm{HRh(CO)}_x\mathrm{(PR_3)}$ only have a feeble hydrogenation activity [8]. However, careful examination of the rhodium-tricyclopentylphosphine catalytic system has revealed that the maximum rate of ethylene glycol production is attained when $\mathrm{P(c\text{-}C_5H_9)_3/Rh}$ is about 1. We are, therefore, rather inclined to suppose that **4** itself is closely related to a key species in the catalytic hydrogenation of carbon monoxide to ethylene glycol.

Experimental

All experiments were performed under dry argon or carbon monoxide. 1,3-Dimethyl-2-imidazolidinone (DMI) was purchased from the Tokyo Kasei Kogyo Co., and used as received. $\mathrm{Rh(CO)_2(acac)}$ and $\mathrm{P(i\text{-}Pr)_3}$ were purchased from Strem Chemicals Inc., and $\mathrm{P(c\text{-}C_5H_9)_3}$ was prepared from phosphorus trichloride and cyclopentyl bromide by the Grignard method [9].

Infrared spectra were recorded on a Shimadzu infrared spectrophotometer IR-435 and calibrated against a polystyrene standard. NMR spectra were obtained using a JEOL JNM-GX270 FT NMR spectrometer (^{1}H, 270.05 MHz) and a JEOL JNM-FX100 FT NMR spectrometer (^{31}P, 40.25 MHz).

[Rh(CO)$_3$P(c-C$_5$H$_9$)$_3$]$_2$ (1)

Into a 35cc Hastelloy C autoclave, containing acetylacetonatobis(carbonyl)rhodium ($\mathrm{Rh(CO)_2(acac)}$, 154.8 mg, 0.6 mmol), tricyclopentylphosphine ($\mathrm{P(c\text{-}C_5H_9)_3}$, 0.18 ml, 0.6 mmol), and 4 ml of DMI, was introduced syngas ($\mathrm{H_2/CO} = 1/1$) at 29.4 MPa, at room temperature. The autoclave was heated to 230°C increasing the reaction pressure to 47.0 MPa. The reaction pressure was maintained at 47.0 MPa and the reaction continued for 45 min. After cooling to room temperature, the autoclave was left to stand for 2 d. The reaction mixture was transferred to a flask under a carbon monoxide atmosphere and the orange precipitate was separated by decantation. The crystals were washed with an n-hexane/toluene (1 : 1) mixture and dried under a stream of carbon monoxide. Yield: 0.14 g (54.9%). IR (Nujol mull, KBr cells): 1950(vs) cm^{-1}. Analysis: Found: C, 50.84; H, 6.33; P, 7.28; Rh, 22.7. $\mathrm{C_{36}H_{54}O_6P_2Rh_2}$ calc: C, 50.8; H, 6.35; P, 7.29; Rh, 24.2%.

[Rh(CO)$_3$P(i-Pr)$_3$]$_2$ (2)

The complex **2** was prepared by the same procedure as described for **1**. Yield: 0.15 g (72.0%). IR (Nujol mull, KBr cells): 1950(vs) cm^{-1}. Analysis: Found: C, 41.90; H, 6.17; P, 9.28; Rh, 27.4. $\mathrm{C_{24}H_{42}O_6P_2Rh_2}$ Calc: C, 41.48; H, 6.05; P, 8.92; Rh, 29.6%.

X-ray crystallography

Crystal data. **1**. $\mathrm{C_{36}H_{54}O_6P_2Rh_2}$, $M = 850.0$, monoclinic, space group $P2_1/n$. a 12.391(6), b 15.547(9), c 10.018(3) Å, β 96.18(3)°, $Z = 2$, D_c 1.425 g cm^{-3}, (Mo-K_α) 9.08 cm^{-1}, F(000) = 1280.

2. $C_{24}H_{42}O_6P_2Rh_2$, $M = 694.4$, monoclinic, space group $P2_1/n$. a 13.271(3), b 11.649(4), c 10.235(4) Å, β 94.86(3)°, $Z = 2$, D_c 1.463 g cm^{-3}, (Mo-K_α) = 10.96 cm^{-1}, F(000) = 720.

The lattice constants were determined by a least-squares refinement of the angular settings of 12 ($2\theta > 15°$) and 10 ($2\theta > 15°$) reflections for **1** and **2**, respectively.

Data were collected on an Enraf–Nonius CAD-4 diffractometer with Mo-K_α radiation ($\lambda = 0.71069$ Å) monochromatized by a graphite crystal. 3848 (**1**) and 3145 (**2**) reflections were measured in the range of $2\theta < 50°$, of which 2863 (**1**) and 2434 (**2**) (with $|F_o| > \sigma(|F_o|)$) were considered as observed and used for the structure

TABLE 5

ATOMIC COORDINATES FOR $[Rh(CO)_3P(c\text{-}C_5H_9)_3]_2$ (**1**) [a]

Atom	*x*	*y*	*z*	*B*
Rh	8972(5)	4618(4)	6287(7)	4.2 [b]
P	2432(2)	1186(1)	1558(2)	3.9 [b]
C(1)	631(11)	−166(11)	2200(13)	8.2 [b]
C(2)	1664(8)	−92(8)	−682(14)	6.8 [b]
C(3)	31(9)	1453(7)	233(15)	7.6 [b]
C(11)	2437(7)	1599(6)	3286(9)	4.8 [b]
C(21)	3676(24)	572(20)	1330(44)	6.7 [b]
C(21)′	3691(17)	509(18)	1625(35)	3.4 [b]
C(31)	3004(20)	2156(17)	796(26)	5.8 [b]
C(31)′	2534(40)	2176(22)	564(32)	6.5 [b]
O(1)	594(19)	−780(20)	2964(23)	9.4(8)
O(1)′	266(19)	−343(19)	3229(23)	7.5(8)
O(2)	2078(12)	−283(15)	−1641(22)	6.4(5)
O(2)′	2192(15)	−599(18)	−1184(29)	5.2(7)
O(3)	−382(18)	2046(13)	−468(35)	6.9(8)
O(3)′	−580(12)	2032(9)	224(24)	6.6(5)
C(12)	2547(10)	887(8)	4380(12)	6.5(2)
C(13)	2130(13)	1348(11)	5554(17)	9.9(4)
C(14)	1457(12)	2075(10)	5073(15)	9.0(4)
C(15)	1420(9)	2121(8)	3536(12)	6.4(2)
C(22)	3634(18)	−422(13)	1784(30)	5.5(5)
C(23)	4779(20)	−695(17)	2207(39)	8.3(8)
C(24)	5435(17)	60(14)	2418(31)	6.1(5)
C(25)	4765(21)	844(18)	1998(34)	7.2(7)
C(22)′	3515(20)	−401(15)	2270(37)	5.0(6)
C(23)′	4645(20)	−604(16)	2934(36)	5.8(7)
C(24)′	5317(25)	129(19)	2978(45)	6.6(8)
C(25)′	4702(18)	916(15)	2412(30)	3.9(5)
C(32)	2235(15)	2931(13)	707(20)	6.8(5)
C(33)	2516(22)	3469(16)	−515(25)	9.0(6)
C(34)	3203(19)	2842(13)	−1408(22)	7.0(5)
C(35)	3177(18)	1960(12)	−735(20)	6.8(5)
C(32)′	3366(22)	2805(19)	1050(28)	6.2(7)
C(33)′	3303(26)	3373(19)	−267(28)	6.7(7)
C(34)′	2670(29)	2907(20)	−1429(33)	7.4(8)
C(35)′	2479(23)	2016(16)	−947(25)	5.2(6)

[a] Atomic coordinates are multiplied by 10^5 for Rh atom and 10^4 for other atoms. [b] B_{eq}.

TABLE 6

ATOMIC COORDINATES FOR $[Rh(CO)_3P(i\text{-}Pr)_3]_2$ (**2**) [a]

Atom	x	y	z	B
Rh	4766(1)	949(1)	772(1)	4.0 [b]
P	4493(4)	2513(4)	2100(5)	4.8 [b]
C(1)	343(1)	36(1)	69(2)	4.5(3)
C(2)	513(2)	179(2)	−66(2)	6.8(5)
C(3)	582(2)	26(2)	191(3)	7.1(5)
O(1)	263(1)	5(2)	65(2)	8.7(5)
O(2)	534(2)	230(2)	−152(3)	11.7(7)
O(3)	663(3)	52(4)	250(4)	8.5(8)
O(3)′	631(2)	2(2)	277(3)	5.4(5)
C(11)	334(2)	352(2)	165(3)	7.0(5)
C(12)	316(7)	349(7)	13(4)	10.9(22)
C(13)	233(2)	282(3)	171(5)	10.3(10)
C(12)′	331(6)	397(5)	24(5)	10.0(16)
C(21)	556(2)	368(2)	210(4)	8.5(7)
C(22)	670(3)	346(6)	202(8)	10.7(15)
C(23)	564(13)	487(8)	282(14)	15.6(53)
C(22)′	658(3)	318(5)	262(6)	6.8(11)
C(23)′	518(12)	485(6)	265(15)	14.8(46)
C(31)	420(5)	208(4)	375(5)	8.1(16)
C(32)	357(5)	96(4)	389(7)	6.7(14)
C(33)	521(5)	256(8)	441(9)	8.8(22)
C(31)′	463(3)	221(4)	387(4)	6.7(11)

[a] Atomic coordinates are multiplied by 10^4 for Rh and P atoms, and 10^3 for other atoms. [b] B_{eq}.

determination. Lorentz, polarization and empirical absorption corrections were applied.

The structure was solved by the conventional Patterson and Fourier method and refined by a full-matrix least-squares method. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = 0.5531/(\sigma^2(F) + 0.012470F^2)$ for **1**. All non-hydrogen atoms, except disordered C atoms, were refined anisotropically. The final residual values were $R = 0.084$ and $R_w = 0.095$ for **1**. The largest parameter shifts in the final cycle were less than 0.1 of their estimated standard deviations, and the maximum peak height on the difference map was 0.74 eÅ^{-3}.

The residual values in the final stage of refinement were $R = 0.143$ and $R_w = 0.159$ for **2**.

Atomic coordinates are collected in Table 5 for **1** and Table 6 for **2**.

For both complexes extensive atomic disorders were observed with respect to carbonyl oxygens and cyclopentyl or isopropyl groups.

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