Ligand migrations during the formation of some palladium–rhodium heterodinuclear complexes

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Abstract

A new Pd(I)–Rh(II) heterodinuclear complex, $trans$-$(NC)_2$–$(CH_3O)_3PRh(\mu$-dppm$)_2PdCl$ (2a), was prepared by treatment of $[(cod)RhCl]_2$ with $(CH_3O)_3P$ and $trans$-$(NC)_2Pd(dppm)_2$ (1) (dppm = bis(diphenylphosphino)methane, cod = 1,5-cyclooctadiene) and characterized by ^{31}P NMR spectroscopy and single-crystal X-ray structure determination. The single crystal of complex 2a is triclinic; its space group $P\bar{1}$(No.2); $a = 15.684(6)$, $b = 16.059(5)$, $c = 12.274(4)$ Å, $\alpha = 94.43(3)$, $\beta = 106.55(3)$, $\gamma = 87.86(3)°$. The Rh–Pd bond distance is 2.7835(5) Å. The molecular structure of this complex suggests that its formation reaction includes: (i) ligand migrations of the Cl^- from the Rh center to the Pd center and the two CN^- groups from the Pd center to Rh center; (ii) the intermetallic one-electron transfer indicated by the alteration from Rh(I) and Pd(II) to Rh(II) and Pd(I) respectively; (iii) the Pd(I)–Rh(II) bond formation by pairing one electron from Rh(II) with one electron from Pd(I). The differences of chemical shifts of the phosphorus atoms coordinated to the Pd center in the Pd–Ag complexes and the Pd–Rh complexes are discussed.

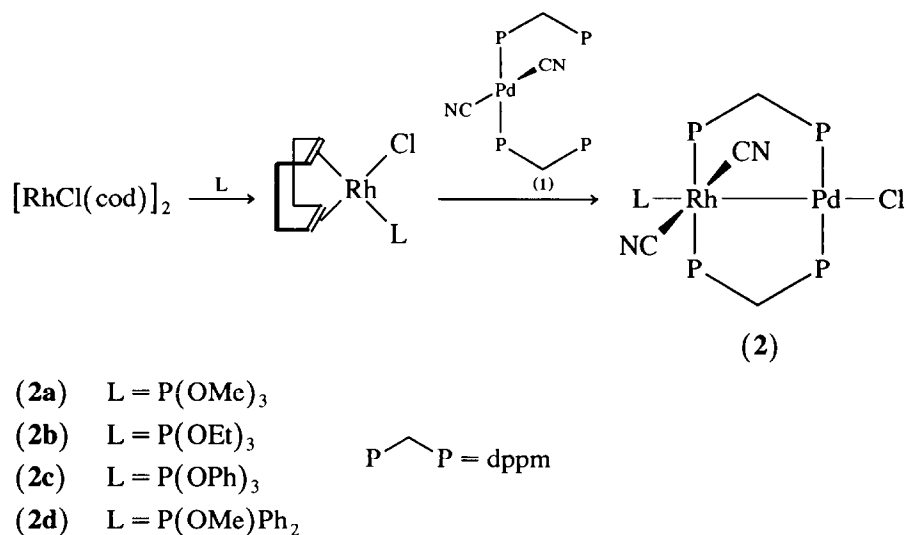*Keywords:* Heterobimetallics; Rhodium; Palladium; Cyanide; Chloride; Diphosphine

1. Introduction

Heterodinuclear complexes are very attractive because of their structural and reactive features and their potential applications for catalysis [1]. In these complexes, two different metal atoms or ions in the same molecule may cooperate to facilitate some reactions, which could not be handled by a single metal center, leading to new types of reaction and affording new opportunities. Four Pd–Ag heterodinuclear complexes bridged with dppm have been prepared and characterized by elemental analysis, IR and NMR spectroscopy [2], and the molecular structure of $trans$-$(NC)_2Pd(\mu$-dppm$)_2Ag(NO_2)$ has been reported [3a]. Now our interest is extended to a series of Pd–Rh complexes [3b]. In this paper the molecular structure of $trans$-$(NC)_2(CH_3O)_3PRh(\mu$-dppm$)_2PdCl$ (2a) and its formation reaction, including ligand migrations and intermetallic electron transfer, are presented.

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2. Results and discussion

Many heterobimetallic complexes has been prepared from dppm complexes of platinum or palladium dicyanides [4]. We have prepared a series of Pd–Rh heterobimetallic complexes by treatment of complex $trans$-$Pd(CN)_2(dppm)_2$ (1) with $[Rh(cod)Cl]_2$ and other tertiary phosphine ligands. For example, a mixture of $[Rh(cod)Cl]_2$ and 2 equimolar $P(OMe)_3$ in dichloromethane was treated with 2 equimolar $trans$-$Pd(CN)_2(dppm)_2$ (1) for 8 h, an orange complex was formed [3b] (see Scheme 1). This complex was formulated as $[ClPd(\mu$-dppm$)_2Rh(CN)_2P(OMe)_3]$ (2a) on the basis of elemental analysis, ^{31}P-$\{^1H\}$ NMR, ^1H NMR and IR spectroscopy. Complex 2a in KBr pellet has a strong IR absorption at 2100.6 cm^{-1} owing to the CN^- stretching. This IR singlet band may rule out the existence of $(CN)ClPd(\mu$-dppm$)_2Rh(CN)P(OMe)_3$, which should have two bands of absorption around 2100 cm^{-1} owing to the two CN^- groups at the Pd and Rh center, respectively. The ^1H NMR (in CDCl$_3$) spectrum shows that the chemical shift of the methylene of dppm bridg-

$$[RhCl(cod)]_2 \xrightarrow{\ L\ } \left[\text{Rh}\begin{array}{c}Cl\\L\end{array}\right] \xrightarrow{(1)} \quad (2)$$

(2a)   L = P(OMe)$_3$

(2b)   L = P(OEt)$_3$

(2c)   L = P(OPh)$_3$ P$\frown$P = dppm
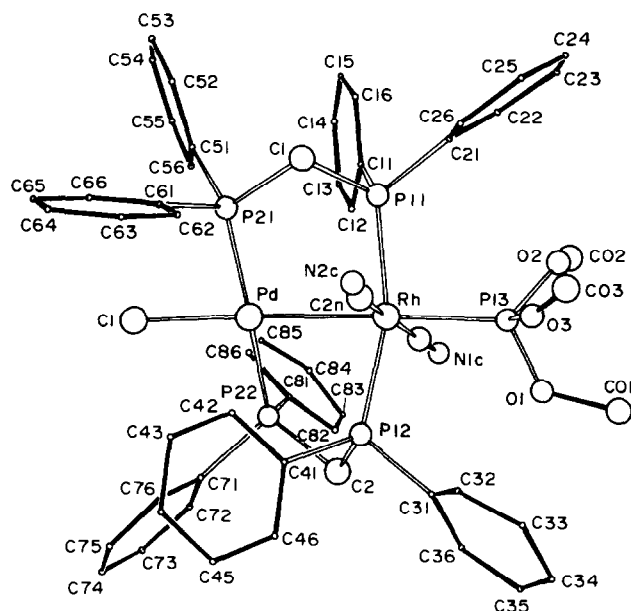
(2d)   L = P(OMe)Ph$_2$

Scheme 1.

ing between the metals changes from 3.55 ppm (1) to 3.0 ppm (2a). The ^{13}C NMR spectrum of complex 2a does not give any information about the CN$^-$ groups, because their resonance lines are masked by strong and broad resonance lines of 24 carbon atoms of the phenyl groups. In the ^{31}P NMR spectrum (Fig. 1), there are three groups of resonance lines. The first group is quartet around -3.66 ppm owing to P$_{21}$ and P$_{22}$. The
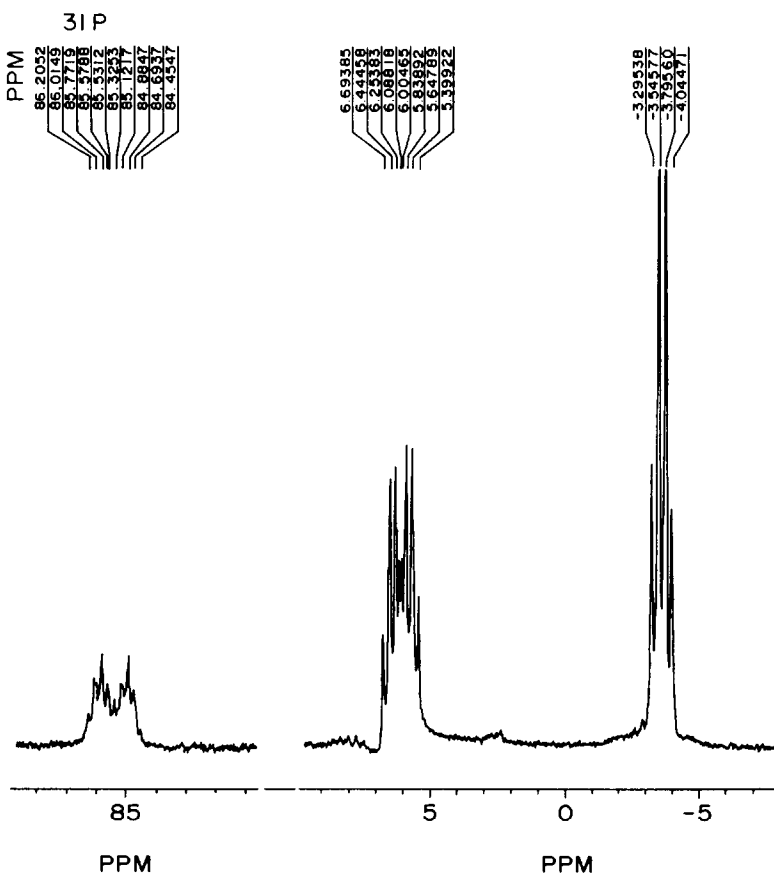
Fig. 1. The ^{31}P NMR spectrum of complex 2a.

Fig. 2. The molecular structure of complex 2a.

Table 2
Selected bond angles (°) for complex 2a

Rh–Pd–Cl	175.49(4)	C(1n)–Rh–C(2n)	177.0(2)
Rh–Pd–P(21)	93.04(3)	Rh–P(11)–C(1)	109.2(1)
Rh–Pd–P(22)	90.23(3)	Rh–P(11)–C(11)	120.9(2)
Cl–Pd–P(21)	86.65(4)	Rh–P(11)–C(21)	117.7(2)
Cl–Pd–P(22)	90.52(4)	Rh–P(12)–C(2)	110.0(1)
P(21)–Pd–P(22)	173.62(4)	Rh–P(12)–C(31)	117.2(1)
Pd–Rh–P(11)	83.99(3)	Rh–P(12)–C(41)	119.2(1)
Pd–Rh–P(12)	80.49(3)	Rh–P(13)–O(1)	112.6(1)
Pd–Rh–P(13)	174.87(4)	Rh–P(13)–O(2)	121.6(2)
Pd–Rh–C(1n)	92.4(1)	Rh–P(13)–O(3)	114.4(3)
Pd–Rh–C(2n)	92.0(2)	Pd–P(21)–C(1)	115.1(1)
P(11)–Rh–P(12)	163.51(4)	Pd–P(21)–C(51)	116.2(2)
P(11)–Rh–P(13)	97.38(4)	Pd–P(21)–C(61)	113.9(1)
P(11)–Rh–C(1n)	96.8(1)	Pd–P(22)–C(2)	114.5(1)
P(11)–Rh–C(2n)	86.1(1)	Pd–P(22)–C(71)	110.1(2)
P(12)–Rh–P(13)	98.57(4)	Pd–P(22)–C(81)	109.8(1)
P(12)–Rh–C(1n)	89.4(1)	P(11)–C(1)–P(21)	105.9(2)
P(12)–Rh–C(2n)	88.9(2)	P(12)–C(2)–P(22)	105.2(2)
P(13)–Rh–C(1n)	82.5(1)	Rh–C(1n)–N(1c)	176.7(4)
P(13)–Rh–C(2n)	93.0(2)	Rh–C(2n)–N(2c)	171.0(5)

second is octet around 6.05 ppm owing to P_{11} and P_{12}. The third is also octet around 85.45 ppm owing to P_{13}. The area ratios of the three groups are $2:2:1$.

The molecular structure of complex 2a is shown in Fig. 2. Selected bond lengths and bond angles are listed in Tables 1 and 2, respectively. The interatomic distance of Pd–Rh (2.7835(5) Å) shows the existence of the Pd–Rh bond. In this molecule the Pd atom locates at the center of a square plane composed of the two P atoms of the two dppm ligands, the Cl atom and the Rh atom. The oxidation number of the palladium is formally considered to be +1. The Rh atom locates at the center of an octahedron composed of the three P atoms, the two CN^- groups and the Pd atom. The oxidation number of the rhodium is considered to be +2. The Pd atom and Rh atom each contribute one electron to form an Rh–Pd bond, which seems mainly to be a covalent rather than a dative bond. No unpairing electrons exist in the complex molecule 2a, resulting in its diamagnetism. In this molecule (2a), the two five-membered

Table 1
Selected bond distances (–) for complex 2a

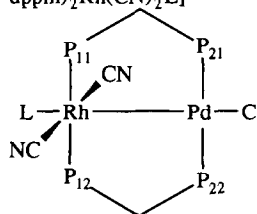|			
Pd–Rh	2.7835(5)	P(12)–C(2)	1.827(5)
Pd–Cl	2.413(1)	P(12)–C(31)	1.840(4)
Pd–P(21)	2.290(1)	P(12)–C(41)	1.839(5)
Pd–P(22)	2.307(1)	P(13)–O(1)	1.565(3)
Rh–P(11)	2.341(1)	P(13)–O(2)	1.554(4)
Rh–P(12)	2.323(1)	P(13)–O(3)	1.578(7)
Rh–P(13)	2.314(1)	P(21)–C(1)	1.836(4)
Rh–C(1n)	2.000(6)	P(21)–C(15)	1.839(4)
Rh–C(2n)	2.013(6)	P(21)–C(61)	1.847(6)
P(11)–C(1)	1.835(5)	P(22)–C(2)	1.844(4)
P(11)–C(11)	1.847(5)	P(22)–C(71)	1.865(4)
P(11)–C(21)	1.820(5)	P(22)–C(81)	1.832(5)

rings $Pd–Rh–P_{11}–C_1–P_{21}$ and $Pd–Rh–P_{12}–C_2–P_{22}$ are not planar. The $Rh–P_{11}$ bond is not parallel to the $Pd–P_{21}$ bond. Also the $Rh–P_{12}$ bond is not parallel to the $Pd–P_{22}$ bond. Their torsion angles are 41.91° and 30.84°, respectively. The dihedral angle between the $Cl–P_{21}–Rh–P_{22}$ plane with the Pd center and the $P_{11}–P_{12}–Pd–P_{13}$ plane in the octahedron with the Rh center is 143.80°. The dihedral angle between the $Cl–P_{21}–Rh–P_{22}$ plane with the Pd center and the $C_1N_1–C_2N_2–Rh–P_{13}$ plane is 50.88°. Therefore, the square plane surrounding the Pd center and the octahedron surrounding the Rh center is staggered.

We have proposed that the formation reaction of complex 2a and its analogues includes the following three processes: ligand migration, intermetallic electron transfer, and Pd–Rh bond formation. The cyanide ion has been shown to be an excellent strong ligand for stabilizing the fluxional dppm complexes *trans*-$[M(CN)_2(dppm)_2]$ (M = Pt or Pd), which can be used as key starting materials in the systematic synthesis of dppm-bridged heterobimetallic complexes [4]. In the series of Pd–Rh complexes prepared, we found that before the reaction the two CN^- groups coordinated to the Pd center in *trans*-$Pd(CN)_2(dppm)_2$ (1) and then coordinated to the Rh center in complex 2a after the reaction: the Cl^- bonded to the Rh before the reaction coordinated to the Pd after the reaction. This result shows that the ligand migrations of the Cl^- from the Rh center to the Pd center and the CN^- groups from the Pd center to the Rh center happened during the formation reation of 2a. The reason may be that the cyanide ions have a stronger affinity with the Rh(II) center coordinated by a phosphite ligand than with the Pd(I) center. This affinity is enhanced by the presence of the phosphite ligand at the Rh center. In complex 2a, the

Table 3
^{31}P NMR chemical shifts (ppm) of complexes [ClPd(μ-dppm)$_2$Rh(CN)$_2$L]

L	P(OMe)$_3$	P(OEt)$_3$	P(OPh)$_3$	PPh$_2$(OMe)
P$_{11}$,P$_{12}$	6.05	5.65	5.08	5.62
P$_{21}$,P$_{22}$	−3.66	−3.40	−3.48	−2.96
P$_{13}$	85.45	79.56	65.53	92.44

oxidation numbers of Rh and Pd are + 1 and + 2 before the formation reaction respectively. During the formation of complex 2a, the Rh(I) is oxidated to Rh(II) and the Pd(II) is reduced to Pd(I). One electron from Rh(II) and the other from Pd(I) pair with each other to form a Pd–Rh bond. No unpairing electrons exist in the complex molecule 2a, resulting in its diamagnetism.

2.1. The ^{31}P-{^{1}H} NMR parameters

Four Pd–Ag heterodinuclear complexes have been prepared [2]. Complex *trans*-(NC)$_2$Pd(μ-dppm)$_2$Ag-(NO$_2$) (3) is one of them. The molecular structure of complex 3 has been determined by X-ray diffraction [3a]. The chemical shifts of the P atoms coordinated with Pd are − 3.66 ppm in complex 2a and 19.8 ppm in complex 3 respectively. We have obtained three other Pd–Rh complexes (2b, 2c, 2d) similar to complex 2a by addition of P(OEt)$_3$, P(OPh)$_3$ and PPh$_2$(OMe) respectively, instead of P(OMe)$_3$ [3b]. Their ^{31}P NMR data [3b] are shown in Table 3. The chemical shifts of the P atoms coordinated with the Pd centers are all about − 3 ppm in these three Pd–Rh complexes. Comparing these P chemical shifts of complexes 2a (− 3.66 ppm) and complex 3 (19.8 ppm), they are very different in the Pd–Rh complexes and in the Pd–Ag complexes, indicating that their chemical environments are not the
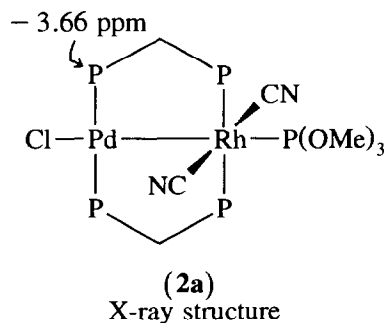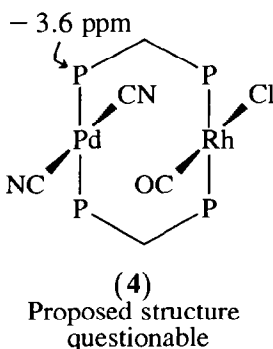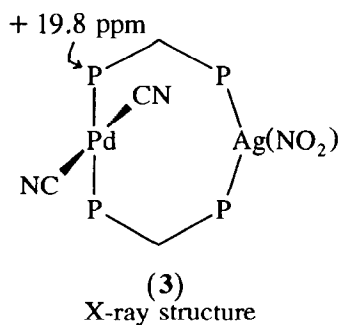
same because of ligand migrations, Pd(I)–Rh(II) bond formation, and no Pd–Ag bond in the dppm-bridged Pd–Ag complexes. The proposed molecular structure of complex *trans*-(NC)$_2$Pd(μ-dppm)$_2$RhCl(CO) (4) in the literature [5] seems unlikely because of its phosphorus chemical shift values (− 3.6 ppm), very close to that of complex 2a.

3. Experimental

The complexes *trans*-Pd(CN)$_2$(dppm)$_2$ and [Rh-(cod)Cl]$_2$ were prepared as described in the literature [5,6]. The infrared spectrum was obtained on a Nicolet 10 DXFT-IR (KBr pellet), NMR spectra were measured on a Bruker AM-400 spectrometer. Tetramethylsilane was used as the internal reference (0.00 ppm) for proton NMR spectra. H$_3$PO$_4$ (85%) was used as the external reference for phosphorus NMR spectra. The elemental analysis was carried out on a Carlo-Erba 1106.

3.1. Preparation of [ClPd(μ-dppm)$_2$Rh(CN)$_2$P(OMe)$_3$] (2a)

A mixture of [Rh(cod)Cl]$_2$ (0.049 g, 0.10 mmol) and P(OMe)$_3$ (0.0248 g, 0.2 mmol) in dichloromethane (10 cm^3) was stirred under a nitrogen atmosphere. Then a solution of *trans*-Pd(CN)$_2$(dppm)$_2$ (0.185 g, 0.20 mmol) in CH$_2$Cl$_2$ (5 cm^3) was added. The mixture was stirred under nitrogen atmosphere for 8 h then filtered and methanol (ca. 50 ml) was added to the filtrate. The desired product was precipitated as an orange solid (0.152 g, 64%; m.p. 175°C). Anal. Found: C, 55.49; H, 4.73; N, 2.24. C$_{55}$H$_{53}$O$_3$N$_2$P$_5$ClPdRh. Calc.: C, 55.53; H, 4.79; N, 2.35%; ν_{max} (cm^{-1}) (CN) 2100.6. ^{1}H NMR (400 MHz, CDCl$_3$), 3.0 (4H, t, CH$_2$), 1.62 (9H, s, CH$_3$).

3.2. Crystallography

Suitable crystals of [ClPd(μ-dppm)$_2$Rh(CN)$_2$-P(OMe)$_3$](C$_3$H$_6$O)$_2$ were grown from acetone + hexane (3:1).

+ 19.8 ppm

(3)
X-ray structure

− 3.6 ppm

(4)
Proposed structure
questionable

− 3.66 ppm

(2a)
X-ray structure

Table 4

Positional parameters and their estimated standard deviations for [PdRh(dppm)$_2$(CN)$_2$P(OMe)$_2$Cl](C$_3$H$_5$O)$_2$

Atom	x	y	z	B (Å^2)
Pd	0.73551(4)	0.24870(3)	0.13366(4)	2.97(1)
Rh	0.75275(4)	0.20588(4)	0.35546(4)	2.95(1)
Cl	0.7100(2)	0.2918(2)	−0.0582(2)	6.28(7)
P(11)	0.7366(2)	0.0695(1)	0.2748(2)	3.54(5)
P(12)	0.7501(2)	0.3503(1)	0.3815(2)	2.96(5)
P(13)	0.7805(2)	0.1727(2)	0.5434(2)	4.89(6)
P(21)	0.6450(2)	0.1391(1)	0.0557(2)	3.20(5)
P(22)	0.8373(2)	0.3529(1)	0.2013(2)	3.13(5)
C(1)	0.6336(6)	0.0638(5)	0.1573(6)	3.8(2)
C(2)	0.8448(6)	0.3937(5)	0.3473(6)	3.6(2)
C(1n)	0.8856(5)	0.2071(5)	0.3966(5)	3.3(2)
C(2n)	0.6200(6)	0.2074(6)	0.3286(7)	4.5(2)
N(1c)	0.9616(5)	0.2096(5)	0.4250(6)	5.5(2)
N(2c)	0.5497(5)	0.2035(5)	0.3267(5)	5.3(2)
O(1)	0.8410(4)	0.2375(3)	0.6282(4)	4.9(2)
O(2)	0.8213(7)	0.0866(4)	0.5849(5)	9.7(3)
O(3)	0.6951(6)	0.1728(7)	0.5872(8)	13.1(3)
C(01)	0.8621(8)	0.2363(7)	0.7522(7)	7.2(3)
C(02)	0.914(1)	0.0626(8)	0.590(1)	10.8(5)
C(03)	0.6430(9)	0.142(1)	0.627(1)	13.2(6)
C(11)	0.8202(6)	0.0212(5)	0.2096(6)	4.5(2)
C(12)	0.8927(6)	0.0654(6)	0.2035(7)	4.9(2)
C(13)	0.9553(7)	0.0287(7)	0.1500(8)	6.4(3)
C(14)	0.9419(7)	−0.0516(7)	0.1035(9)	7.0(3)
C(15)	0.8683(8)	−0.0954(6)	0.1086(8)	6.9(3)
C(16)	0.8077(7)	−0.0596(5)	0.1617(7)	5.5(3)
C(21)	0.7201(7)	−0.0124(5)	0.3626(6)	5.7(3)
C(22)	0.787(1)	−0.0703(6)	0.4113(8)	9.0(4)
C(23)	0.769(1)	−0.1276(7)	0.4854(9)	14.4(6)
C(24)	0.687(1)	−0.1274(8)	0.501(1)	14.1(5)
C(25)	0.627(1)	−0.0746(8)	0.459(1)	13.7(4)
C(26)	0.6407(8)	−0.0154(6)	0.3863(8)	8.2(3)
C(31)	0.7564(6)	0.3941(5)	0.5255(6)	3.5(2)
C(32)	0.6868(6)	0.3758(6)	0.5692(7)	4.7(2)
C(33)	0.6901(7)	0.4032(7)	0.6804(7)	6.7(3)
C(34)	0.7599(8)	0.4492(6)	0.7449(7)	7.4(3)
C(35)	0.8279(8)	0.4687(6)	0.7020(7)	6.8(3)
C(36)	0.8261(7)	0.4415(6)	0.5910(7)	5.4(2)
C(41)	0.6545(6)	0.4103(5)	0.2966(6)	3.8(2)
C(42)	0.5930(6)	0.3759(5)	0.1998(6)	4.0(2)
C(43)	0.5262(6)	0.4247(6)	0.1348(7)	5.0(2)
C(44)	0.5182(7)	0.5073(6)	0.1641(8)	6.2(3)
C(45)	0.5776(7)	0.5433(6)	0.2577(8)	6.4(3)
C(46)	0.6454(7)	0.4948(5)	0.3250(7)	5.0(2)
C(51)	0.6791(5)	0.0709(5)	−0.0510(6)	3.5(2)
C(52)	0.6247(6)	0.0056(5)	−0.1076(7)	5.0(2)
C(53)	0.6532(7)	−0.0479(5)	−0.1827(7)	5.6(3)
C(54)	0.7336(7)	−0.0397(6)	−0.2005(7)	6.3(3)
C(55)	0.7878(7)	0.0232(6)	−0.1461(7)	5.8(3)
C(56)	0.7600(6)	0.0800(5)	−0.0705(7)	4.4(2)
C(61)	0.5295(6)	0.1706(5)	−0.0181(6)	3.9(2)
C(62)	0.4668(6)	0.1867(6)	0.0397(7)	4.9(2)
C(63)	0.3823(7)	0.2159(7)	−0.0170(9)	6.2(3)
C(64)	0.3620(7)	0.2297(6)	−0.1299(9)	6.9(3)
C(65)	0.4237(8)	0.2140(6)	−0.1893(8)	6.8(3)
C(66)	0.5091(7)	0.1853(6)	−0.1331(7)	5.7(3)
C(71)	0.8246(6)	0.4505(5)	0.1226(6)	3.9(2)
C(72)	0.8971(6)	0.4859(6)	0.1013(8)	5.8(3)
C(73)	0.8875(7)	0.5596(6)	0.0456(9)	6.8(3)
C(74)	0.8056(7)	0.5985(5)	0.0133(8)	5.9(3)
C(75)	0.7336(7)	0.5643(6)	0.0337(8)	5.9(3)
C(76)	0.7420(6)	0.4888(6)	0.0882(7)	4.9(2)
C(81)	0.9481(5)	0.3149(5)	0.1977(7)	3.8(2)

Table 4 (continued)

Atom	x	y	z	B (Å^2)
C(82)	1.0240(6)	0.3341(7)	0.2816(8)	6.4(3)
C(83)	1.1067(7)	0.3071(8)	0.2709(9)	8.2(3)
C(84)	1.1106(7)	0.2590(7)	0.179(1)	8.9(4)
C(85)	1.0360(7)	0.2453(7)	0.088(1)	9.2(3)
C(86)	0.9520(7)	0.2730(7)	0.0958(8)	7.0(3)
C(1a)	0.935(2)	0.686(1)	0.321(2)	7.5(6) *
C(2a)	0.903(1)	0.6410(8)	0.378(1)	4.0(3) *
C(3a)	0.822(1)	0.655(1)	0.385(1)	5.5(4) *
O(a)	0.9469(9)	0.5859(8)	0.424(1)	6.1(3) *
C(1b)	0.442(2)	0.397(1)	0.426(2)	7.4(6) *
C(2b)	0.374(1)	0.3425(9)	0.390(1)	4.9(3) *
C(3b)	0.353(2)	0.319(1)	0.287(2)	7.0(5) *
O(b)	0.3303(9)	0.3342(9)	0.450(1)	6.6(3) *

* Refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $(4/3)[a^2\beta(1, 1) + b^2\beta(2, 2) + c^2\beta(3, 3) + ab(\cos \gamma)\beta(1, 2) + ac(\cos \beta)\beta(1, 3) + bc(\cos \alpha)\beta(2, 3)]$.

3.3. Crystal data

[ClPd(μ-dppm)$_2$Rh(CN)$_2$P(OMe)$_3$](C$_3$H$_6$O)$_2$, C$_{61}$H$_{65}$ClPdRhN$_2$O$_5$P$_5$ MW = 1305.84, triclinic; a = 15.684(2), b = 16.059(3), c = 12.274(3) Å, α = 93.43(3), β = 106.65(3), γ = 87.86(2)°, V = 2957.5 Å^3; space group $P\bar{1}$(No. 2); Z = 2, D_c = 1.479 (g cm^{-3}), $F(000)$ = 1336. Orange, crystal dimensions of 0.50 × 0.80 × 1.00 mm^3, radiation Mo Kα (λ = 0.71069 Å); μ(Mo Kα) = 8.0 cm^{-1}.

3.4. Data collection and processing

MSC/RigaKu diffractometer, ω–2θ mode with ω scan width 0.80 + 0.350 tan θ, ω scan speed 16° min^{-1} (in omega); graphic-monochromated Mo Kα radiation (λ = 0.71069 Å); 7979 reflections were measured (2θ < 50.1 + h + k + l), 7560 unique (merging R = 0.070 after absorption correction (max., min. transmission factor 0.999, 0890)) giving 6162 I > 3.0 $\sigma(I)$.

3.5. Structure analysis and refinement

The structure was solved by direct methods. A total of eight atoms were located from an E-map. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. The structure was refined in full-matrix least-squares, where refinement minimized was $w([F_0] - [F_c])^2$ and the weight w is defined as for the Killean and Lawrence method with terms of 0.010 and 1.0. Final R and R' values are 0.047, 0.071, respectively. All calculations were performed on a VAX computer using SDP/VAX [7]. The final atomic coordinates and their standard deviations are listed in Table 4.

Acknowledgements

References

[1] (a) B. Delavaux, B. Chaudred, J. Evillers, F. Dahan, G. Commenges and R. Poiblanc, *J. Am. Chem. Soc., 108* (1986) 3707.
(b) S.W. Carr, B.L. Shaw and M. Thornton-pett, *J. Chem. Soc., Dalton Trans.* (1987) 1763.
(c) B. Chaudret, B. Delavaux and R. Poilblance, *Coord. Chem. Rev. 86* (1988) 191.

(d) M. Krumm, B. Lippert, L. Randaccio and E. Zangrando, *J. Am. Chem. Soc., 113* (1991) 5129.
(e) R.J. Puddephatt, *Chem. Soc. Rev., 12* (1983) 99.
(f) S.A. Laneman and G.G. Stanley, in W.R. Moser and D.W. Slocum (eds.), *Homogeneous Transition Metal Catalyzed Reactions,* Adv. Chem. Ser. 230, Washington, D.C., 1992, p. 349.
[2] S.-j. Lu, *JIEGOUHAXUE 10* (1991) 70.
[3] (a) S.-j. Lu, F.R. Fronczek and J. Selbin, *JIEGOUHAXUE 9* (1990) 154.
(b) S.-j. Lu and J. Selbin, *JIEGOUHAXUE 11* (1992) 24.
[4] P.G. Pringle and B.L. Shaw, *J. Chem. Soc., Chem. Commun.,* (1982) 956.
[5] F.S.M. Hassan, D.P. Markam, P.G. Pringle and B.L. Shaw, *J. Chem. Soc., Dalton Trans.,* (1985) 279.
[6] J. Chatt and L.M. Venanzi, *J. Chem. Soc.,* (1975) 4735. G. Giordano and R.H. Crabtree, *Inorg. Synth., XIX* (1982) 218.
[7] B.A. Frenz, in H. Schenk, R. Olthof-Hazelkam, H. Vankonigsveld and G.C. Bassi (eds.), *The Enraf-Nonius CAD 4SDP — A Real-time System for Concurrent X-Ray Data Collection and Crystallography,* Delft University Press, Delft, Netherlands, 1978, p. 64.