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Steric Effects of the 2-(Diphenylphosphino)-6-methoxypyridine Short-Bite Bridging Ligand in the Synthesis of Binuclear Complexes. Crystal and Molecular Structure of $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4\cdot CH_2Cl_2$

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Treatment of $[Rh(COD)(\mu\text{-}Cl)]_2$ (COD = cycloocta-1,5-diene) with 2-(diphenylphosphino)-6-methoxypyridine ($Ph_2PPyOMe$) in benzene solution yielded the complex $[Rh(COD)(Ph_2PPyOMe)Cl]$ (**1**), in which $Ph_2PPyOMe$ acts as an η^1 P-bonded ligand. The COD ligand was easily displaced when CO was bubbled into a CH_2Cl_2 solution of **1**, and the presence in solution of *cis*-$[Rh(CO)_2(Ph_2PPyOMe)Cl]$ (**2**) was established by IR and NMR spectroscopy. By the addition of $Ph_2PPyOMe$ to a CH_2Cl_2 solution containing **2** (molar ratio 1:1) or $[Rh(CO)_2(\mu\text{-}Cl)]_2$ (molar ratio 4:1), *trans*-$[Rh(CO)(Ph_2PPyOMe)_2Cl]$ (**3**) was obtained. The lack of formation in these reactions of the A-frame complex $[Rh_2(\mu\text{-}CO)(Ph_2PPyOMe)_2Cl_2]$, as was observed in the analogous reactions with 2-(diphenylphosphino)pyridine (Ph_2PPy), is discussed. The reaction of **3** with $[Cu(NCCH_3)_4]BF_4$, in CH_2Cl_2 solution, gave nearly quantitatively the complex $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4\cdot CH_2Cl_2$ (**4**), whose structure was established by an X-ray diffraction study. Attempts to obtain a Rh_2Au complex, analogous to **4**, failed. Crystals of **4** are monoclinic, of space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 32.852$ (8) Å, $b = 10.452$ (4) Å, $c = 12.945$ (5) Å, and $\beta = 97.17$ (2)°. The structure was solved from diffractometric data by Patterson and Fourier methods and refined by full-matrix least-squares techniques on the basis of 4842 observed reflections to R and R_w values of 0.0500 and 0.0661, respectively. The cationic complex of **4** is a trinuclear Rh_2Cu species containing two rhodium atoms linked by two bridging chloride ligands; the CO and the $Ph_2PPyOMe$ (P-bonded to Rh) ligands complete the coordination of each rhodium center. The two CO ligands are mutually trans. The copper center is almost linearly coordinated by the pyridine nitrogen atoms of the $Ph_2PPyOMe$ ligands. The copper and rhodium atoms are not involved in a metal–metal bond. The reaction of **1** with $[AuPPh_3]PF_6$ afforded $[Rh(COD)(\mu\text{-}Cl)]_2$ and $[Au(PPh_3)(Ph_2PPyOMe)]PF_6$ (**6**). Transfer of the $Ph_2PPyOMe$ ligand from one metal center to another occurred also in the reactions of **1** with *cis*-$[Pd(CN^tBu)_2Cl_2]$ and $[Pd(COD)Cl_2]$. The reaction products were $[Rh(CO)_2(\mu\text{-}Cl)]_2$ and respectively *cis*-$[Pd(CN^tBu)(Ph_2PPyOMe)Cl_2]$ (**7**) and $[Pd(Ph_2PPyOMe)Cl(\mu\text{-}Cl)]_2$ (**8**), $Ph_2PPyOMe$ acting as an η^1 P-bonded ligand in the last two. The effect of the small bite angle of the $Ph_2PPyOMe$ ligand on the pathway of these reactions is discussed, and a comparison with the results of analogous reactions of complexes containing the Ph_2PPy ligand is made.

Introduction

The reaction of metal-containing ligands with coordinatively unsaturated metal species provides easy access to binuclear complexes in which two metal atoms are surrounded by the binucleating ligand.[2,3] We have successfully used this synthetic route to prepare new binuclear complexes containing Ph_2PPy as a bridging ligand.[4]

We recently reported[5] the synthesis of rhodium–palladium complexes by reaction of the metal-containing ligand $[Rh(COD)(Ph_2PPy)Cl]$ (COD = cycloocta-1,5-diene; Ph_2PPy = 2-(diphenylphosphino)pyridine), in which Ph_2PPy acts as monodentate P-bonded ligand, with palladium(II) species. The outcome of these reactions was strongly dependent on the steric requirements of Ph_2PPy when coordinated as a bridging ligand. In fact, breaking of the Rh–P bond in the intermediate formed by coordination of the pyridine nitrogen atom of $[Rh(COD)(Ph_2PPy)Cl]$ to the palladium(II) center and concomitant transfer of Ph_2PPy to palladium have been achieved. The presence on the palladium(II) substrate of labile ligands or of potentially bridging ligands may also determine the reaction course. Thus the tetranuclear formally Rh^{II}–Pd^{I} complex $\{[(^tBuNC)_2Cl_2Rh(\mu\text{-}Ph_2PPy)Pd(\mu\text{-}Cl)]_2\}$ and the binuclear complex $[(COD)Rh(\mu\text{-}Ph_2PPy)(\mu\text{-}Cl)PdCl_2]$ were isolated from the reactions of $[Rh(COD)(Ph_2PPy)Cl]$ with *cis*-$[Pd(^tBuNC)_2Cl_2]$ and $[Pd(COD)Cl_2]$, respectively. These reactions involve changes in the coordination of the Ph_2PPy ligand from P- to N-bonded to the Rh center; reaction schemes have been proposed.

In light of these results and with the aim of gaining further insight into the pathways of these reactions, we have synthesized the ligand 2-(diphenylphosphino)-6-methoxypyridine ($Ph_2PPyOMe$) and examined the reactions of its rhodium(I) complexes with palladium(II) substrates and with group 11 atom electrophiles. In these reactions, we would expect the steric factors

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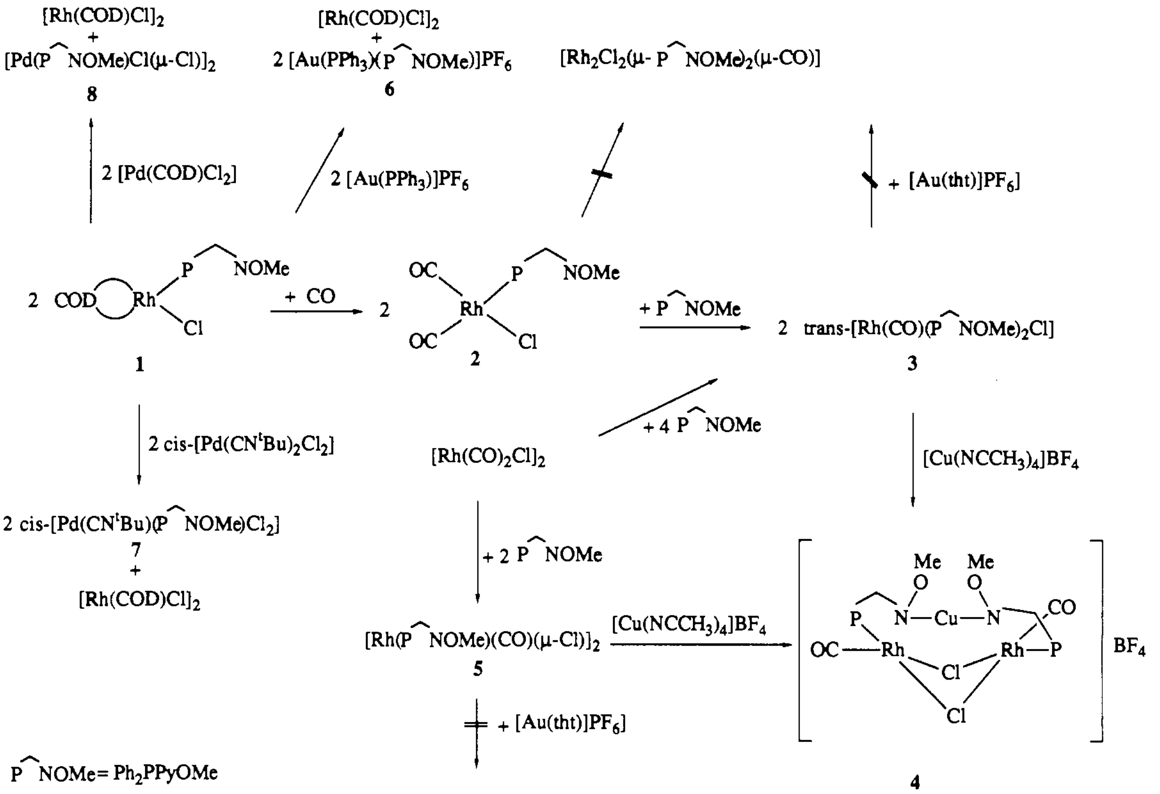
Scheme I



P^NOMe = $Ph_2PPyOMe$

COD = cyclooctadiene ; tht = tetrahydrothiophene

associated with the bridging coordination mode of $Ph_2PPyOMe$ to be enhanced with respect to the Ph_2PPy complexes because of the presence of the OCH_3 substituent on the 6-position of the pyridine ring. In this paper, we report the results of this investigation together with the X-ray structure of $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4\cdot CH_2Cl_2$.

Results

The reactions studied are summarized in Scheme I.

Synthesis of $Ph_2PPyOMe$–Rh^I Complexes. Treatment of $[Rh(COD)Cl]_2$ with 2 molar equiv of $Ph_2PPyOMe$ led to the formation of $[Rh(COD)(Ph_2PPyOMe)Cl]$ (**1**) as a yellow solid, which was nonconducting in benzene solution and soluble in diethyl ether, benzene, and dichloromethane to give air-stable solutions.

$Ph_2PPyOMe$ acts as a monodentate P-bonded ligand in **1**. Thus the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 solution shows a doublet at δ 30.3 ppm ($^1J_{RhP}$ = 150.4 Hz). In the ^1H NMR spectrum in $CDCl_3$ solution at 305 K, the olefinic protons of the COD ligand appear as two broad resonances centered at δ 5.60 ppm (trans to P) and δ 3.35 ppm. The methylene protons give rise to two sets of resonances centered at δ 2.0 and 2.4 ppm. Mutual exchange of the olefinic double bonds is likely to be responsible for the large line width observed for the olefinic protons. We have reported[6] that the ^1H NMR spectrum at low temperature of the analogous Ph_2PPy complex shows two resonances which collapse to a single resonance in the room-temperature spectrum. The double-bond scrambling has been related to the existence of a fast equilibrium between the square-planar complex and small amounts of a pentacoordinated complex formed by chelation of the pyridine nitrogen to the metal. Line shape analysis shows that exchange takes place more rapidly for $Ph_2PPyOMe$ than for PPh_3 but more slowly for the Ph_2PPy analog. This is consistent with the reduced capability of $Ph_2PPyOMe$ to give pentacoordinated complexes by chelation through nitrogen. The frequency of the OCH_3 proton resonance does not show significant change upon coordination of the ligand; this is consistent with the absence of interaction between either the pyridine nitrogen atom or the methoxy oxygen atom and the metal. Thus, IR and NMR data support a structure for **1** in which the rhodium(I) center is four-coordinate.

The COD ligand was easily displaced when CO was bubbled into a CH_2Cl_2 solution of **1**. The presence in the IR spectrum of the resulting solution of two very strong ν(CO) bands at 2010 and 2080 cm^{-1} indicated the formation of *cis*-$[Rh(CO)_2(Ph_2PPyOMe)Cl]$ (**2**). The $^{31}P\{^1H\}$ NMR spectrum of **2** in toluene at 235 K showed a doublet at δ 26.6 ppm (J_{RhP} = 126 Hz). A ^{13}CO-enriched sample, obtained when ^{13}CO was bubbled into a toluene solution of **2**, showed, in addition to the doublet at δ 26.6 ppm, a triplet centered at the same frequency ($^2J_{PC}$ = $^1J_{RhP}$ = 126.0 Hz). The ^{13}C NMR spectrum of the ^{13}CO-enriched sample showed a doublet of doublets ($^1J_{RhC}$ = 71.4 Hz, $^2J_{PC}$ = 16.3 Hz) at δ 183.1 ppm for the carbonyl cis to the phosphine and a doublet of doublets ($^1J_{RhC}$ = 60.3 Hz, $^2J_{PC}$ = 124.2 Hz) at δ 181.8 ppm for the carbonyl trans to the phosphine (the carbon–carbon coupling is too small to be observed).

On addition of $Ph_2PPyOMe$ to a CH_2Cl_2 solution of **2**, the mononuclear complex *trans*-$[Rh(CO)(Ph_2PPyOMe)_2Cl)]$ (**3**) was obtained. This was also obtained by reacting $[Rh(CO)_2(\mu\text{-}Cl)]_2$ with $Ph_2PPyOMe$ in the molar ratio 1:4, in CH_2Cl_2 solution. Compound **3** is a yellow-orange, air-stable solid, soluble in diethyl ether, benzene, and chlorinated solvents; it was characterized by elemental analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. Compounds analogous to **3** have been isolated with both PPh_3[7] and Ph_2PPy[8] ligands.

Reactions of 3 with Copper and Gold Complexes. On addition of a CH_2Cl_2 solution of $[Cu(NCCH_3)_4]BF_4$ to a solution of **3**

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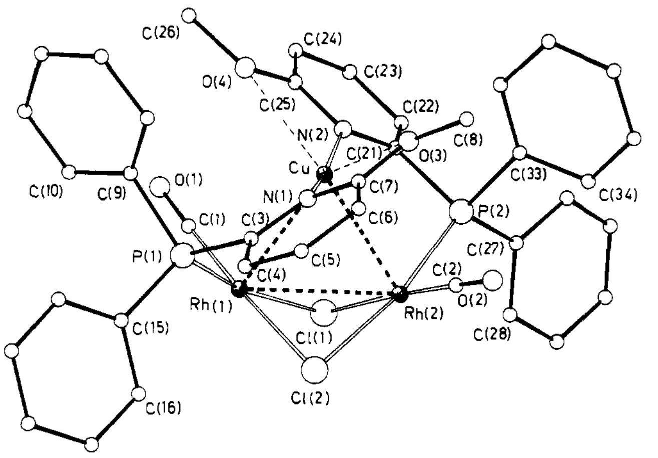

Figure 1. View of the structure of the cationic complex $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]^+$ with the atomic numbering scheme.

(molar ratio 1:2) in the same solvent, the color rapidly turned from yellow to orange; the dilution of the resulting solution with diethyl ether produced $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4\cdot CH_2Cl_2$ (**4**) nearly quantitatively. Compound **4** was isolated as an orange solid, whose methanol solution is conducting and which is air stable as a solid over long periods. Compound **4** was further characterized by a single-crystal X-ray diffraction study (see Figure 1 and Discussion). The complex cation of **4** displays a trinuclear Rh_2Cu cluster with the two rhodium atoms linked by two bridging chloride ligands; the CO and the $Ph_2PPyOMe$ (P-bonded to Rh) ligands complete the coordination of each rhodium center. The two CO ligands are mutually trans. The copper center is almost linearly coordinated by the pyridine nitrogen atoms of the $Ph_2PPyOMe$ ligands. The spectroscopic data are fully consistent with the X-ray structural results. The IR spectrum (Nujol mull) shows one $\nu(CO)$ band at 2002 cm^{-1}. A very strong $\nu(BF)$ band at 1050 cm^{-1} is consistent with the presence of the BF_4^- ion. The ^1H NMR spectrum in $CDCl_3$ at room-temperature shows the OCH_3 resonance as singlet at δ 3.30 ppm, shifted with the respect to the value of the free ligand. This shift suggests an interaction of the methoxy substituent oxygen atom with copper (see X-ray structure). The $^{31}P\{^1H\}$ NMR spectrum, in the same solvent, at 230 K, shows a doublet at δ 48.4 ppm ($^1J_{RhP}$ = 133.3 Hz).

The compounds CuCl, CuI, and $[CuPPh_3]BF_4$ failed to react with **3** or **5**.

The addition of a CH_2Cl_2 solution of $[AuPPh_3]PF_6$ to a solution of **1** in the same solvent led to a reaction. Workup of the resulting solution yielded $[Au(PPh_3)(Ph_2PPyOMe)]PF_6$ (**6**) and $[Rh(COD)Cl]_2$. Compound **6** is an orange solid, soluble in chlorinated solvents and methanol; conductivity measurements performed on methanol solutions are in accord with its formulation as a 1:1 electrolyte. In the ^1H NMR spectrum, in $CDCl_3$ solution, the OCH_3 resonance is observed at a δ value very close to that observed for the free ligand. In the $^{31}P\{^1H\}$ NMR spectrum, in $CDCl_3$ solution, the two phosphines give rise to a single resonance; this is probably due to the small difference in the chemical shift of the phosphorus atoms and to a consequently low $\Delta\nu/J_{PP}$ value.

It is noteworthy that attempts to obtain a compound analogous to **4** containing Au instead of the Cu by reacting **2**, **3**, or **5** with $[Au(tht)]^+$ (tht = tetrahydrothiophene) failed.

Description of the Crystal Structure of $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4\cdot CH_2Cl_2$ (4). In the crystals of **4**, heterotrinuclear cationic complexes $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]^+$, BF_4^-, anions and dichloromethane molecules of solvation are present. The structure of the cation, which shows approximate C_2 symmetry, is depicted in Figure 1 together with the atomic numbering scheme; the most important bond distances and angles are given in Table I. The metal core consists of a Rh_2Cu isosceles triangle, in which the Rh···Rh separation is 3.014 (1) Å and the Rh···Cu distances are 2.800 (2) and 2.753 (2) Å. Two Cl atoms almost symmetrically bridge the Rh–Rh edge [the dihedral angle between the two Rh–Cl–Rh triangles is 113.1 (1)°] whereas the two $Ph_2PPyOMe$ ligands bridge the Rh–Cu edges, being bound to the Rh atoms through the P atoms [Rh(1)–P(1) = 2.234 (2) and Rh(2)–P(2) = 2.223 (2) Å] and to the Cu atoms through the N atoms [Cu(1)–N(1) = 1.948 (7) and Cu–N(2) = 1.949 (7) Å]. Structurally characterized trinuclear Rh_2Cu complexes are rather rare. In $[Rh_2Cu(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ a triangle, in which the metal atoms are positionally disordered at a mean distance of 2.56 (1) Å, is present.[9] The cationic complex $[Rh_2Cu(\mu\text{-}Cl)_2(CO)_2(\eta\text{-}dpma)_2]^+$ [dpma = bis[(diphenylphosphino)methyl]phenylarsine] displays an almost linear Rh–Cu–Rh array in which the Rh and Cu atoms, at a distance of 3.084 (1) Å, are linked by two Cl bridges.[10] Finally, in the metal triangle found in $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}CuI)]$, the two Rh atoms, at a distance of 2.746 (1) Å, are bridged by the carbonyl and dppm ligands; both the Rh–Rh and Rh–Cu distances are consistent with metal–metal bonds,[11] and the two Rh–Cu separations of 2.588 (2) Å are shorter than those found in **4**. In **4**, the metal separations probably correspond only to weak attractive metal–

Table I. Selected Bond Distances (Å) and Angles (deg) for Complex **4**

Distances			
Rh(1)–Rh(2)	3.014 (1)		
Rh(1)–Cu	2.800 (2)	Rh(2)–Cu	2.753 (2)
Rh(1)–Cl(1)	2.421 (2)	Rh(2)–Cl(1)	2.387 (2)
Rh(1)–Cl(2)	2.418 (2)	Rh(2)–Cl(2)	2.425 (2)
Rh(1)–P(1)	2.234 (2)	Rh(2)–P(2)	2.223 (2)
Rh(1)–C(1)	1.836 (9)	Rh(2)–C(2)	1.812 (10)
Cu–N(1)	1.948 (7)	Cu–N(2)	1.949 (7)
P(1)–C(3)	1.817 (9)	P(2)–C(21)	1.852 (9)
P(1)–C(9)	1.824 (8)	P(2)–C(27)	1.817 (9)
P(1)–C(15)	1.835 (8)	P(2)–C(33)	1.808 (9)
O(1)–C(1)	1.117 (11)	O(2)–C(2)	1.139 (13)
O(3)–C(7)	1.298 (11)	O(4)–C(25)	1.355 (10)
O(3)–C(8)	1.413 (14)	O(4)–C(26)	1.423 (12)
N(1)–C(3)	1.365 (10)	N(2)–C(21)	1.366 (10)
N(1)–C(7)	1.366 (12)	N(2)–C(25)	1.320 (11)
Cu···O(3)	2.827 (7)	Cu···O(4)	2.776 (6)
Angles			
P(1)–Rh(1)–C(1)	92.2 (3)	P(2)–Rh(2)–C(2)	92.0 (3)
Cl(2)–Rh(1)–C(1)	175.6 (3)	Cl(1)–Rh(2)–C(2)	176.8 (3)
Cl(2)–Rh(1)–P(1)	91.6 (1)	Cl(1)–Rh(2)–P(2)	90.9 (1)
Cl(1)–Rh(1)–C(1)	93.1 (3)	Cl(2)–Rh(2)–C(2)	94.1 (3)
Cl(1)–Rh(1)–P(1)	167.2 (1)	Cl(2)–Rh(2)–P(2)	169.3 (1)
Cl(1)–Rh(1)–Cl(2)	82.77 (9)	Cl(1)–Rh(2)–Cl(2)	83.3 (1)
Cu–Rh(1)–C(1)	88.7 (3)	Cu–Rh(2)–C(2)	90.5 (3)
Cu–Rh(1)–P(1)	78.82 (8)	Cu–Rh(2)–P(2)	80.39 (8)
Cu–Rh(1)–Cl(2)	89.79 (8)	Cu–Rh(2)–Cl(1)	91.52 (8)
Cu–Rh(1)–Cl(1)	89.67 (8)	Cu–Rh(2)–Cl(2)	90.75 (8)
Rh(2)–Rh(1)–Cu	56.37 (5)	Rh(1)–Rh(2)–Cu	57.88 (5)
Rh(1)–Cu–N(1)	91.3 (2)	Rh(2)–Cu–N(2)	91.7 (2)
Rh(1)–Cu–N(2)	99.9 (2)	Rh(2)–Cu–N(1)	99.5 (2)
Rh(1)–Cu–Rh(2)	65.75 (6)	N(1)–Cu–N(2)	166.7 (3)
Rh(1)–Cl(1)–Rh(2)	77.64 (8)	Rh(1)–Cl(2)–Rh(2)	76.98 (8)
Rh(1)–P(1)–C(15)	118.1 (3)	Rh(2)–P(2)–C(27)	116.3 (3)
Rh(1)–P(1)–C(9)	119.4 (3)	Rh(2)–P(2)–C(33)	118.9 (3)
Rh(1)–P(1)–C(3)	107.0 (3)	Rh(2)–P(2)–C(21)	108.0 (3)
C(9)–P(1)–C(15)	102.6 (4)	C(27)–P(2)–C(33)	103.7 (4)
C(3)–P(1)–C(15)	104.9 (4)	C(21)–P(2)–C(27)	106.7 (4)
C(3)–P(1)–C(9)	103.0 (4)	C(21)–P(2)–C(33)	101.8 (4)
C(7)–O(3)–C(8)	118.0 (9)	C(25)–O(4)–C(26)	119.1 (7)
Cu–N(1)–C(7)	116.9 (6)	Cu–N(2)–C(25)	117.4 (6)
Cu–N(1)–C(3)	122.9 (6)	Cu–N(2)–C(21)	125.0 (6)
Rh(1)–C(1)–O(1)	175.6 (8)	Rh(2)–C(2)–O(2)	178.9 (9)
P(1)–C(3)–N(1)	115.6 (6)	P(2)–C(21)–N(2)	113.4 (6)
P(1)–C(3)–C(4)	123.0 (6)	P(2)–C(21)–C(22)	123.3 (7)
O(3)–C(7)–C(6)	126.2 (8)	O(4)–C(25)–C(24)	123.9 (8)
O(3)–C(7)–N(1)	113.3 (8)	O(4)–C(25)–N(2)	112.1 (7)

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metal interactions. Thus the Rh–Rh one is too long and the Rh–Cu distances, even if not much longer than those expected for a metal–metal bond (2.66 Å)[12] or than those found in the cluster $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]$ (in the range 2.629 (1)–2.693 (1) Å),[13] do not seem to influence the coordination bonding of the Cu atom substantially (see below). It is known that a short metal–metal separation alone is not always a sign of metal–metal bonding, especially when bridging atoms are present.

The coordination of each Rh atom in **4** is approximately square planar, the ligands being two Cl atoms, the P atom of the $Ph_2PPyOMe$ ligand, and a carbon atom of a terminal carbonyl group. The two mean coordination planes around the Rh atoms are tilted by 79.3 (1)°, and the two CO ligands and the two $Ph_2PPyOMe$ ligands are mutually trans. The Cu atom is best considered two-coordinate, the N–Cu–N bond angle being 166.7 (3)°. The distortion from the linearity is probably due to weaker interactions the Cu atom displays with the Rh atoms (in fact, the Cu deviates from the N···N axis toward the Rh atoms). Taking into account these weaker interactions with the Rh atoms, the Cu atom shows a distorted tetrahedral coordination. Also noteworthy are two weak interactions between the Cu atom and the oxygen atoms of the methoxy groups [Cu···O(3) = 2.827 (7) and Cu···O(4) = 2.776 (6) Å]. In the $Ph_2PPyOMe$ ligands, the two pyridine rings are planar with the P atom and the O atom and atoms of the methoxy substituents are practically coplanar, whereas the copper atom deviates by 0.375 (2) and 0.268 (2) Å, respectively, from the two mean planes. The two pyridine rings are at a dihedral angle of 64.5 (3)°, and each of them is roughly parallel to the coordination mean plane of a Rh atom.

Reactions of 1 with $[Pd(CN^tBu)_2Cl_2]$ and $[Pd(COD)Cl_2]$. The addition of 1 equiv of *cis*-$[Pd(CN^tBu)_2Cl_2]$ to a CH_2Cl_2 solution of **1** led to a change of the solution color from yellow to red-brown. Workup of the resulting solution yielded the compound *cis*-$[Pd(CN^tBu)(Ph_2PPyOMe)Cl_2]$ (**7**) together with a rhodium–isocyanide complex which was not fully characterized. The product **7** was characterized by elemental analysis and IR and NMR spectroscopies. Analogously, when **1** was reacted with 1 equiv of $[Pd(COD)Cl_2]$, $Ph_2PPyOMe$ migration from Rh to Pd occurred, the products being $[Rh(COD)Cl]_2$ and $[Pd(Ph_2PPyOMe)Cl(\mu\text{-}Cl)]_2$ (**8**). Compound **8** was characterized only by elemental analysis and IR spectroscopy owing its low solubility. In CH_2Cl_2 solution, the reaction of **8** with CN^tBu rapidly produces a nearly quantitative yield of **7**.

Discussion

The results obtained in the reactions of $[Rh(COD)Cl]_2$ with $Ph_2PPyOMe$ are very similar to those described for the analogous reactions with PPh_3[7] and in some aspects differ from those obtained by Balch et al.[8] using Ph_2PPy as a binucleating ligand.

The formation of the intermediate $[Rh(CO)_2(Ph_2PPy)Cl]$, analogous to **2**, was postulated[5] in the reaction of $[Rh(COD)(Ph_2PPy)Cl]$ with CO to give the known A-frame complex $[Rh_2Cl_2(Ph_2PPy)_2(\mu\text{-}CO)]$ as the final product.[8] The lack of formation of the A-frame complex $[Rh_2Cl_2(Ph_2PPyOMe)_2(\mu\text{-}CO)]$, analogous to $[Rh_2Cl_2(Ph_2PPy)_2(\mu\text{-}CO)]$, in the solution containing **2** is a consequence of the increased steric demand of $Ph_2PPyOMe$ with respect to Ph_2PPy. A computer-generated space-filling model of the A-frame complex $[Rh_2Cl_2(Ph_2PPyOMe)_2(\mu\text{-}CO)]$, obtained from X-ray crystal structure data for $[Rh_2Cl_2(Ph_2PPy)_2(\mu\text{-}CO)]$,[8] clearly showed the strong steric repulsive interaction of the oxygen atom of the CH_3O group with the chlorine atom.

The reaction of **3** with $[Cu(NCCH_3)_4]BF_4$ is very fast, and no traces of products other than the starting material and **4** have been detected by monitoring the reaction by NMR spectroscopy. The mechanism of the reaction is quite obscure, as it formally implies coordination of the nitrogen atom of $Ph_2PPyOMe$ of two 14-electron $[Rh(CO)(Ph_2PPyOMe)Cl]$ moieties to a copper atom and formation of two chloro bridges. Although we do not have any experimental evidence, we think that a rapid equilibrium between species **3** and $[Rh(CO)(Ph_2PPyOMe)Cl]$ may be operating in solution. A similar rapid equilibrium in solution has been considered to occur in the catalytic processes involving *trans*-$[Rh(CO)(PPh_3)_2Cl]$.[14] Both the species **3** and $[Rh(CO)(Ph_2PPyOMe)Cl]$ may be involved in the formation of the Cu–N bond. If the 14-electron species $[Rh(CO)(Ph_2PPyOMe)Cl]$ is initially involved in the reaction with $[Cu(NCCH_3)_4]BF_4$, the rate of production of **4** would diminish dramatically on addition of free $Ph_2PPyOMe$ at the beginning of the reaction. Unfortunately, this experiment has been frustrated because $Ph_2PPyOMe$ reacts easily with $[Cu(NCCH_3)_4]BF_4$ to give a species which does not react with **3**. Compound **4** was also formed easily on addition of $[Cu(NCCH_3)_4]BF_4$ to a CH_2Cl_2 solution of **2**. This suggests that the presence in solution of the 14-electron Rh^I species $[Rh(CO)(Ph_2PPyOMe)Cl]$ might determine the pathway of the reaction. However, we do not rule out the possibility that **2** and **3** could also be in rapid equilibrium with $[Ru(CO)(Ph_2PPyOMe)Cl]$ and $[Rh(CO)(Ph_2PPyOMe)(\mu\text{-}Cl)]_2$ (**5**). Thus **4** could be formed directly from the reaction of species **5** with $[Cu(NCCH_3)_4]BF_4$. We prepared the compound **5** following a method reported for the synthesis of the PPh_3 analog,[7a] and we verified that it reacts with $[Cu(NCCH_3)_4]BF_4$ to give **4**.

Characterization of $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4{\cdot}CH_2Cl_2$ (**4**) provided an example of a new structural type of complex. Several bimetallic complexes in which a rhodium or iridium center and a group 11 metal are held together by the bridging phosphorus short-bite ligands and a metal–metal bond have been reported. Examples are[15,16] $[RhAu(\mu\text{-}PNP)_2]^{2+}$ and $[RhAg(\mu\text{-}PNP)_2]^{2+}$ (PNP = 2-[bis(diphenylphosphino)methyl]pyridine). Related complexes in which a naked metal center is trapped into a metallamacrocycle based on bis[(diphenylphosphino)methyl]phenylarsine have been also reported.[10,17] The formation of **4** can be considered a process in which the Cu^+ ion is incorporated into the framework provided by *trans*-$[Rh(CO)(Ph_2PPyOMe)(\mu\text{-}Cl)]_2$. The size of the metal ion is a determining factor for its complexation into the central cavity. The nonformation of a Rh_2Au complex, analogous to **4**, may be related to steric factors within the cavity in which the gold(I) ion would be positioned and is not entirely unexpected owing to greater ionic radius of Au^+ compared to Cu^+.

The results of the reactions of **1** with *cis*-$[Pd(CN^tBu)_2Cl_2]$ and $[Pd(COD)Cl_2]$ can be explained by considering the behavior of $[Rh(COD)(Ph_2PPy)Cl]$ in the reactions with the same palladium(II) substrates and the greater steric demand of the $Ph_2PPyOMe$ with respect to the Ph_2PPy ligand. Owing to steric factors associated with the presence of the OCH_3 substituent in the pyridine ring, complexes **7** and **8** do not react further with $[Rh(COD)Cl]_2$ to give binuclear RhPd species, as observed in the analogous reactions of the Ph_2PPy derivatives.[5]

Experimental Section

Established methods were used to prepare the compounds $[Rh(COD)(\mu\text{-}Cl)]_2$,[18] *cis*-$[Pd(CNBu^t)_2Cl_2]$,[19] $[Pd(COD)Cl_2]$,[20] $[Cu(PPh_3)]PF_6$,[21] $[Cu(NCCH_3)_4]PF_6$,[22] $[Au(tht)]PF_6$,[23] and $[Au(PPh_3)]PF_6$.[24] Ph_2-

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PPyOCH$_3$ was prepared by a procedure similar to that followed for Ph$_2$PPy,[25] starting from diphenylphosphine and 2-chloro-6-methoxypyridine. All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. IR spectra were obtained as Nujol mulls on KBr or CsI plates using a Perkin-Elmer FTIR 1720 spectrophotometer. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker WP80-SY or a Varian Gemini-300 spectrometer.

^{1}H NMR spectra were referenced to internal tetramethylsilane, and ^{31}P spectra, to external 85% H_3PO_4; positive chemical shifts are to higher frequency for all nuclei. Conductivity measurements were made with a Radiometer CDM 3 conductivity meter. Molecular weights were determined with a Knauer vapor pressure osmometer. Elemental analyses were performed by Malissa-Reuter Mikroanalytishes Laboratorium, Elbach, Germany, and by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan.

Preparation of 2-(Diphenylphosphino)-6-methoxypyridine (Ph$_2$PPyOMe). A solution of *n*-butyllithium (16.8 mL of 1.6 M hexane solution, 27 mmol) was added dropwise to a stirred solution of diphenylphosphine (5 g, 27 mmol) in tetrahydrofuran (100 mL) at room temperature. The resulting red solution was stirred for $^1/_2$ h. Then a solution of 2-chloro-6-methoxypyridine (3.87 g, 27 mmol) in tetrahydrofuran (20 mL) was added dropwise, at room temperature; the red color of the solution dissipated upon addition of 2-chloro-6-methoxypyridine. Then the mixture was stirred for ca. 20 h, 25 mL of ethanol was added, and the solution was stirred for an additional $^1/_2$ h.

Removal of all solvents in vacuo gave a yellow solid. The product was extracted by dissolution in hot hexane (300 mL) to give a light yellow solution. After treatment by charcoal, filtration of the resulting colorless solution, and evaporation of the solvent, the pure product was obtained as white crystals. Yield: 7.12 g (24.3 mmol), 90%. MP: 51 °C. Anal. Calcd for $C_{18}H_{16}NOP$: C, 73.71; H, 5.50; N, 4.78. Found: C, 73.65; H, 5.48; N, 4.77. ^{1}H NMR (CDCl$_3$): δ 3.80 (s, OCH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −5.7 (s).

Preparation of [Rh(C$_8$H$_{12}$)(Ph$_2$PPyOMe)Cl] (1). A benzene solution (10 mL) of Ph$_2$PPyOMe (0.250 g, 0.852 mmol) was added to a solution of [(C$_8$H$_{12}$)Rh(μ-Cl)]$_2$ (0.210 g, 0.426 mmol) in the same solvent (20 mL). The mixture was stirred for 2 h and filtered. The volume of filtrate was reduced to 10 mL, and then 20 mL of petroleum ether was added to induce the precipitation of the product as a yellow-orange powder. This was filtered off, washed with petroleum ether, and recrystallized in diethyl ether to give the pure product (0.346 g, 0.639 mmol) in 75% yield. Anal. Calcd for $C_{26}H_{28}ClNOPRh$: C, 57.74; H, 5.40; N, 2.59; Cl, 6.55. Found: C, 57.75; H, 5.43; N, 2.61; Cl, 6.60. IR (CsI, Nujol): ν(RhCl) 278 cm^{-1}. ^{1}H NMR (CDCl$_3$, 305 K): δ 3.78 (s, OCH$_3$), 3.35 and 5.60 (s br, C$_8$H$_{12}$), 2.0 and 2.4 (m, C$_8$H$_{12}$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 30.3 (d, $^1J_{RhP}$ = 150.4 Hz).

Reaction of 1 with CO. When CO was bubbled through a dichloromethane solution (10 mL) of **1** (0.085 g, 0.157 mmol), a slight change of the yellow color of the solution immediately occurred, while the IR spectrum in the (CO) region showed bands at 2080 and 2010 cm^{-1} assigned to compound **2** (see Results). The reaction was completed in a few minutes. On addition, under CO atmosphere, of 30 mL of petroleum ether, a mixture of *cis*- and *trans*-[Rh(CO)(Ph$_2$PyOMe)(μ-Cl)]$_2$ precipitated.

Preparation of *trans*-[Rh(CO)(Ph$_2$PPyOMe)$_2$Cl] (3). A dichloromethane solution (10 mL) of [Rh(CO)$_2$(μ-Cl)]$_2$ (0.160 g, 0.412 mmol) was added dropwise to a stirred solution of Ph$_2$PPyOMe (0.483 g, 1.65 mmol) in the same solvent (20 mL). After 15 min, the volume of the resulting solution was reduced to ca. 10 mL; the addition of 30 mL of petroleum ether afforded the product as a yellow-orange precipitate. This was removed by filtration, washed with petroleum ether, and vacuum-dried. Yield: 0.544 g (0.659 mmol), 80%. Anal. Calcd for $C_{37}H_{32}ClN_2O_3P_2Rh$: C, 58.86; H, 4.54; N, 3.71; Cl, 4.70. Found: C, 58.83; H, 4.53; N, 3.70; Cl, 4.65. IR (Nujol): ν(CO) 1973, ν(RhCl) 310 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.78 (s, OCH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 230 K): δ 28.6 (d, $^1J_{RhP}$ = 128.2 Hz).

Preparation of [Rh$_2$Cu(CO)$_2$(Ph$_2$PPyOMe)$_2$(μ-Cl)$_2$]BF$_4$·CH$_2$Cl$_2$ (4). Procedure a. Solid [Cu(NCCH$_3$)$_4$]BF$_4$ (0.019 g, 0.061 mmol) was added to a well-stirred dichloromethane solution (20 mL) of **3** (0.092 g, 0.122 mmol). The resultant mixture was stirred for ca. 15 min, during which a color change from yellow-orange to orange occurred. The solution was reduced in volume (10 mL), and on addition of diethyl ether, compound **4** was obtained as an orange microcrystalline solid. This was removed by filtration, washed with diethyl ether, and vacuum-dried. Yield: 0.061 g (0.053 mmol), 87%. Anal. Calcd for $C_{39}H_{34}BCl_4F_4N_2O_4P_2CuRh_2$: C, 40.57; H, 2.97; N, 2.43; Cl, 12.28. Found: C, 40.59; H, 2.98; N, 2.45; Cl, 12.32. IR (Nujol): ν(CO) 2002, ν(BF) 1050 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.30 (s, OCH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 230 K): δ 48.4 (d, $^1J_{RhP}$ = 133.3 Hz).

Procedure b. Solid [Cu(NCCH$_3$)$_4$]BF$_4$ (0.387 g, 0.123 mmol) was added to a stirred solution of **5** (0.140 g, 0.123 mmol) in dichloromethane solution (20 mL). After 20 min, the resulting orange solution was reduced in volume (10 mL), and on addition of diethyl ether, product **4** was obtained. This was removed by filtration, washed with diethyl ether, and vacuum-dried.

Procedure c. Carbon monoxide was bubbled through a dichloromethane solution (10 mL) of **1** (0.120 g, 0.222 mmol). After about 15 min, solid [Cu(NCCH$_3$)$_4$]BF$_4$ (0.035 g, 0.111 mmol) was added, and the resulting solution was stirred for 20 min. The orange solution was reduced in volume (about 10 mL), and diethyl ether (20 mL) was added to induce precipitation of the product as an orange, microcrystalline solid. This was removed by filtration, washed with diethyl ether, and vacuum-dried. Yield: 0.060 g (0.052 mmol), 85%.

Preparation of *trans*-[Rh(CO)(Ph$_2$PPyOMe)(μ-Cl)]$_2$ (5). A benzene solution (10 mL) of Ph$_2$PPyOMe (0.180 g, 0.614 mmol) was added dropwise to a stirred solution of [Rh(CO)$_2$(μ-Cl)]$_2$ (0.119 g, 0.307 mmol) in the same solvent (10 mL). After 15 min, the volume of the solution was reduced to ca. 10 mL. By addition of hexane (30 mL) an orange precipitate was obtained. This was removed by filtration, washed with hexane, and dried. Spectroscopic data (see Results) indicated that it is a mixture of *cis*-[Rh(CO)(Ph$_2$PPyOMe)(μ-Cl)]$_2$ and *trans*-[Rh(CO)(Ph$_2$PPyOMe)(μ-Cl)]$_2$. Recrystallization of the mixture from hot benzene gave the pure trans isomer **5**, as an orange solid (0.197 g, 0.215 mmol). Yield: 70%. Anal. Calcd for $C_{38}H_{32}Cl_2N_2O_4P_2Rh_2$: C, 49.65; H, 3.51; N, 3.05; Cl, 7.71. Found: C, 49.63; H, 3.49; N, 3.02; Cl, 7.69. IR (Nujol): ν(CO) 1980 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 40.9 (d, $^1J_{RhP}$ = 136.4 Hz).

Reaction of 1 with [Au(PPh$_3$)]PF$_6$. Solid AgPF$_6$ (0.047 g, 0.186 mmol) was added to a stirred solution of AuPPh$_3$Cl (0.092 g, 0.186 mmol) in dichloromethane (20 mL). Stirring was continued for ca. 10 min to ensure complete reaction, and the AgCl precipitate was filtered off. The filtrate was added to a solution of **1** (0.100 g, 0.186 mmol) in the same solvent (20 mL), and the mixture was stirred for about 1 h. The volume was reduced to 10 mL, and on addition of 30 mL of diethyl ether [Au(PPh$_3$)(Ph$_2$PPyOMe)]PF$_6$ (**6**) was obtained as an orange microcristalline solid (0.111 g, 0.132 mmol) in 71% yield. Anal. Calcd for $C_{36}H_{31}F_6NOP_3Au$: C, 48.15; H, 3.48; N, 1.56. Found: C, 47.89; H, 3.44; N, 1.57. IR (Nujol): ν(PF) 840 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.76 (s, OCH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 43.9 (s, see Results). [Rh(COD)Cl]$_2$ was recovered from the mother liquor and identified by comparison with an authentic sample (0.031 g, 0.063 mmol, yield 71%).

Reaction of 1 with *cis*-[Pd(^{t}BuNC)$_2$Cl$_2$]. A dichloromethane solution (15 mL) of *cis*-[Pd(^{t}BuNC)$_2$Cl$_2$] (0.51 g, 0.148 mmol) was added to a solution (10 mL) of **1** (0.080 g, 0.148 mmol) in the same solvent, and the mixture was stirred for about 1 h. During this time, the color of the solution turned from yellow to red-brown. The volume of the solution was then reduced to ca. 10 mL; the addition of the diethyl ether gave the product [Pd(^{t}BuNC)(Ph$_2$PPyOMe)Cl$_2$] (**7**) as a yellow solid. This was removed by filtration, washed several times with diethyl ether, and vacuum-dried to give the pure product (0.042 g, 0.768 mmol) in 60% yield. Anal. Calcd for $C_{23}H_{25}Cl_2N_2OPPd$: C, 49.89; H, 4.55; N, 5.06; Cl, 12.80. Found: C, 49.91; H, 4.57; N, 5.10; Cl, 12.76. IR (Nujol): ν(CN) 2220, ν(PdCl) 340, 300 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.80 (s, OCH$_3$), δ 1.0 (s, CN^{t}Bu). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 24.6 (s). By complete evaporation of the mother liquor, an intractable material containing an isocyanide–rhodium complexes, which was not characterized, was obtained.

Reaction of 1 with [Pd(COD)Cl$_2$]. A dichloromethane solution (10 mL) of [Pd(C$_8$H$_{12}$)Cl$_2$] (0.035 g, 0.123 mmol) was added dropwise to a stirred solution of **1** (0.066 g, 0.123 mmol) in the same solvent (10 mL). The color of the solution turned from yellow to orange. Stirring was continued for 1 h to ensure complete reaction. The volume of solution was reduced to ca. 10 mL; the addition of diethyl ether afforded an orange precipitate of [Pd(Ph$_2$PPyOMe)Cl(μ-Cl)]$_2$ (**8**), which was removed by filtration, washed with diethyl ether, and vacuum-dried. Yield: 0.045 g (0.048 mmol), 78%. Anal. Calcd for $C_{36}H_{32}Cl_4N_2O_2P_2Pd_2$: C, 45.94; H, 3.43; N, 2.98; Cl, 15.07. Found: C, 45.91; H, 3.41; N, 2.97; Cl, 15.11. IR (Nujol): ν(PdCl) 300, 280 cm^{-1}. [Rh(COD)Cl]$_2$ was recovered from

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Table II. Crystallographic Data for Complex **4**

chem formula	$[C_{38}H_{32}Cl_2CuN_2O_4P_2Rh_2][BF_4]\cdot CH_2Cl_2$
fw	1154.63
cryst syst	monoclinic
space group	$P2_1/a$
radiatn	Ni-filtered Cu Kα (λ = 1.541 84 Å)
a, Å	32.852 (8)
b, Å	10.452 (4)
c, Å	12.945 (5)
β, deg	97.17 (2)
V, Å^3	4410 (3)
Z	4
D_{calcd}, g cm^{-3}	1.739
F(000)	2288
cryst dimens, mm	0.20 × 0.23 × 0.28
μ, cm^{-1}	101.86
$R(F_o)^a$	0.0500
$R_w(F_o)^b$	0.0661

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

the mother liquor and identified by comparison with an autentic sample (0.023 g, 0.046 mmol, yield 71%).

X-ray Crystal Structure Determination of $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4\cdot CH_2Cl_2$ (4). The crystallographic data are summarized in Table II. Unit cell parameters were determined from the *θ* values of 30 carefully centered reflections, having 20.6 < *θ* < 32.4°. Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the Ni-filtered Cu Kα radiation. All reflections with *θ* in the range 3–70° were measured; of 8373 independent reflections, 4842, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analyzed according to the technique of Lehmann and Larsen.[26] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.336 and 0.806).[27] Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson (SHELXS-86)[28] and Fourier methods and refined by full-matrix least-squares techniques (SHELX-76)[28] first with isotropic and then with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms of the cation. All hydrogen atoms were placed at their geometrically calculated positions and refined isotropically "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 493 variables; after the last cycles, no parameters (excepting those of the carbon atom of the solvent) shifted by more than 0.7 esd. The largest remaining peak (close to the Cl atom of the solvent) in the final difference map was equivalent to about 1.2 e/Å^3. In the final cycles of refinement, the weighting scheme $w = K/[\sigma^2(F_o) + gF_o^2]$ was used; at convergence, the *K* and *g* values were 0.479 and 0.0033, respectively. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 29.

All calculations were carried out on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio, Bologna, Italy) and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy. The final atomic coordinates for the non-hydrogen atoms are given in Table III. The atomic coordinates and isotropic thermal parameters of the hydrogen atoms are given in Table SI, the thermal parameters for the non-hydrogen atoms are given in Table SII, and a complete listing of bond distances and angles is given in Table SIII (supplementary material).

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Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for the Non-Hydrogen Atoms of Complex **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
Rh(1)	430 (1)	−252 (1)	4334 (1)	34.7 (2)^a
Rh(2)	1330 (1)	254 (1)	4971 (1)	36.0 (2)^a
Cu	1058 (1)	−1562 (1)	3505 (1)	38.3 (4)^a
Cl(1)	822 (1)	−359 (2)	6044 (2)	43.7 (6)^a
Cl(2)	802 (1)	1730 (2)	4232 (2)	47.0 (7)^a
P(1)	205 (1)	−187 (2)	2633 (2)	34.4 (6)^a
P(2)	1726 (1)	−1379 (2)	5562 (2)	36.9 (7)^a
O(1)	44 (2)	−2751 (6)	4638 (6)	61 (3)^a
O(2)	1942 (2)	1179 (8)	3661 (6)	75 (3)^a
O(3)	1638 (2)	−1025 (7)	2123 (5)	60 (3)^a
O(4)	691 (2)	−3958 (6)	3442 (5)	50 (2)^a
N(1)	991 (2)	−491 (7)	2265 (5)	39 (2)^a
N(2)	1159 (2)	−2937 (6)	4523 (6)	37 (2)^a
C(1)	178 (3)	−1796 (9)	4492 (7)	39 (3)^a
C(2)	1705 (3)	811 (9)	4160 (8)	50 (3)^a
C(3)	643 (2)	195 (8)	1962 (7)	37 (2)^a
C(4)	633 (3)	1143 (9)	1191 (7)	47 (3)^a
C(5)	985 (3)	1374 (10)	738 (8)	57 (4)^a
C(6)	1336 (3)	682 (10)	1024 (8)	54 (3)^a
C(7)	1332 (3)	−291 (10)	1780 (7)	44 (3)^a
C(8)	2008 (3)	−888 (15)	1681 (10)	91 (5)^a
C(9)	2 (2)	−1639 (8)	1976 (7)	37 (3)^a
C(10)	−360 (2)	−2157 (9)	2261 (7)	45 (3)^a
C(11)	−541 (3)	−3221 (10)	1731 (9)	57 (4)^a
C(12)	−362 (3)	−3749 (10)	923 (8)	56 (4)^a
C(13)	−9 (3)	−3221 (10)	627 (9)	59 (4)^a
C(14)	176 (3)	−2178 (9)	1160 (7)	48 (3)^a
C(15)	−184 (2)	1011 (8)	2174 (7)	38 (3)^a
C(16)	−171 (3)	2208 (8)	2700 (7)	42 (3)^a
C(17)	−471 (3)	3088 (10)	2402 (9)	55 (4)^a
C(18)	−779 (3)	2873 (10)	1607 (8)	56 (4)^a
C(19)	−787 (3)	1723 (10)	1085 (8)	62 (4)^a
C(20)	−488 (3)	791 (10)	1377 (7)	53 (4)^a
C(21)	1408 (2)	−2847 (8)	5448 (7)	37 (3)^a
C(22)	1425 (3)	−3758 (9)	6204 (8)	47 (3)^a
C(23)	1179 (3)	−4833 (10)	6025 (8)	52 (3)^a
C(24)	928 (3)	−4955 (9)	5095 (8)	52 (3)^a
C(25)	928 (3)	−3971 (8)	4377 (7)	38 (3)^a
C(26)	426 (3)	−5013 (9)	3159 (10)	68 (4)^a
C(27)	1956 (2)	−1280 (9)	6910 (7)	43 (3)^a
C(28)	1835 (3)	−300 (10)	7535 (8)	51 (3)^a
C(29)	2034 (3)	−142 (13)	8544 (9)	73 (4)^a
C(30)	2327 (4)	−961 (14)	8924 (9)	81 (5)^a
C(31)	2454 (3)	−1945 (14)	8316 (10)	83 (5)^a
C(32)	2267 (3)	−2112 (12)	7300 (9)	68 (4)^a
C(33)	2149 (2)	−1831 (9)	4870 (7)	43 (3)^a
C(34)	2509 (3)	−1069 (13)	5038 (11)	77 (4)^a
C(35)	2843 (4)	−1328 (14)	4496 (11)	85 (6)^a
C(36)	2818 (4)	−2304 (14)	3803 (11)	81 (5)^a
C(37)	2466 (3)	−3027 (12)	3602 (9)	69 (5)^a
C(38)	2136 (3)	−2779 (10)	4137 (8)	56 (4)^a
C(39)	1585 (6)	−4911 (20)	1512 (17)	151 (8)
Cl(3)	1546 (2)	−5794 (5)	2638 (4)	150 (2)
Cl(4)	1131 (2)	−3988 (6)	1185 (5)	177 (2)
B	6697 (5)	1407 (16)	8733 (13)	75 (4)
F(1)	6682 (3)	2055 (10)	9631 (8)	137 (3)
F(2)	6476 (4)	338 (11)	8826 (9)	164 (4)
F(3)	6517 (3)	2127 (8)	7927 (7)	109 (3)
F(4)	7081 (3)	1135 (11)	8655 (9)	156 (4)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Supplementary Material Available: Hydrogen atom coordinates and isotropic thermal parameters (Table SI), anisotropic thermal parameters for the non-hydrogen atoms (Table SII), complete bond distances and angles (Table SIII), and crystallographic data (Table SIV) (7 pages). Ordering information is given on any current masthead page.

Registry No. 1, 143890-17-9; **2**, 143890-18-0; **3**, 143890-19-1; **4**, 143890-22-6; **5**, 143890-23-7; **6**, 143890-25-9; **7**, 143890-26-0; **8**, 143890-27-1; $Ph_2PPyOMe$, 132682-80-5; $[Rh(COD)(\mu\text{-}Cl)]_2$, 12092-47-6; $[Cu(NCCH_3)_4]BF_4$, 15418-29-8; $[Rh(CO)_2(\mu\text{-}Cl)]_2$, 14523-22-9; $AuPPh_3Cl$, 14243-64-2; *cis*-$[Pd(t\text{-}BuNC)_2Cl_2]$, 34710-33-3; $[Pd(COD)Cl_2]$, 12107-56-1; diphenylphosphine, 829-85-6; 2-chloro-6-methoxypyridine, 17228-64-7.

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