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Steric Effects of the 2-(Diphenylphosphino)pyridine Bridging Ligand in the Synthesis of Binuclear RhPd Complexes. Crystal Structures of $[(CN^tBu)_2Cl_2Rh(\mu\text{-}Ph_2PPy)Pd(\mu\text{-}Cl)]_2$ and $[(C_8H_{12})Rh(\mu\text{-}Cl)(\mu\text{-}Ph_2PPy)PdCl_2]$

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The reaction of $[Rh(COD)(\mu\text{-}Cl)]_2$ (COD = cycloocta-1,5-diene) with 2-(diphenylphosphino)pyridine (Ph_2PPy), in benzene solution, gave the complex $[Rh(COD)(Ph_2PPy)Cl]$, (**1**) in which the Ph_2PPy acts as monodentate P-bonded ligand. The P,N chelation of the Ph_2PPy to the rhodium(I) center to give the cationic complex $[Rh(COD)(Ph_2PPy)]X$ ($X = ClO_4$, **2a**; $X = PF_6$, **2b**) was achieved by treating **1** with $AgClO_4$ or $AgPF_6$. The uncoordinated pyridine nitrogen atom of **1** was protonated by HPF_6, giving $[Rh(COD)(Ph_2PPyH)Cl]PF_6$ (**3**). The known A-frame complex $[Rh_2Cl_2(Ph_2PPy)_2(\mu\text{-}CO)]$ was obtained by bubbling CO into a dichloromethane solution of **1**. In the presence of PPh_3, the reaction of **1** with CO gave the compound $[Rh(CO)(PPh_3)(Ph_2PPy)Cl]$ (**4**). The reaction of **1** with *cis*-$[Pd(CN^tBu)_2Cl_2]$, in CH_2Cl_2 solution, gave nearly quantitatively the tetranuclear formal $Rh^{II}Pd^{I}$ complex $\{[(^tBuNC)_2Cl_2Rh(\mu\text{-}Ph_2PPy)Pd(\mu\text{-}Cl)]_2\}$ (**5**) whose structure was also established by X-ray diffraction methods. Compound **5** was also obtained by adding in succession Ph_2PPy and $[Rh(COD)(\mu\text{-}Cl)]_2$, in the appropriate stoichiometric ratio, to a CH_2Cl_2 solution of *cis*-$[Pd(CN^tBu)_2Cl_2]$. The addition of Ph_2PPy to a CH_2Cl_2 solution of *cis*-$[Pd(CN^tBu)_2Cl_2]$ afforded the mixed isocyanide–tertiary phosphine complex *cis*-$[Pd(CN^tBu)(Ph_2PPy)Cl_2]$ (**6**). Crystals of **5** are monoclinic, space group $P2_1/a$ with $Z = 2$ in a unit cell of dimensions $a = 19.420$ (8) Å, $b = 11.700$ (5) Å, $c = 15.006$ (6) Å, and $\beta = 110.80$ (2)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1959 observed reflections to R and R_w values of 0.0738 and 0.0987, respectively. The tetranuclear complex is centrosymmetric with the inversion center relating two PdRh dimeric units in which the Pd–Rh separation is 2.612 (3) Å. Two Cl atoms asymmetrically bridge the Pd atoms. The Ph_2PPy ligand also acts as a bridge being bound to the Pd atom through the P atom and to the Rh atom through the pyridine N atom. The reaction of **1** with $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$, in CH_2Cl_2 solution, gave quantitatively the palladium–allyl complex $\{Pd[CH_2C(CH_3)CH_2](Ph_2PPy)Cl\}$ (**9**), together with $[Rh(COD)(\mu\text{-}Cl)]_2$. Complexes $[Pd(COD)Cl_2]$ and $[Pd(C_6H_5CN)_2Cl_2]$ reacted with **1** to give quantitatively the binuclear complex $[(COD)Rh(\mu\text{-}Cl)(\mu\text{-}Ph_2PPy)PdCl_2]$ (**10**) characterized by IR and NMR spectroscopy. The structure of the dichloromethane solvate of **10** was determined by a X-ray diffraction study. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 9.282$ (5) Å, $b = 10.564$ (5) Å, $c = 14.690$ (6) Å, $\alpha = 84.35$ (3)°, $\beta = 86.32$ (3)°, and $\gamma = 79.01$ (3)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1443 observed reflections to R and R_w values of 0.0730 and 0.0932, respectively. The binuclear complex consists of the (COD)Rh and $PdCl_2$ moieties held together by Ph_2PPy and chloride bridges, with the Pd···Rh separation of 3.210 (4) Å. The compound $[Pd(Ph_2PPy)Cl_2]$ (**11**) was isolated by reacting $[Pd(COD)Cl_2]$ or $[Pd(C_6H_5CN)_2Cl_2]$ with Ph_2PPy in the molar ratio 1:1; it is a very reactive species and was found to react with $[Rh(COD)(\mu\text{-}Cl)]_2$ to give **10**. Interestingly, compound **5** was also obtained almost quantitatively, by reacting **10** with CN^tBu. In the bimetallic complexes **5** and **10** important bond changes in the Ph_2PPy coordination to the rhodium center, with respect to **1**, occurred. Reaction sequences for the formation of these compounds were proposed. The presence of unfavorable interactions between the hydrogens of COD ligand and the phenyl groups in the bimetallic intermediates containing the bridging Ph_2PPy ligand P bonded to Rh was considered the factor determining the course of reaction.

Introduction

There is currently considerable interest in binuclear complexes in which interactions take place between the metal atoms.[1] To explore such interactions, binucleating ligands have been developed and used for connecting two metal centers. The obtained bimetallic complexes in some cases exhibit unusual and unexpected structures and react with unsaturated substrates or small molecules by a process in which both metals participate simultaneously to give new substrate reactivity.[2,3] For these reasons, such bimetallic systems are interesting for their potential applications in catalysis.[4]

We have been recently interested in the synthesis, reactivity, structural studies, and catalysis of d^8–d^8 homo- and heterobinuclear complexes in which the metal centers are surrounded by one short-bite bis(diphenylphosphino)methane (dppm) or 2-(diphenylphosphino)pyridine (Ph_2PPy) ligand.[5-14] We have reported the

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symmetric $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}dppm)Rh(\eta^5\text{-}C_5H_5)]$[5] and the unsymmetric $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)M(CO)Cl]$ (M = Rh, Ir) complexes.[11] In these complexes, the metal centers are surrounded by only one short-bite bridging ligand and are held in close proximity by the steric requirements of these ligands; this makes the space between the metal centers favorable for the occurrence of an activation process. Thus, the complex $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}dppm)Rh(\eta^5\text{-}C_5H_5)]$ easily reacts with electrophiles containing group 11 metals and with $HgCl_2$, giving the neutral or cationic triangular clusters $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}X)(\mu\text{-}dppm)Rh(\eta^5\text{-}C_5H_5)]$[6-10] (X = $AgCF_3COO$, $AgCH_3COO$, $AgPF_2O_2$, $AgS_2CN(C_2H_5)_2$, CuI, $AuPPh_3$, $HgCl_2$). The complex $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ reacts with activated acetylenes $RO_2CC_2CO_2R$ (R = CH_3, C_2H_5), giving the tetranuclear complexes $\{[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}RO_2CC_2CO_2R)(\mu\text{-}Ph_2PPy)Rh(CO)(\mu\text{-}Cl)]_2\}$.[12]

Here we report the synthesis of rhodium–palladium complexes by reaction of the metal-containing ligand $[Rh(COD)(Ph_2PPy)Cl]$ (COD = cycloocta-1,5-diene), in which the Ph_2PPy acts as monodentate P-bonded ligand, with palladium(II) substrates.

The reactions proceed by coordination of the pyridine nitrogen atom of $[Rh(COD)(Ph_2PPy)Cl]$ to the palladium(II) center and appear to be strongly dependent on the steric factors of the Ph_2PPy bridging ligand; the presence on the palladium(II) center of labile ligands or of ligands that can give rise to bridging coordination is also very important in determining the course of reaction. The crystal and molecular structures of the tetranuclear formal $Rh^{II}Pd^{I}$ complex $[({}^tBuNC)_2Cl_2Rh(\mu\text{-}Ph_2PPy)Pd(\mu\text{-}Cl)]_2$ (**5**) and of the $Rh^{I}Pd^{II}$ complex $[(COD)Rh(\mu\text{-}Cl)(\mu\text{-}Ph_2PPy)PdCl_2]$ (**10**) are also reported.

Results and Discussion

Synthesis of Mononuclear Ph_2PPyRh^I Complexes. The compound $[Rh(COD)(\mu\text{-}Cl)]_2$ (COD = cycloocta-1,5-diene) reacts with Ph_2PPy, in benzene solution, to give the rhodium(I) complex $[Rh(COD)(Ph_2PPy)Cl]$ (**1**). The product complex results from cleavage of the chloro bridge by the tertiary phosphine Ph_2PPy, which acts as a monodentate P-bonded ligand. The $^{31}P\{^1H\}$ NMR spectrum, in CD_2Cl_2 solution, shows the phosphorus resonance as a doublet at δ 29.3 ($^1J_{RhP}$ = 150.1 Hz); in the ^1H NMR spectrum the 6-hydrogen of the pyridine ring gives a distinct resonance at δ 8.75. When the pyridine nitrogen atom is coordinated, the ortho hydrogen resonance is usually shifted to higher frequency.[13] These NMR spectral data clearly support the formulation of **1** as having a planar four-coordinate geometry with the pyridine nitrogen atom of Ph_2PPy uncoordinated.

Complex **1** is a crystalline yellow solid, nonconducting in dichloromethane solution, soluble in diethyl ether, benzene, and chlorinated solvents; both complex **1** and its solution are air stable.

Coordination of the pyridine nitrogen atom to rhodium(I) in **1** has been achieved by removing the chloride ligand with a silver ion. Thus, treating **1** with $AgClO_4$ or $AgPF_6$ in CH_3CN or CH_2Cl_2 solution results in the precipitation of AgCl and the formation of the cationic complexes $[Rh(COD)(Ph_2PPy)]X$ (X = ClO_4, **2a**; X = PF_6, **2b**). The P,N chelation is supported by microanalyses, spectroscopic IR data, and conductivity values. The IR spectra of **2a,b** are very similar to that of **1** except for the lack of the ν(RhCl) at 285 cm^{-1} and the presence of bands associated with the ionic ClO_4 and PF_6 at 1094 and 840 cm^{-1} in **2a** and **2b**, respectively. The low solubility of both **2a** and **2b** complexes prevented obtaining reliable NMR spectra. In methanol solution the conductivity of both **2a** and **2b** (5×10^{-4}–5×10^{-3} M solution) is appropriate for a 1:1 electrolyte.[15] Complexes **2a,b** have also been obtained by adding Ph_2PPy to the cationic complexes $[Rh(COD)(solv)_2]X$ (X = ClO_4, PF_6) in CH_2Cl_2 solution.

The pyridine nitrogen atom of **1** can be protonated readily with HPF_6, in CH_2Cl_2 solution, and the corresponding adduct cationic species $[Rh(COD)(Ph_2PPyH)Cl]PF_6$ (**3**) has been obtained as a yellow precipitate in high yields. The IR spectrum of **3** is very similar to that of the precursor **1** except for the presence of bands associated with the NH (ν(NH) 3200 cm^{-1} and δ(NH) 1611 cm^{-1}) and the PF_6 ion (811 cm^{-1}). In the ^1H NMR spectrum, in $CDCl_3$, the 6-hydrogen of the pyridine ring gives a resonance at δ 9.0 while the cyclooctadiene hydrogens give a broad singlet at δ 4.1.

When CO was bubbled into a dichloromethane solution of **1**, the color immediately turned from yellow orange to red brown; the known A-frame complex $[Rh_2Cl_2(Ph_2PPy)_2(\mu\text{-}CO)]$[16,17] has been isolated almost quantitatively by adding petroleum ether to the solution. Presumably, the reaction involves the formation of the intermediate $[Rh(CO)_2(Ph_2PPy)Cl]$ by displacement of COD with CO from **1**; an intermolecular nucleophilic attack of the uncoordinated pyridine nitrogen atom on the 16-electron rhodium(I) center and loss of CO could be the subsequent reaction steps.

In the presence of PPh_3, the reaction of **1** with CO gives the compound $[Rh(CO)(PPh_3)(Ph_2PPy)Cl]$ (**4**) as a yellow solid, stable in the air for long time, nonconducting in acetone solution; on standing, CH_2Cl_2 solutions of **4** give solid $[Rh(CO)(PPh_3)_2Cl]CH_2Cl_2$. In compound **4** the rhodium(I) center is four-coordinate, being uncoordinated by the pyridine nitrogen atom of the Ph_2PPy ligand. The ν(CO) at 1962 cm^{-1} and the ν(RhCl) at 312 cm^{-1} indicate the trans arrangement of CO and Cl ligands as in the related $[Rh(CO)(PPh_3)_2Cl]$ complex. The $^{31}P\{^1H\}$ NMR spectrum in toluene solution shows a doublet centered at δ 27.8 (J_{RhP} = 128 Hz); this spectrum, in our opinion, is caused by the almost equal chemical shift and J_{RhP} of the differently coordinated tertiary phosphines. As usual, when the nitrogen of the Ph_2PPy is uncoordinated, in the ^1H NMR spectrum, in CD_2Cl_2 solution, the 6-hydrogen of the pyridine ring resonance is observed at δ 8.76.

We have attempted the preparation of heterobinuclear complexes using bridge-assisted reactions in which the uncoordinated pyridine nitrogen atom of **1** displaces a labile ligand from a second metal center.

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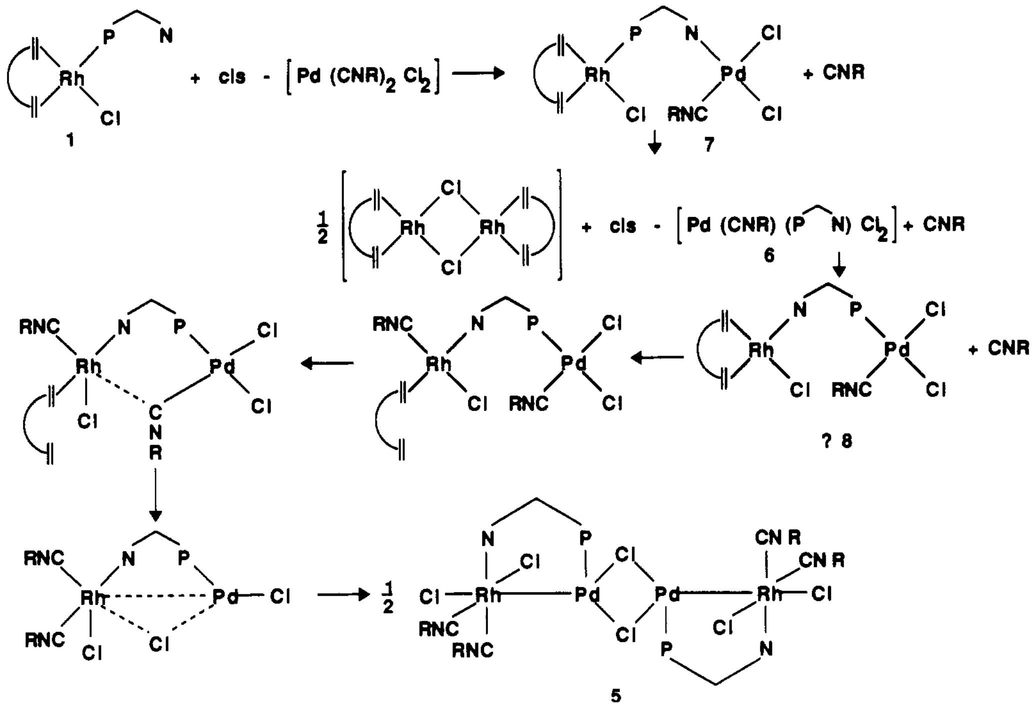
Scheme I



Reactions of 1 with Palladium(II) Metal Complexes. Reaction with *cis*-[Pd(CN^{t}Bu)$_2$Cl$_2$]. The reaction of 1 with *cis*-[Pd(CN^{t}Bu)$_2$Cl$_2$] in CH_2Cl_2 solution occurs rapidly and produces an almost quantitative yield of [(^{t}BuNC)$_2$Cl$_2$Rh(μ-Ph$_2$PPy)Pd(μ-Cl)]$_2$ (5). Complex 5 has been isolated as a red-brown crystalline solid, soluble in chlorinated solvents and air stable for long time. It has been fully characterized by a single-crystal X-ray diffraction analysis; see Figure 1. The crystal structure of 5 will be discussed below. Complex 5 is a tetranuclear species containing two bimetallic units linked by two chloride ligands bridging the palladium atoms. Each bimetallic unit contains the bridging Ph$_2$PPy ligand coordinated to rhodium through the pyridine nitrogen atom; two CN^{t}Bu and two chloride ligands mutually in cis position complete the coordination sphere of rhodium while the phosphorus and the bridging chloride ligands complete that of palladium center. The rhodium and palladium atoms are involved in a metal–metal bond.

The IR spectrum of 5 is fully consistent with the X-ray crystal structure; it shows two terminal isocyanide ν(CN) bands at 2226 and 2178 cm^{-1} and, in the ν(MCl) region, bands at 330, 300, and 275 cm^{-1}, indicating the presence of both terminal and bridging chloride ligands. The ^{1}H NMR spectra, in $CDCl_3$ solution, are consistent with the presence in solution of two species. In fact, the resonances of the two ^{t}Bu groups of the main product at δ 1.37 and 1.12 are flanked by two resonances at δ 1.34 and 1.26 of lower intensity (ratio 6:1) attributable to ^{t}Bu groups of a different species. Its presence can also be inferred by the ^{31}P{^{1}H} NMR spectrum, in the same solvent, which shows two singlets at δ 10.3 and 11.1 with intensity ratio 6:1. The absence of any detectable coupling with rhodium for the two resonances implies structures with the phosphorus atom coordinated to palladium for both species. The NMR data are consistent with the presence in solution of two species with very similar structures, each with the phosphorus atom and one of the two ^{t}Bu groups in very similar chemical environments. The only significant difference concerns the proton resonances of one of the two ^{t}Bu groups. On this basis, the most likely structure for the minor product is that of an isomer of 5 containing the CN^{t}Bu groups mutually in cis positions and in trans to the Rh–Pd and to Rh–N bonds.

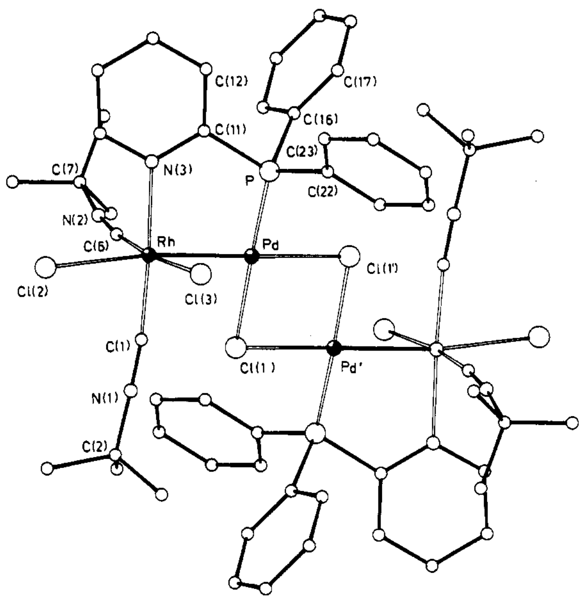


Figure 1. View of the molecular structure of the complex [(^{t}BuNC)$_2$Cl$_2$Rh(μ-Ph$_2$PPy)Pd(μ-Cl)]$_2$ (5) with the atomic numbering scheme.

Compound 5 can be considered a Rh^{II}Pd^I species; the full mechanism of its formation is actually unknown although some speculations are reasonable (Scheme I). The reaction formally involves (i) oxidative addition of a Pd–Cl bond across the rhodium center of 1 with the formation of a Rh–Pd bond; (ii) displacement of the COD by transfer of the isocyanide ligands from palladium to rhodium; (iii) important bond changes in the coordination of the Ph$_2$PPy ligand (from P to N bonded to rhodium center); and (iv) formation of chloro bridges between the palladium atoms. The reaction is very fast, and only the presence of the starting materials and of 5 has been detected monitoring the reaction by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

Balch and co-workers have been able to isolate, from the reaction of $[Rh(CO)_2Cl]_2$ with *cis*-$[Pt(Ph_2PPy)_2Cl_2]$, the ionic product $[Rh(CO)_2Cl_2][Pt(Ph_2PPy)_2Cl]$, which must be considered the intermediate in the formation of the $Rh^{II}Pt^{I}$ complex $[RhPt(Ph_2PPy)_2(CO)Cl_3]$;[18] an analogous ionic intermediate has not been detected in the synthesis of the $Rh^{II}Pd^{I}$ complex $[RhPd(Ph_2PPy)_2(CO)Cl_3]$[19,20] from $[Rh(CO)(Ph_2PPy)_2Cl]$ and $[Pd(COD)Cl_2]$.

To gain some insight into the reaction of 1 with *cis*-$[Pd(CN^tBu)_2Cl_2]$, we have explored some related reactions. We have found that 1 does not react with $[Ph_4As]Cl$ to give a *cationic rhodium(I) species*, namely $[Rh(Ph_2PPy)Cl_2]AsPh_4$. Thus, the initial formation of an ionic intermediate, as observed by Balch,[18] by transfer of a chloride ligand from *cis*-$[Pd(CN^tBu)_2Cl_2]$ to the rhodium(I) center seems unlikely.

Compound **5** has also been obtained by a different route. The addition of Ph_2PPy to a CH_2Cl_2 solution of *cis*-$[Pd(CN^tBu)_2Cl_2]$ results in the replacement of a CN^tBu ligand by the Ph_2PPy and formation of $[Pd(CN^tBu)(Ph_2PPy)Cl_2]$ (**6**), in which the Ph_2PPy acts as monodentate P-bonded ligand. The reaction is similar to that of $[Pd(CN^tBu)_2Cl_2]$ with tertiary phosphines.[21] When $[Rh(COD)(\mu\text{-}Cl)]_2$ was added, in the appropriate molar ratio, to the CH_2Cl_2 reaction mixture containing **6** and free CN^tBu, compound **5** was obtained almost quantitatively.

Compound **6** is a pale yellow crystalline solid and soluble in chlorinated solvents and methanol, nonconducting in CH_2Cl_2 and CH_3OH solution. Its IR spectrum shows the $\nu(CN)$ at 2228 cm^{-1} and the $\nu(PdCl)$ at 339 and 294 cm^{-1}, indicating a cis configuration. ^1H and $^{31}P\{^1H\}$ NMR spectra, in $CDCl_3$, support a structure in which the Ph_2PPy is P bonded to palladium; in agreement, the resonance of the 6-hydrogen of the pyridine ring was observed at δ 8.77 and that of ^tBu as singlet at δ 1.14; in the $^{31}P\{^1H\}$ NMR spectrum a singlet was observed at δ 24.5.

It is very likely that the reaction of 1 with *cis*-$[Pd(CN^tBu)_2Cl_2]$ initially gives free isocyanide and the transient binuclear species $[(COD)ClRh(\mu\text{-}Ph_2PPy)Pd(CN^tBu)Cl_2]$ (**7**), in which the Rh–P bond is retained. As a consequence of steric interactions between the COD ligand and the phenyl groups of the bridged Ph_2PPy ligand, the binuclear structure of **7** can be disrupted to give complexes **6** and $[Rh(COD)(\mu\text{-}Cl)]_2$ in the appropriate stoichiometric ratio. It is well-known that because of its rigidity and small bite angle bridging coordination of Ph_2PPy requires small ligands cis to the P atom. Bimetallic complexes in which two d^8 metal centers are surrounded by two "head-to-tail" Ph_2PPy have been synthesized only when CO, halogenides, and $CNCH_3$ are the coordinated ligands cis to phosphorus;[3,17,20] besides, the rigidity of the Ph_2PPy ligand allows only a low torsion angle about the metal–metal vector.[11-13] Molecular modeling considerations clearly show the presence of **7** of strong unfavorable interactions between the hydrogens of the COD ligand and the phenyl groups or the ligands coordinated to the palladium(II) center. We have verified in a separate experiment that, in the absence of free CN^tBu, compound **6** reacts with $[Rh(COD)(\mu\text{-}Cl)]_2$ to give a binuclear complex containing the bridging Ph_2PPy N bonded to rhodium. Very likely, the species $[(COD)ClRh(\mu\text{-}Ph_2PPy)Pd(CN^tBu)Cl_2]$ (**8**) could be formed in the reaction mixture containing **6**, $[Rh(COD)(\mu\text{-}Cl)]_2$, and free CN^tBu. The COD displacement from **8** can be started by an external attack of the free isocyanide and finished by the isocyanide ligand coordinated to palladium center.

Table I. Selected Bond Distances (Å) and Angles (deg) for Complex 5[a]

Distances			
Pd-Rh	2.612 (3)	Rh-Cl(2)	2.520 (7)
Pd-Cl(1)	2.388 (7)	Rh-Cl(3)	2.380 (6)
Pd-Cl(1′)	2.479 (9)	Rh-N(3)	2.10 (2)
Pd-P	2.185 (6)	Rh-C(1)	1.89 (2)
P-C(11)	1.82 (3)	Rh-C(6)	1.91 (3)
P-C(16)	1.80 (1)	P-C(22)	1.82 (2)
C(1)-N(1)	1.14 (3)	C(6)-N(2)	1.08 (3)
N(1)-C(2)	1.48 (3)	N(2)-C(7)	1.53 (5)
Angles			
Cl(1)-Pd-Cl(1′)	82.6 (2)	Pd-Rh-Cl(3)	90.5 (2)
Cl(1)-Pd-Rh	98.2 (2)	Pd-Rh-N(3)	94.5 (5)
Rh-Pd-P	84.6 (2)	Pd-Rh-C(1)	89.3 (7)
P-Pd-Cl(1′)	94.6 (3)	Pd-Rh-C(6)	82.6 (8)
Pd-Cl(1)-Pd′	97.4 (3)	Cl(2)-Rh-Cl(3)	93.3 (2)
Pd-P-C(11)	117.0 (9)	Cl(2)-Rh-N(3)	93.2 (5)
P-C(11)-N(3)	116 (2)	Cl(2)-Rh-C(1)	83.0 (8)
Rh-N(3)-C(11)	122 (2)	Cl(2)-Rh-C(6)	94.0 (7)
Rh-C(1)-N(1)	172 (2)	Cl(3)-Rh-N(3)	90.0 (6)
C(1)-N(1)-C(2)	174 (3)	Cl(3)-Rh-C(1)	89.3 (8)
Rh-C(6)-N(2)	171 (2)	N(3)-Rh-C(6)	87.0 (9)
C(6)-N(2)-C(7)	172 (3)	C(1)-Rh-C(6)	94.2 (11)

[a] The primed atoms are related to the unprimed ones by the transformation $-x, -y, 1 - z$.

The transfer of the isocyanide and chloride ligands from the palladium to the rhodium center, with concomitant formation of the Rh–Pd bond, to give the formal $Rh^{II}Pd^{I}$ species, probably occurs through reaction steps in which these ligands are bridging. A similar reaction sequence has been proposed[13] to explain both the formation of the $Rh^{II}Pt^{I}$ complex $[(\eta^5\text{-}C_5H_5)RhCl(\mu\text{-}Ph_2PPy)Pt(CO)Cl]$, from $[(\eta^5\text{-}C_5H_5)Rh(CO)(Ph_2PPy)]$ and *cis*-$[Pt(DMSO)_2Cl_2]$, and the isocyanide ligand transfer from Pd to Rh in the formation of $[(\eta^5\text{-}C_5H_5)(CN^tBu)Rh(\mu\text{-}Ph_2PPy)Pd(CN^tBu)Cl]PF_6$. The formation of **10** (see below) and its reaction with CN^tBu to give **5** provide support for the proposal that oxidative addition of the Pd–Cl bond across the rhodium center in the reaction of 1 with *cis*-$[Pd(CN^tBu)_2Cl_2]$ occurs subsequently to the COD displacement by the CN^tBu ligands. In the $Rh^{II}Pd^{I}$ species, the palladium(I) is an unsaturated 14-electron center; it becomes a tetracoordinated 16-electron center, as in **5**, by an intermolecular formation of chloro bridges.

Description of the Crystal Structure of $[(CN^tBu)_2Cl_2Rh(\mu\text{-}Ph_2PPy)Pd(\mu\text{-}Cl)]_2$ (5). The structure of **5** is depicted in Figure 1 together with the atomic numbering scheme; selected bond distances and angles are given in Table I. The tetranuclear PdRh complex has a crystallographic inversion center relating two PdRh dimeric units in which the Pd–Rh separation (2.612 (3) Å) is consistent with a single metal–metal bond. Two centrosymmetrically related Cl atoms asymmetrically bridge the Pd atoms (Pd–Cl(1) = 2.388 (7), Pd–Cl(1′) = 2.479 (9) Å). The square-planar coordination around each Pd atom is completed by the P atom from the Ph_2PPy ligand (Pd–P = 2.185 (6) Å) bridging also the Rh atom through the pyridinic nitrogen atom (Rh–N(3) = 2.10 (2) Å). The coordination around the Rh atom involves, beyond the Pd and N(3) atoms, two Cl atoms in cis position (Rh–Cl(2) = 2.520 (7), Rh–Cl(3) = 2.380 (6) Å) and two carbon atoms from ^tBuNC ligands (Rh–C(1) = 1.89 (2), Rh–C(6) = 1.91 (3) Å). The value of the Pd–Rh metal–metal bond is comparable with the one found in the neutral complex $[RhPd(\mu\text{-}Ph_2PPy)_2(CO)Cl_3]$[19,20] (2.594 (1) Å) and slightly

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shorter than the one found in the cationic complex $[Rh_2Pd(CO)_2(\mu\text{-}Cl)Cl_2(\mu\text{-}dpma)_2]^+$ (2.699 (1) Å) (dpma = bis[(diphenylphosphino)methyl]phenylarsine).[22] As shown above, the values of the Rh–Cl(2) and Pd–Cl(1′) bonds, significantly longer than those of the Rh–Cl(3) and Pd–Cl(1) bonds, indicate the high trans effect of the metal-metal (Pd–Rh) bond. Both values of the Pd–P and Rh–N bonds are shorter than the ones found in the complex $[RhPd(Ph_2PPy)_2(CO)Cl_3]$ with the same Ph_2PPy ligand (2.220 (4) and 2.16 (1) Å, respectively).[19,20]

The PdPC(11)N(3)Rh ring is puckered, maximum deviation from the mean plane through the five atoms being 0.61 (2) Å for N(3), with a P···N(3) separation of 2.68 (2) Å, slightly longer than the metal–metal one. The N(3)–Rh–Pd–P torsion angle is 20.2 (6)° and is indicative of a rather strong steric hindrance in the complex, probably due to the need to reduce the repulsion between the two coordinating atoms trans to N(3) and P, i.e., C(1) and Cl(1), and between Cl(2) and the pyridinic C(15) atoms. In spite of this distortion, the C(1)···Cl(1) and Cl(2)···C(15) separations are 3.08 (3) and 3.21 (3) Å, respectively.

Reaction with $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$. Complex **1** reacts with $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$ in dichloromethane solution to give quantitatively the palladium–allyl complex $\{Pd[CH_2C(CH_3)CH_2](Ph_2PPy)Cl\}$ (**9**) together with $[Rh(COD)(\mu\text{-}Cl)]_2$. The separation of the products has been achieved by using their different solubility in a CH_2Cl_2–diethyl ether mixture. Compound **9** has also been obtained, as a yellow-orange solid, by reacting $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$ with Ph_2PPy in CH_2Cl_2 solution. Its ^1H NMR spectrum, in $CDCl_3$ solution, at 255 K, shows two doublets at δ 4.54 ($^3J_{PH}$ = 6.9 Hz; $^4J_{H_{syn}H_{anti}}$ = 2.9 Hz) and δ 3.02 ($^4J_{H_{syn}H_{syn}}$ = 2.9 Hz; $^2J_{H_{anti}H_{syn}}$ = 1.7 Hz), doublets at δ 3.58 ($^3J_{PH}$ = 9.9 Hz) and δ 2.73 ($^2J_{H_{syn}H_{anti}}$ = 1.7 Hz), and a singlet at δ 1.95 for the methyl group; the spectrum also shows a resonance for the 6-hydrogen of the pyridine ring at δ 8.76. In the $^{31}P\{^1H\}$ NMR spectrum at 255 K, a singlet at δ 24.3 is present. These NMR spectral data clearly support for **9** a structure in which the Ph_2PPy acts as monodentate P-bonded ligand and the methylallyl group is η^3 coordinated. The reaction appears to be similar to that of pyridine with $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$ to give $\{Pd[CH_2C(CH_3)CH_2](py)Cl\}$.[23] As for the reaction of **1** with the *cis*-$[Pd(CN^tBu)_2Cl_2]$, steric factors give rise to the breaking of the Rh–P bond in the very likely intermediate $\{(COD)ClRh(\mu\text{-}Ph_2PPy)Pd[CH_2C(CH_3)CH_2]Cl\}$ to give $[Rh(COD)(\mu\text{-}Cl)]_2$ and the isomer of **9** containing the Ph_2PPy ligand N bonded to palladium atom. Reaction enthalpies of the bridge cleavage of $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$ by pyridine and PPh_3 support the change in the bonding mode of Ph_2PPy from N to P bonded in this isomer of **9**.[23] The reaction of **1** with *cis*-$[Pt(DMSO)_2Cl_2]$ proceeds similarly to give as final products $[Rh(COD)(\mu\text{-}Cl)]_2$ and *cis*-$[Pt(DMSO)(Ph_2PPy)Cl_2]$.[23] The formation of **9** and $[Rh(COD)(\mu\text{-}Cl)]_2$ from the reaction of **1** with $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$ strongly supports the initial steps suggested for the reaction of **1** with *cis*-$[Pd(CN^tBu)_2Cl_2]$.

We do not understand the reason why **9** and $[Rh(COD)(\mu\text{-}Cl)]_2$ do not react to give a binuclear species.

Reaction with $[Pd(COD)Cl_2]$ and $[Pd(C_6H_5CN)_2Cl_2]$. Complex **1** reacts with $[Pd(COD)Cl_2]$ and $[Pd(C_6H_5CN)_2Cl_2]$ to give quantitatively the binuclear complex $[(COD)Rh(\mu\text{-}Cl)(\mu\text{-}Ph_2PPy)PdCl_2]$ (**10**), whose structure has been fully established by X-ray diffraction analysis. The molecule consists of the (COD)Rh and $PdCl_2$ moieties held together by Ph_2PPy and chloride bridges (Figure 2). The crystal structure of **10** will be discussed below. Compound **10** is a red-brown solid, stable in the air and moderately soluble in chlorinated solvents. Its IR spectrum exhibits bands at 341, 291, and 273 cm^{-1}, indicating the presence of terminal and bridging chloride ligands. The low solubility of the compound prevented obtaining reliable NMR spectra.

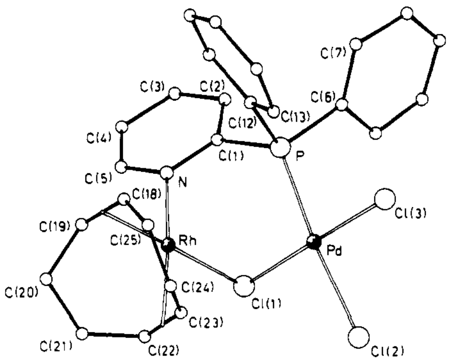

Figure 2. View of the molecular structure of the complex $[(COD)Rh(\mu\text{-}Cl)(\mu\text{-}Ph_2PPy)PdCl_2]$ (**10**) with the atomic numbering scheme.

The reactions of **1** with $[Pd(COD)Cl_2]$ and $[Pd(C_6H_5CN)_2Cl_2]$ in some aspects resemble those of **1** with *cis*-$[Pd(CN^tBu)_2Cl_2]$ and $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$; significantly, the oxidative addition of the PdCl across the rhodium center does not occur, probably owing to the low basicity of the rhodium(I) center and the presence of two bridging ligands.

The reactions of **1** with $[Pd(COD)Cl_2]$ and $[Pd(C_6H_5CN)_2Cl_2]$ involve initially displacement of the C_6H_5CN or COD ligand by the pyridine nitrogen atom to give a transient intermediate containing the Ph_2PPy as bridging ligand. Owing to the unfavorable interactions of the bridging Ph_2PPy ligand withe the COD, the dimeric structure is disrupted to give $[Rh(COD)(\mu\text{-}Cl)]_2$ and $[Pd(Ph_2PPy)Cl_2]$ (**11**). Compound **11** has been isolated by reacting $[Pd(COD)Cl_2]$ with Ph_2PPy (molar ratio 1:1) in dichloromethane solution and has been found to react with $[Rh(COD)(\mu\text{-}Cl)]_2$ to give **10**. The sequence reported in Scheme II seems to be very likely for the reaction. Compound **11** is a yellow-orange solid, moderately soluble in chlorinated solvents; on standing in CH_2Cl_2, it gives a yellow insoluble solid that has not been fully characterized. In the IR spectrum the ν(PdCl) at 335 and 293 cm^{-1} indicate the presence of chloride in a cis position. Although the low solubility prevented obtaining reliable NMR data, we consider the Ph_2PPy to be chelated to Pd in compound **11**.

It is worthwhile mentioning that **10** reacts with CN^tBu, in CH_2Cl_2 solution, to give **5** almost quantitatively. The reaction is very fast, and only the presence of the starting material and **5** can be demonstrated spectroscopically.

Description of the Crystal Structure of $[(C_8H_{12})Rh(\mu\text{-}Cl)(\mu\text{-}Ph_2PPy)PdCl_2]\cdot CH_2Cl_2$ (10). The structure of **10** is depicted in Figure 2 together with the atomic numbering scheme; selected bond distances and angles are given in Table II. In the binuclear PdRh complex, the Ph_2PPy ligand bridges the two metal centers coordinating to the Pd atom through the P atom (Pd–P = 2.246 (9) Å) and to the Rh atom through the pyridinic N atom (2.05 (2) Å). The two metal atoms are also slightly asymmetrically bridged by a Cl atom (Pd–Cl(1) = 2.345 (7), and Rh–Cl(1) = 2.399 (8) Å). The Pd–Rh separation of 3.210

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Scheme II

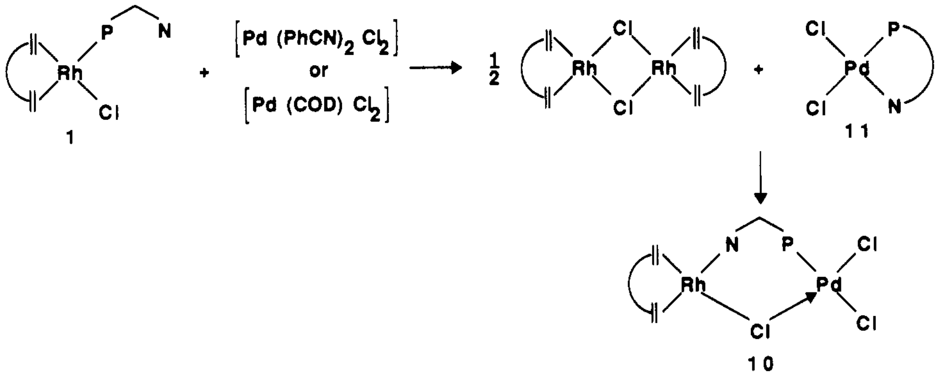

Table II. Selected Bond Distances (Å) and Angles (deg) for Complex 10

	Distances		
Pd-Rh	3.210 (4)	Rh-Cl(1)	2.399 (8)
Pd-Cl(1)	2.345 (7)	Rh-N	2.05 (2)
Pd-Cl(2)	2.362 (10)	Rh-M(1)[a]	2.05 (4)
Pd-Cl(3)	2.278 (7)	Rh-M(2)	2.07 (4)
Pd-P	2.246 (9)	C(18)-C(19)	1.28 (4)
P-C(1)	1.93 (3)	C(22)-C(23)	1.27 (5)
C(1)-N	1.38 (3)		
	Angles		
Cl(1)-Pd-Cl(2)	89.4 (3)	Cl(1)-Rh-N	85.7 (6)
Cl(2)-Pd-Cl(3)	89.8 (3)	Cl(1)-Rh-M(2)	93 (1)
Cl(3)-Pd-P	86.6 (3)	M(1)-Rh-M(2)	87 (1)
P-Pd-Cl(1)	94.0 (3)	N-Rh-M(1)	95 (1)
Pd-Cl(1)-Rh	85.1 (3)	Rh-N-C(1)	126 (2)
Pd-P-C(1)	115.4 (9)	P-C(1)-N	109 (2)

[a] M(1) and M(2) are the midpoints of the C(18)-C(19) and C(22)-C(23) bonds, respectively.

(4) Å is too long to be considered indicative of a metal-metal interaction. The square-planar coordination of the Pd atom is completed by two terminal Cl atoms (Pd-Cl(2) = 2.362 (10), Pd-Cl(3) = 2.278 (7) Å), with a narrow Pd-Cl(1)-Rh angle of 85.1 (3)°. The coordination of the Rh atom also involves a COD molecule interacting through the two double bonds. If the midpoints of the two double bonds, M(1) and M(2), are taken into account, the Rh atom is in a square-planar arrangement (Rh-M(1) = 2.05 (4), Rh-M(2) = 2.07 (4) Å). The two mean coordination planes are almost perpendicular to one another, the dihedral angle being 93.8 (4)°. The complex is strongly tensioned as the Ph_2PPy ligand is obliged to span the two metals separated by a long distance (the N···P separation is 2.72 (2) Å), and the pyridinic ring cannot be placed perpendicularly to the Rh coordination plane to avoid the steric hindrance with the COD ligand (the dihedral angle between the pyridinic ring and Rh mean coordination plane is 66.3 (7)°).

Conclusions

Although many binuclear metal complexes containing Ph_2PPy have been synthesized, its steric requirements when coordinated as a bridging ligand, on the reaction course, are relatively unknown.

This work offers insight into these steric demands by showing that the coordination of the pyridine nitrogen atom of 1 to the palladium(II) center gives rhodium-palladium intermediates whose binuclear structure is disrupted by the breaking of the Rh-P bond, owing to the strong unfavorable interactions between the hydrogens of the COD ligand and the phenyl groups or the ligands coordinated to palladium(II) center. Formally, the transfer of the Ph_2PPy from rhodium to palladium is achieved; in the resulting palladium(II) complexes the Ph_2PPy is bonded through the phosphorus or is chelated (in the product of the reaction with $[Pd(COD)Cl_2]$ and $[Pd(C_6H_5CN)_2Cl_2]$) to the metal center. These palladium(II) complexes are very reactive species; they react with the $[Rh(COD)(\mu\text{-}Cl)]_2$ complex to give stable heterobinuclear complexes containing the Ph_2PPy bridging ligand N bonded to rhodium atom. This mode of bonding of the Ph_2PPy gives stability to the bimetallic complex. The subsequent reaction path appears to be strongly dependent on both the nature of the ligands bound to the palladium(II) center and the basicity of the rhodium(I) center. Transfer of ligands from palladium to rhodium atoms has been demonstrated in the presence of ligands that can give rise to bridging coordination mode. If the rhodium center is sufficiently basic, oxidative addition of the Pd-Cl bond across the rhodium center can also be observed. We are inclined to consider that the oxidative addition process occurs by partial formation at the same time of both the chloride bridge and the metal-metal bond. The rigidity and the short bite angle of the Ph_2PPy bridging ligand are very important in these processes.

Experimental Section

Established methods were used to prepare the compounds $[Rh(COD)(\mu\text{-}Cl)]_2$,[25] $\{Pd[CH_2C(CH_3)CH_2]Cl\}_2$,[26] *cis*-$[Pd(CN^tBu)_2Cl_2]$,[27] $[Pd(COD)Cl_2]$,[28] and $[Pd(C_6H_5CN)_2Cl_2]$.[29] 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 plates with use of a Perkin-Elmer FTIR 1720 spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker WP80-SY or a Varian Model Gemini-300 spectrometer.

^1H NMR spectra were referenced to internal tetramethylsilane and ^{31}P spectra to external 85% H_3PO_4; positive chemical shifts are for all nuclei to higher frequency. 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, West Germany, and by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan.

Preparation of $[Rh(C_8H_{12})(Ph_2PPy)Cl]$ (1). A benzene solution (10 mL) of Ph_2PPy (0.160 g, 0.608 mmol) was added to a solution of $[(C_8H_{12})Rh(\mu\text{-}Cl)]_2$ (0.150 g, 0.304 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 precipitation of the product as a yellow-orange powder. This was filtered, washed

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with petroleum ether, and crystallized by diethyl ether to give the pure product (0.220 g, 0.432 mmol) in 71% yield. Anal. Calcd for $C_{25}H_{26}ClNPRh$: C, 58.90; H, 5.14; N, 2.75; Cl, 6.95. Found: C, 58.81; H, 5.15; N, 2.55; Cl, 6.70. IR (CsI, Nujol): ν(RhCl) 285 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.75 (6-H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.3 (d, $^1J_{RhP}$ = 150.1 Hz).

Preparation of [Rh(C_8H_{12})(Ph_2PPy)]X (X = ClO_4, 2a; X = PF_6, 2b). Solid $AgClO_4$ (0.044 g, 0.211 mmol) was added to a well-stirred dichloromethane solution (20 mL) of 1 (0.108 g, 0.212 mmol). After 15 min, the precipitate of AgCl was separated by filtration and the volume of the resulting orange solution reduced to ca. 8 mL. When 20 mL of petroleum ether was added an orange precipitate formed. This was removed by filtration, washed with diethyl ether, and vacuum dried. Yield: 0.097 g (0.169 mmol), 80%. Anal. Calcd for $C_{25}H_{26}ClNO_4PRh$: C, 52.33; H, 4.56; N, 2.44. Found: C, 52.17; H, 4.52; N, 2.65. IR (KBr, Nujol): ν(ClO_4) 1094 cm^{-1}. Compound **2b** was similarly prepared from 1 and $AgPF_6$. Yield: 82%. Anal. Calcd for $C_{25}H_{26}F_6NP_2Rh$: C, 48.48; H, 4.23; N, 2.26. Found: C, 48.45; H, 4.21; N, 2.22. IR (CsI, Nujol): ν(PF_6) 840 cm^{-1}.

Preparation of [Rh(C_8H_{12})(Ph_2PPyH)Cl]PF_6 (3). A few drops of HPF_6 (solubility 60% by weight in H_2O) was added to a stirred solution (10 mL) of 1 (0.100 g, 0.197 mmol) in benzene. A yellow precipitate was formed. After about 20 min, this was removed by filtration, washed several times with small portions of benzene and diethyl ether, and vacuum dried. Yield: 0.090 g (0.138 mmol), 70%. Anal. Calcd for $C_{25}H_{27}ClF_6NP_2Rh$: C, 45.79; H, 4.15; N, 2.14; Cl, 5.41. Found: C, 45.60; H, 4.17; N, 4.18; Cl, 5.31. IR (Nujol): ν(NH) 3200, δ(NH) 1611, ν(PF_6) 811 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.1 (s br, C_8H_{12}), 9.0 (6-H).

Reaction of 1 with CO. Carbon monoxide was bubbled through a dichloromethane solution (10 mL) of 1 (0.253 g, 0.496 mmol). Immediately, the color changed from yellow-orange to red-brown. On addition of 30 mL of petroleum ether, a red-brown solid precipitated. This was removed by filtration, washed with diethyl ether, and vacuum dried to give [$Rh_2(Ph_2PPy)_2(\mu$-CO)Cl_2]. This was characterized by comparison with an authentic sample obtained by a different route.

Preparation of [Rh(PPh_3)(CO)(Ph_2PPy)Cl] (4). Carbon monoxide was bubbled through a stirred dichloromethane solution (20 mL) containing 1 (0.145 g, 0.284 mmol) and PPh_3 (0.075 g, 0.284 mmol). A yellow precipitate was immediately formed. After about 10 min, this was removed by filtration, washed with diethyl ether, and dried to give the product (0.147 g, 0.213 mmol) in 75% yield. Anal. Calcd for $C_{36}H_{29}ClNOP_2Rh$: C, 62.49; H, 4.22; N, 2.02; Cl, 5.12. Found: C, 62.58; H, 4.24; N, 2.19; Cl, 5.23. IR (CsI, Nujol): ν(CO) 1962, ν(Rh–Cl) 312 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.76 (6-H). $^{31}P\{^1H\}$ NMR (toluene): δ 27.8 (d, $^1J_{RhP}$ = 128 Hz).

Preparation of [($^tBuNC)_2Cl_2Rh(\mu$-Ph_2PPy)Pd(μ-Cl)]$_2$ (5). Procedure a. A dichloromethane solution (10 mL) of [Pd($^tBuNC)_2Cl_2$] (0.120 g, 0.349 mmol) was added dropwise to 0.178 g (0.350 mmol) of 1 in the same solvent (10 mL). Immediately, the color of the solution turned from yellow to dark red. After 15 min, the volume of the solution was reduced to ca. 10 mL. By addition of petroleum ether (25 mL) a red precipitate was obtained. This was filtered, washed with diethyl ether, and dried in vacuo to give the product (0.252 g, 0.169 mmol) in 97% yield. Anal. Calcd for $C_{54}H_{64}Cl_6N_6P_2Pd_2Rh_2$: C, 43.52; H, 4.33; N, 5.64; Cl, 14.27. Found: C, 43.45; H, 4.30; N, 5.62; Cl, 14.22. IR (CsI, Nujol): ν(CN) 2226, 2178, ν(Rh–Cl) 330, 300, 275 cm^{-1}. NMR: see Results and Discussion.

Procedure b. A dichloromethane solution (10 mL) of Ph_2PPy (0.056 g, 0.215 mmol) was added to a solution (10 mL) of [Pd($^tBuNC)_2Cl_2$] (0.072 g, 0.215 mmol) in the same solvent. Immediately, the color of the solution turned from pale yellow to yellow. The addition of a solution of [(C_8H_{12})Rh(μ-Cl)]$_2$ (0.053 g, 0.107 mmol) in the same solvent (10 mL) soon resulted in a color change to dark red. After 15 min, the solution was reduced in volume to ca. 10 mL and diethyl ether (20 mL) was added. The red solid obtained was filtered, washed with diethyl ether, and dried in vacuo to give the product (0.152 g, 0.102 mmol) in 95% yield. Anal. Calcd for $C_{54}H_{64}Cl_6N_6P_2Pd_2Rh_2$: C, 43.52; H, 4.33; N, 5.64; Cl, 14.27. Found: C, 43.47; H, 4.32; N, 5.61; Cl, 14.24.

Preparation of [Pd(^tBuNC)(Ph_2PPy)Cl_2] (6). A dichloromethane solution of Ph_2PPy (0.085 g, 0.322 mmol) was added to a solution (10 mL) of [Pd($^tBuNC)_2Cl_2$] (0.108 g, 0.322 mmol) in the same solvent. Immediately, the color of the solution turned from pale yellow to yellow. After addition of 20 mL of petroleum ether, a pale yellow precipitate formed. This was removed by filtration, washed several times with small portion of diethyl ether and vacuum dried. Yield: 0.140 g (0.289 mmol), 90%. Anal. Calcd for $C_{22}H_{18}ClN_2PPd$: C, 54.68; H, 3.75; N, 5.80; Cl, 7.34. Found: C, 54.66, H, 3.74; N, 5.78; Cl, 7.30. IR (CsI, Nujol): ν(CN) 2228, ν(PdCl) 339, 294 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.77 (6-H), 1.14 (s, ^tBu). $^{31}P\{^1H\}$ NMR: δ 24.5 (s).

Preparation of {Pd[$CH_2C(CH_3)CH_2$](Ph_2PPy)Cl} (9). A dichloromethane solution (5 mL) of {Pd[$CH_2C(CH_3)CH_2$]Cl}$_2$ (0.025 g, 0.126 mmol) was added to a solution of 1 (0.128 g, 0.252 mmol) in the same solvent (10 mL) and the resulting mixture stirred for about 2 h. The volume of the solution was then reduced to ca. 10 mL; the addition of petroleum ether–diethyl ether (1:1, 20 mL) gave a yellow-orange precipitate. This was filtered, washed with diethyl ether, and vacuum dried to give **9** (0.111 g, 0.239 mmol) in 95% yield. [(C_8H_{12})Rh(μ-Cl)]$_2$ was recovered from the mother liquor and identified by comparison with an authentic sample. Anal. Calcd for $C_{21}H_{22}ClNPPd$: C, 54.69; H, 4.81; N, 3.04; Cl, 7.69. Found: C, 54.73; H, 4.86; N, 3.05; Cl, 7.73. ^1H NMR ($CDCl_3$, 255 K): δ 4.54 (dd, $^3J_{PH}$ = 6.9, $^4J_{H_{syn}H_{anti}}$ = 2.9 Hz), 3.02 (dd, $^4J_{H_{syn}H_{syn}}$ = 2.9, $^2J_{H_{anti}H_{syn}}$ = 1.7), 3.58 (d, $^3J_{PH}$ = 9.9 Hz), 2.73 (d, $^2J_{H_{syn}H_{anti}}$ = 1.7 Hz), 1.95 (s, CH_3), 8.76 (6-H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 255 K): δ 24.3 (s).

Synthesis of [(C_8H_{12})Rh(μ-Cl)(μ-Ph_2PPy)PdCl_2] (10). Procedure a. A dichloromethane solution (10 mL) of [Pd(C_8H_{12})Cl_2] (0.086 g, 0.301 mmol) was added dropwise to a stirred solution of 1 (0.154 g, 0.302 mmol) in the same solvent (10 mL). Immediately, the color of solution turned from yellow to dark red. After about 15 min, the volume of the solution was reduced to ca. 10 mL; by addition of petroleum ether (20 mL) a red precipitate was formed. This was filtered, washed with diethyl ether, and vacuum dried to give the product (0.198 g, 0.289 mmol) in 96% yield. Anal. Calcd for $C_{25}H_{26}Cl_3NPPdRh$: C, 43.70; H, 3.81; N, 2.03; Cl, 15.48. Found: C, 43.68; H, 3.79; N, 1.99; Cl, 15.44. IR (CsI, Nujol): ν(Rh–Cl) 341, 291, 273 cm^{-1}.

The product was analogously obtained by reaction of [Pd($PhCN)_2Cl_2$] with 1.

Procedure b. A dichloromethane solution of Ph_2PPy (0.111 g, 0.421 mmol) was added to a solution (10 mL) of [Pd(C_8H_{12})Cl_2] (0.120 g, 0.421 mmol) in the same solvent. Immediately, the color of the solution turned from yellow to orange. The subsequent addition of [(C_8H_{12})Rh(μ-Cl)]$_2$ (0.104 g, 0.211 mmol) in the same solvent (10 mL), to the reaction mixture, soon resulted in a color change to dark red. The solution was reduced in volume to ca. 10 mL, and diethyl ether (20 mL) was added to give the product as a red solid. This was filtered, washed with diethyl ether, and vacuum dried. Yield: 0.275 g (0.399 mmol), 95%. Anal. Calcd for $C_{25}H_{26}Cl_3NPPdRh$: C, 43.70; H, 3.81; N, 2.03; Cl, 15.48. Found: C, 43.67; H, 3.78; N, 2.01; Cl, 15.46.

Reaction of 10 with ^tBuNC. To a suspension of **10** (0.10 g, 0.145 mmol) in dichloromethane (10 mL) was added a ^tBuNC solution in the same solvent dropwise until the IR spectrum indicated that the reaction was complete. During this time, the suspension disappeared and the solution turned to dark red. The addition of petroleum ether (20 mL) afforded a red solid. This was filtered, washed with diethyl ether, and vacuum dried to give **5** in nearly quantitative yield. Anal. Calcd for $C_{54}H_{64}Cl_6N_6P_2Pd_2Rh_2$: C, 43.52; H, 4.33; N, 5.64. Cl, 14.27. Found: C, 43.50; H, 4.36; N, 5.63; Cl, 14.31.

Preparation of [Pd(Ph_2PPy)Cl_2] (11). To a dichloromethane solution (10 mL) of [Pd(C_8H_{12})Cl_2] (0.054 g, 0.188 mmol) was added Ph_2PPy (0.049 g, 0.188 mmol) in the same solvent dropwise, with stirring. Immediately, the color of the solution turned from yellow to orange. After 20 mL of petroleum ether was added, an orange precipitate formed. This was removed by filtration, washed with diethyl ether, and vacuum dried. Anal. Calcd for $C_{17}H_{14}Cl_2NPPd$: C, 46.34; H, 3.2; N, 3.18; Cl, 16.09. Found: C, 46.40; H, 3.18; N, 3.19; Cl, 16.12. IR (CsI, Nujol): ν(PdCl) 335, 293 cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for [($^tBuNC)_2Cl_2Rh(\mu$-Ph_2PPy)Pd(μ-Cl)]$_2$ (5) and [(C_8H_{12})Rh(μ-Cl)(μ-Ph_2PPy)PdCl_2]·CH_2Cl_2 (10). Crystals of both compounds were of very small size and very poor quality, so accurate structural determinations were prevented. Crystal

Table III. Experimental Data for the X-ray Diffraction Studies

	complex 5	complex 10
mol formula	$C_{54}H_{64}Cl_6N_6P_2Pd_2Rh_2$	$C_{25}H_{26}Cl_3NPPdRh{\cdot}CH_2Cl_2$
mol wt	1490.42	772.06
cryst system	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$
radiatn	Ni-filtered Cu Kα (λ = 1.54178 Å)	
a, Å	19.420 (8)	9.282 (5)
b, Å	11.700 (5)	10.564 (5)
c, Å	15.006 (6)	14.690 (6)
α, deg	90	84.35 (3)
β, deg	110.80 (2)	86.32 (3)
γ, deg	90	79.01 (3)
V, Å^3	3187 (2)	1406 (1)
Z	2	2
D_{calcd}, g cm^{-3}	1.553	1.824
F(000)	1488	764
cryst dimens, mm	0.10 × 0.13 × 0.18	0.12 × 0.15 × 0.15
μ(Cu Kα), cm^{-1}	119.76	153.49
2θ range, deg	6–130	6–110
reflcns measd	$\pm h,k,l$	$\pm h,\pm k,l$
unique total data	5960	3541
unique obsd data	1959 [$I > 3\sigma(I)$]	1443 [$I > 2\sigma(I)$]
R	0.0738	0.0730
R_w	0.0987	0.0932

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for the Non-Hydrogen Atoms of Complex 5

atom	x/a	y/b	z/c	U
Pd	8 (1)	17 (2)	3785 (1)	63.0 (7)[a]
Rh	497 (1)	1246 (2)	2683 (1)	53.8 (7)[a]
Cl(1)	459 (4)	1172 (7)	5185 (5)	105 (3)[a]
Cl(2)	1031 (3)	2641 (6)	1823 (4)	79 (3)[a]
Cl(3)	1352 (3)	−216 (5)	2696 (4)	69 (3)[a]
P	−451 (3)	−1075 (5)	2532 (4)	64 (3)[a]
N(1)	1669 (11)	2354 (18)	4366 (16)	78 (10)[a]
N(2)	−752 (11)	2778 (17)	2600 (16)	82 (11)[a]
N(3)	−256 (9)	582 (17)	1414 (13)	59 (9)[a]
C(1)	1209 (15)	1893 (19)	3778 (17)	59 (13)[a]
C(2)	2204 (14)	3023 (23)	5137 (20)	81 (8)
C(3)	1838 (18)	3571 (30)	5749 (25)	133 (12)
C(4)	2545 (20)	4034 (30)	4689 (27)	145 (12)
C(5)	2796 (18)	2218 (29)	5751 (24)	127 (12)
C(6)	−272 (13)	2261 (21)	2701 (16)	62 (10)[a]
C(7)	−1493 (22)	3352 (33)	2424 (29)	168 (16)
C(8)	−1535 (26)	4533 (34)	2012 (34)	211 (21)
C(9)	−2087 (25)	2577 (35)	1727 (33)	222 (21)
C(10)	−1596 (42)	3392 (53)	3363 (32)	224 (26)
C(11)	−564 (12)	−444 (24)	1383 (16)	73 (11)[a]
C(12)	−1010 (16)	−928 (27)	505 (20)	97 (14)[a]
C(13)	−1153 (14)	−336 (25)	−349 (19)	81 (12)[a]
C(14)	−857 (13)	772 (27)	−294 (19)	79 (13)[a]
C(15)	−385 (14)	1171 (27)	610 (17)	95 (13)[a]
C(16)	−1408 (6)	−1369 (14)	2311 (11)	59 (5)
C(17)	−1713 (6)	−2432 (14)	1967 (11)	87 (8)
C(18)	−2472 (6)	−2599 (14)	1688 (11)	93 (8)
C(19)	−2926 (6)	−1704 (14)	1755 (11)	111 (11)
C(20)	−2621 (6)	−641 (14)	2100 (11)	98 (9)
C(21)	−1862 (6)	−474 (14)	2378 (11)	88 (8)
C(22)	−38 (8)	−2474 (12)	2566 (14)	72 (7)
C(23)	63 (8)	−3000 (12)	1788 (14)	106 (9)
C(24)	343 (8)	−4109 (12)	1872 (14)	111 (9)
C(25)	520 (8)	−4693 (12)	2736 (14)	118 (10)
C(26)	419 (8)	−4167 (12)	3514 (14)	162 (16)
C(27)	139 (8)	−3058 (12)	3430 (14)	109 (10)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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

atom	x/a	y/b	z/c	U
Pd	−2158 (2)	1348 (2)	2995 (2)	45 (1)[a]
Rh	1174 (3)	1180 (3)	2211 (2)	52 (1)[a]
Cl(1)	−78 (7)	−298 (7)	3149 (5)	54 (3)[a]
Cl(2)	−3399 (8)	−113 (8)	2390 (6)	71 (4)[a]
Cl(3)	−4232 (7)	2896 (7)	2905 (6)	61 (3)[a]
P	−1173 (8)	2769 (7)	3681 (5)	42 (3)[a]
N	1722 (22)	1742 (19)	3419 (14)	34 (6)
C(1)	755 (27)	2119 (25)	4136 (19)	36 (7)
C(2)	945 (29)	2296 (26)	4984 (20)	49 (8)
C(3)	2422 (32)	1882 (28)	5248 (22)	62 (9)
C(4)	3486 (33)	1418 (28)	4633 (21)	56 (9)
C(5)	3088 (35)	1317 (29)	3724 (22)	63 (9)
C(6)	−2258 (29)	3131 (27)	4723 (19)	42 (8)
C(7)	−2687 (32)	4410 (29)	4941 (21)	61 (9)
C(8)	−3645 (35)	4712 (34)	5733 (23)	76 (11)
C(9)	−4048 (34)	3683 (32)	6290 (24)	67 (10)
C(10)	−3555 (33)	2405 (31)	6079 (22)	61 (9)
C(11)	−2704 (31)	2114 (31)	5267 (21)	58 (9)
C(12)	−913 (28)	4307 (25)	3046 (18)	35 (7)
C(13)	−1900 (35)	4866 (32)	2422 (23)	67 (10)
C(14)	−1819 (33)	6147 (29)	2040 (22)	57 (9)
C(15)	−735 (32)	6785 (31)	2292 (22)	56 (9)
C(16)	246 (37)	6208 (31)	2840 (23)	64 (10)
C(17)	95 (31)	4947 (29)	3353 (21)	54 (9)
C(18)	1661 (38)	2850 (34)	1398 (25)	77 (11)
C(19)	2841 (37)	1994 (32)	1393 (24)	74 (11)
C(20)	3539 (40)	1150 (34)	692 (27)	85 (12)
C(21)	2724 (66)	86 (57)	576 (46)	235 (29)
C(22)	1364 (42)	−51 (38)	1091 (27)	89 (12)
C(23)	282 (40)	867 (36)	950 (25)	78 (11)
C(24)	76 (61)	2046 (52)	378 (38)	162 (22)
C(25)	623 (40)	3162 (35)	619 (26)	88 (12)
C(1S)	4083 (59)	6950 (58)	1306 (39)	159 (21)
C(2S)	3811 (76)	5836 (72)	1147 (52)	207 (31)
C(3S)	3324 (71)	5348 (66)	263 (52)	229 (28)
C(4S)	3656 (61)	6469 (58)	−281 (42)	192 (23)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

of **10** for the X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution. The presence of CH_2Cl_2 in the crystals has been ascertained by the mass spectra of the crystals. The crystallographic data for both compounds are summarized in Table III. Unit cell parameters were determined from the θ values of 28 (**5**) and 30 (**10**) carefully centered reflections, having 23 < θ < 35° (**5**) and 18 < θ < 30° (**10**). Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the nickel-filtered Cu Kα radiation and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of 3–12° min^{-1} and a scan width from $\theta - 0.65°$ to $\theta + 0.65 + 0.142 \tan \theta°$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen.[30] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.049 and 0.938 for **5** and 1.297 and 0.878 for **10**).[31] Only the observed reflections were used in the structure solution and refinement.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for the Pd, Rh, Cl, P, N, C(1), C(6), and C(11)–C(15) atoms of **5** and for the Pd, Rh, Cl, and P atoms of **10**. The two phenyl groups in **5** were treated as rigid groups (C–C = 1.395 Å). Some peaks were found in the final ΔF map of **10** due to the presence of a disordered dichloromethane molecule of solvation (see above), but it was not possible to find among them an acceptable image of the solvent. The four biggest peaks, practically of the same height, were considered as carbon atoms and refined isotropically. All hydrogen atoms were placed at their geometrically calculated positions (C–H

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[31] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158. Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

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= 1.08 Å) and introduced in the final structure factor calculations. The final cycles of refinement were carried out on the basis of 201 (**5**) and 176 (**10**) variables; after the last cycles, no parameters shifted by more than 1.49 (**5**) and 1.20 (**10**) esd. The biggest remaining peak (close to the Pd atom) in the final difference map was equivalent to about 1.08 (**5**) and 0.81 (**10**) e/Å^3. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence, the K and g values were 1.019 and 0.0041 for **5** and 0.5856 and 0.0062 for **10**, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 32. 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) and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, with use of the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[33] The final atomic coordinates for the non-hydrogen atoms for **5** and **10** are given in Tables IV and V, respectively. The atomic coordinates of the hydrogen atoms are given in Tables SI (**5**) and SII (**10**) and the thermal parameters in Tables SIII (**5**) and SIV (**10**) of the supplementary material.

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Registry No. 1, 135973-06-7; **2a**, 135973-08-9; **2b**, 135973-09-0; 3, 135973-13-6; 4, 135973-10-3; **5** (isomer 1), 135973-11-4; **5** (isomer 2), 136031-57-7; **6**, 135973-12-5; **9**, 135973-14-7; **10**, 135973-15-8; **10**·CH$_2$Cl$_2$, 135973-17-0; 11, 135973-16-9; [(C$_8$H$_{12}$)Ru(μ-Cl)]$_2$, 12092-47-6; Ph$_2$PPy, 37943-90-1; [Rh$_2$(Ph$_2$PPy)$_2$(μ-CO)Cl$_2$], 75361-61-4; CO, 630-08-0; *cis*-[Pd(^{t}BuNC)$_2$Cl$_2$], 34710-33-3; {Pd[CH$_2$C(CH$_3$)CH$_2$]Cl}$_2$, 12081-18-4; [Pd(C$_8$H$_{12}$)Cl$_2$], 12107-56-1; [Pd(PhCN)$_2$Cl$_2$], 14220-64-5; *t*-BuNC, 7188-38-7.

Supplementary Material Available: Tables of hydrogen atom coordinates (Tables SI and SII), thermal parameters for the non-hydrogen atoms (Tables SIII and SIV), and bond distances and angles (Tables SV and SVI) (8 pages); a listing of observed and calculated structure factors (Tables SVII and SVIII) (19 pages). Ordering information is given on any current masthead page.

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[33] Sheldrick, G. M. SHELX-76, *Program for crystal structure determination*, Univesity of Cambridge, England, 1976; SHELXS-86, *Program for the solution of crystal structures*, University of Göttingen, 1986.

Catalytic Disproportionation of Aldehydes with Ruthenium Complexes

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It was discovered that the ruthenium complex [(C$_4$Ph$_4$COHOCC$_4$Ph$_4$)(μ-H)][(CO)$_4$Ru$_2$] (**2**), as well as other isostructural Ru complexes, in the presence of a catalytic amount of formic acid, catalyzes the homogeneous bimolecular disproportionation reaction of aldehydes to give esters: 2RCHO → RCOOCH$_2$R. The reaction was found to be general and compatible with a variety of aliphatic and aromatic aldehydes and can be carried out in the presence or absence of solvent under mild conditions. It is characterized by an excellent efficiency with an initial turnover frequency reaching 5000 h^{-1}, a measured overall turnover number of ca. 20 000, and high conversion, yield, and selectivity. Increasing the electron density on the metal and the ligand was found to accelerate the reaction. Kinetic studies indicate that the rate = k[catalyst]$^{1/2}$[aldehyde]. The rate also depends on the initial formic acid concentration. A stoichiometric reaction of complex **2** with formic acid, monitored by infrared spectroscopy, shed light on the identity of the active catalytic species. No kinetic isotope effect could be detected by using PhCDO and DCOOD as reactants. Consequently, a mechanism and a detailed catalytic cyle for the bimolecular transformation of aldehydes to esters were proposed.

Introduction

Several years ago we reported that primary alcohols undergo oxidative coupling to esters using dodecacarbonyltriruthenium(0) as a catalyst.[1] Later, Murahashi et al.[2] reported a similar reaction using H$_2$Ru(PPh$_3$)$_4$ as a catalyst. In both works[1,2] the oxidative coupling was found to proceed in the presence and absence of H acceptors. Our experimental observations, in particular the persistence throughout the reaction period of a steady-state concentration of aldehyde,[1] led us to propose a reaction sequence that may account for the chemical transformations of the organic components (Scheme I; the role of the catalyst is omitted).

Scheme I

$$\mathrm{RCH_2OH + Ph_2C_2 \rightarrow RCHO + PhCH{=}CHPh} \quad (1)$$

$$\mathrm{RCHO + RCH_2OH \rightleftharpoons RCH(OH)OCH_2R} \quad (2)$$

$$\mathrm{RCH(OH)OCH_2R + Ph_2C_2 \rightarrow RCOOCH_2R + PhCH{=}CHPh} \quad (3)$$

While reactions 1 and 3 definitely require a catalyst, reaction 2 is a simple aldehyde–hemiacetal equilibrium system. The most effective H acceptor was found to be diphenylacetylene, which was irreversibly reduced to

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[2] (a) Murahashi, S. I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem.* **1987**, *52*, 4319. (b) Murahashi, S. I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *Tetrahedron Lett.* **1981**, *22*, 5327.

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