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**Supplementary Material Available:** Crystallographic in-

formation for 2a including bond lengths and angles (Table S1), anisotropic temperature factors for non-hydrogen atoms (Table S2), and atomic parameters for hydrogen atoms (Table S3) (3 pages); a table of observed and calculated structure factors (Table S4) (9 pages). Ordering information is given on any current masthead page.

## Rhodium-Palladium and Rhodium-Platinum Heterobinuclear Complexes Containing the 2-(Diphenylphosphino)pyridine Short-Bite Bridging Ligand. X-ray Crystal Structure of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^t)\text{Cl}]\text{PF}_6$

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Some new RhPd and RhPt heterobinuclear complexes containing the 2-(diphenylphosphino)pyridine ( $\text{Ph}_2\text{PPy}$ ) bridging ligand have been prepared by reacting  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (1) with  $d^8$  palladium(II) and platinum(II) complexes. The reaction of 1 with *cis*- $[\text{Pd}(\text{CNBu}^t)_2\text{Cl}_2]$  gave  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^t)\text{Cl}]\text{Cl}$  (2b); if the reaction was performed in the presence of  $\text{TIPF}_6$ , the corresponding  $\text{PF}_6^-$  salt (2a) was isolated. The structure of 2a, containing benzene and methanol molecules of solvation, has been determined by X-ray crystallography. The crystal is monoclinic, with space group  $P2_1/n$ , and the cell constants are  $a = 24.485$  (3) Å,  $b = 10.262$  (2) Å,  $c = 17.626$  (3) Å,  $\beta = 101.40$  (4)°, and  $Z = 4$ . The structure has been refined to a final  $R$  value of 0.045. The cation consists of the  $(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}$  and  $(\text{CNBu}^t)\text{ClPd}$  moieties held together by the  $\text{Ph}_2\text{PPy}$  bridge and the Rh-Pd bond. The Pd atom exhibits a nearly square-planar coordination geometry, and the ligands about rhodium are disposed in a distorted tetrahedral environment. The angles at rhodium between the centroid of the cyclopentadienyl ring and the other ligands are larger than those formed by the other ligands. The Rh-Pd bond distance is 2.631 (2) Å; the  $\text{Ph}_2\text{PPy}$  is twisted by 35.4 (2)° about the Rh-Pd bond to avoid unfavorable contacts. Compound 2b readily undergoes metathesis with KI, giving the corresponding iodo derivative  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^t)\text{I}]\text{I}$  (4); compound 4 was also the product of the reaction of 2b with  $\text{CH}_3\text{I}$  or  $\text{CH}_2\text{I}_2$ . The reaction of 1 with  $[\text{Pd}(\text{COD})\text{Cl}_2]$  (COD = cycloocta-1,5-diene) occurs by displacement of COD to give  $[(\text{C}_5\text{H}_5)\text{Rh}(\text{CO})(\mu\text{-Ph}_2\text{PPy})\text{PdCl}_2]$  (5). Reaction of 1 with *cis*- $[\text{Pt}(\text{DMSO})_2(\text{CH}_3)_2]$  (DMSO = dimethyl sulfoxide) gave the compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CH}_3)_2]$  (6) in which a rhodium-platinum bond is present. The analogous reaction with *cis*- $[\text{Pt}(\text{DMSO})_2\text{Cl}_2]$  yielded the  $\text{Rh}^{\text{II}}\text{-Pt}^{\text{I}}$  complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{RhCl}(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CO})\text{Cl}]$  (8); the reaction formally involves the oxidative addition of a  $d^8$  platinum species to a  $d^8$  five-coordinated rhodium(I) complex. The results show that the rigid short-bite  $\text{Ph}_2\text{PPy}$  ligand and the nature of the ligands coordinated to palladium(II) or platinum(II) complexes strongly influence the course of the reactions described.

The synthesis and reactivity of binuclear transition-metal complexes continue to be the subject of considerable interest; this is due to their potential for novel stoichiometric and catalytic reactions.<sup>1-4</sup> In principle, in a heterobimetallic complex each metal center could undergo the reactions observed in their mononuclear compounds; in addition, when the metals are held in close proximity by bridging ligands, novel modes of reactivity, as a consequence of intermediate steps involving formation or breaking of a metal-metal bond, insertion into the metal-metal bond, ligand mobility from terminal to bridging site, and bridging modes involving the substrate molecules, can be observed. Our goal is to prepare homo- and heterobimetallic compounds in which two metal centers are held together by short-bite ligands and to investigate their

behavior in small molecule activation processes.

We have recently reported<sup>5,6</sup> the 2-(diphenylphosphino)pyridine ( $\text{Ph}_2\text{PPy}$ ) complex  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$ , in which the  $\text{Ph}_2\text{PPy}$  acts as a monodentate P-bonded ligand, and its reactions with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  and  $[\text{Ir}(\text{CO})_2(p\text{-toluidineCl})]$  to give the unsymmetric complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})(\mu\text{-Ph}_2\text{PPy})\text{M}(\text{CO})\text{Cl}]$  (M = Rh, Ir); interestingly, the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})(\mu\text{-Ph}_2\text{PPy})\text{Rh}(\text{CO})\text{Cl}]$  reacts<sup>6</sup> with alkynes activated by electron-withdrawing groups, giving the tetranuclear species  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-acetylene})(\mu\text{-Ph}_2\text{PPy})\text{Rh}(\text{CO})(\mu\text{-Cl})]_2$  (acetylene =  $\text{CH}_3\text{O}_2\text{CC}_2\text{CO}_2\text{CH}_3$ ,  $\text{C}_2\text{H}_5\text{O}_2\text{CC}_2\text{CO}_2\text{C}_2\text{H}_5$ ).

The monodentate metal-containing ligand  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (1) would be suitable for the synthesis of new kinds of heterobimetallic complexes. Here, we report the reactions of 1 with  $d^8$  metal complexes of

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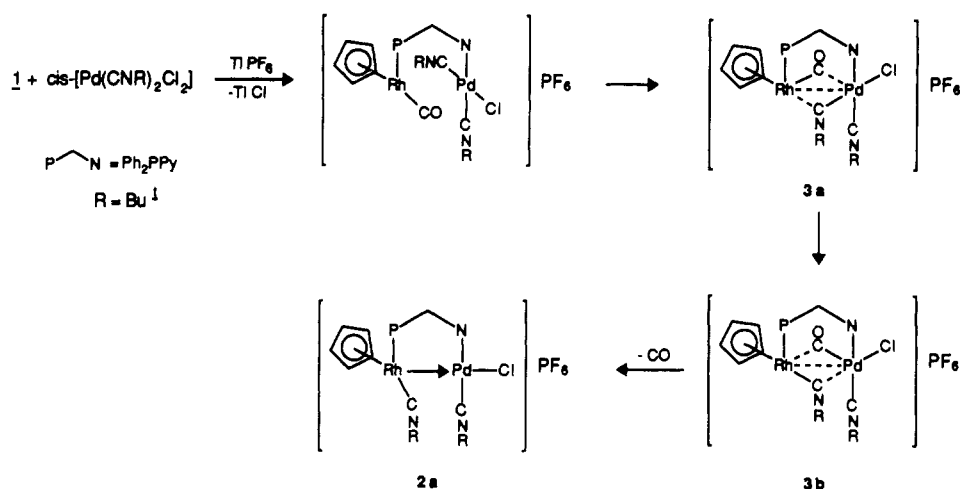
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Scheme I



palladium and platinum, some simple reaction chemistry of the heterobimetallic RhPd complexes as well as the crystal and molecular structure of the rhodium–palladium metal–metal-bonded complex  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBU}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBU}^t)\text{Cl}]\text{PF}_6$  (**2a**). The heterobinuclear complexes reported here are good candidates for the study of site selectivity in their reactions with electrophilic and nucleophilic reagents; the results will be the subject of further publications.

## Results and Discussion

### Synthesis and Characterization of the Complexes.

The addition of monodentate metal-containing ligands to coordinatively unsaturated metal–ligand species, or their precursors, has already been shown to constitute a route to heterobimetallic complexes containing bridging ligands.<sup>1,7</sup> We have used this synthetic route to prepare new rhodium–palladium and rhodium–platinum bimetallic complexes containing Ph<sub>2</sub>PPy as bridging ligand.

The reaction of  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (**1**) with *cis*- $[\text{Pd}(\text{CNBU}^t)_2\text{Cl}_2]$ , in the presence of TlPF<sub>6</sub>, in dichloromethane solution, gives as the final product the cationic complex  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBU}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBU}^t)\text{Cl}]^+$  as the PF<sub>6</sub><sup>-</sup> salt (**2a**). Complex **2a** was isolated in good yields as an orange crystalline, air-stable solid and was fully characterized by IR and <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and a single-crystal X-ray diffraction analysis. The <sup>1</sup>H NMR spectrum, in CDCl<sub>3</sub>, shows resonances for the *tert*-butyl group at  $\delta$  1.16 and 1.61 ppm, as singlets, and a doublet of doublets for the cyclopentadienyl protons at  $\delta$  5.51 ppm (<sup>3</sup>J<sub>PH</sub> = 1.45 Hz; <sup>2</sup>J<sub>RhH</sub> = 0.50 Hz). As usual the 6-hydrogen of the pyridine ring gives a distinct resonance that is further shifted toward higher frequency by the coordination of the nitrogen to the palladium ( $\delta$  = 8.72 ppm for **1** and  $\delta$  = 9.62 ppm for **2a**). NOE experiments allowed the unambiguous assignment of the resonances of the two nonequivalent *tert*-butyl protons. Signal enhancement of the resonance at  $\delta$  1.16 ppm could be detected by irradiating the proton in the 6-position on the pyridine ring. Enhancement of the signal at  $\delta$  1.61 ppm could be detected when the cyclopentadienyl protons were

irradiated. This supports a structure in which the Pd and Rh atoms each coordinate a CNBU<sup>t</sup> group, as in **2a**. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, in CDCl<sub>3</sub>, shows a doublet at  $\delta$  37.19 ppm (<sup>1</sup>J<sub>RhP</sub> = 148.4 Hz). The NMR spectra are not temperature dependent, and this excludes exchange processes in solution. In the IR spectrum the  $\nu(\text{CN})$  bands at 2180 and 2170 cm<sup>-1</sup> are consistent with the presence of two different terminal isocyanide ligands; the strong  $\nu(\text{PdCl})$  at 276 cm<sup>-1</sup> supports a structure in which the chlorine atom is nearly trans to the Rh–Pd bond. It is well-known that a metal–metal bond acts as a ligand with a strong trans-labilizing effect.<sup>8</sup>

In the absence of TlPF<sub>6</sub>, complex **1** reacts with *cis*- $[\text{Pd}(\text{CNBU}^t)_2\text{Cl}_2]$  to give the cation  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBU}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBU}^t)\text{Cl}]^+$  as the Cl<sup>-</sup> salt (**2b**); several recrystallizations are required to obtain the product in an analytically pure form.

The capability of both CO and CNBU<sup>t</sup> ligands to act as bridging ligands together with the tendency of Ph<sub>2</sub>PPy to induce metal–metal bond formation support the reaction sequence reported in Scheme I. All the reaction steps following the nucleophilic attack of the pyridine nitrogen atom are very fast, and only the presence of the starting material and **2** can be demonstrated spectroscopically. Concomitant transfer of carbon monoxide from rhodium to palladium and of CNBU<sup>t</sup> from palladium to rhodium probably occurs through the intermediates **3a** and **3b** in which both these ligands are bridging. Subsequently the palladium center releases carbon monoxide giving **2a**. Although there is no spectroscopic evidence, the intermediate coordination of CO to the palladium center seems very likely; the Pd–CO bond normally appears to be weak due to the lack of an efficient  $\pi$  back-bonding.<sup>9</sup> The formation of such a palladium carbonyl intermediate is also supported by the isolation of the platinum derivative **8**. The rhodium–palladium bond arises from donation of an electron pair from the 18-electron Rh<sup>I</sup> center to the unsaturated 14-electron Pd<sup>II</sup> center. This interaction can be induced by the rigid, short-bite ligand Ph<sub>2</sub>PPy.

The complex **2b** reacts easily with KI, in CH<sub>2</sub>Cl<sub>2</sub> solution, to give the corresponding iodide derivative  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBU}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBU}^t)\text{I}]\text{I}$  (**4**). Analytical,

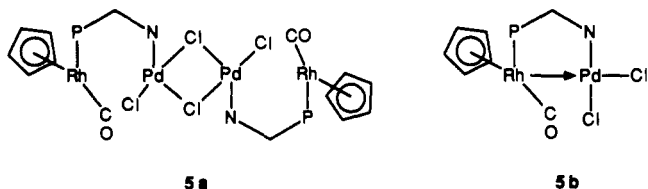
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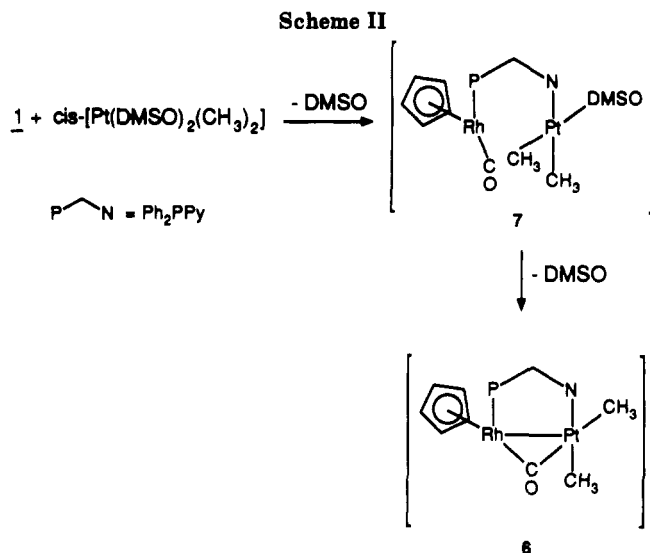
conductivity, IR, and NMR data were all consistent with a formulation of 4 as an iodo derivative analogous to 2b. The complex 4 is also the product of the reaction of 2b with  $\text{CH}_3\text{I}$  and  $\text{CH}_2\text{I}_2$ . Although the mechanism of the formation of 4 in these reactions is unknown, it seems unlikely that the reaction occurs by initial oxidative addition of  $\text{CH}_3\text{I}$  or  $\text{CH}_2\text{I}_2$  to the rhodium(I) center. Probably the  $\text{Rh} \rightarrow \text{Pd}$  dative bond makes the rhodium center not sufficiently basic to promote the oxidative-addition reaction. Also the charge on the complex does not favor such a process, which requires the formation of a cationic intermediate.<sup>10</sup> Taking into account the nature of the reaction product, the most plausible possibility seems to be the oxidative addition of  $\text{CH}_3\text{I}$  or  $\text{CH}_2\text{I}_2$  to the palladium(II) center, which subsequently loses the corresponding chloro derivative by reductive elimination. However, it is not possible to rule out a radical mechanism.

The reaction of 1 with  $[\text{Pd}(\text{COD})\text{Cl}_2]$  (COD) = cycloocta-1,5-diene involves COD displacement to give a neutral product. Compound 1 reacts with  $[\text{Pd}(\text{COD})\text{Cl}_2]$ , in  $\text{CH}_2\text{Cl}_2$  solution, giving a green-black solid, nonconducting in dichloromethane solution, which analyzes as  $\text{RhPd}(\text{C}_5\text{H}_5)(\text{Ph}_2\text{PPy})(\text{CO})\text{Cl}_2$  (5), together with compounds that we were not able to characterize owing to their extensive decomposition. The  $^1\text{H}$  NMR spectrum, in  $\text{CDCl}_3$  solution, shows the cyclopentadienyl protons as a doublet of doublets at  $\delta$  5.53 ppm ( $^2J_{\text{RhH}} = 0.6$  Hz;  $^3J_{\text{PH}} = 1.4$  Hz); the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a doublet at  $\delta$  38.92 ppm ( $^1J_{\text{RhP}} = 158.7$  Hz). The  $^{13}\text{C}$  NMR spectrum of a sample obtained starting from  $^{13}\text{C}$ -enriched 1 shows the carbonyl resonance as a doublet of doublets centered at  $\delta$  196.3 ppm ( $^1J_{\text{RhC}} = 74.12$  Hz;  $^2J_{\text{CP}} = 14.6$  Hz), indicating that the CO coordination to the rhodium is retained. In the IR spectrum the compound shows bands at 333 and 270  $\text{cm}^{-1}$  in the  $\nu(\text{MCl})$  region; the former indicates the presence of a terminal chloride bonded to a palladium center while the band at lower frequency supports the presence of bridging chloride or of a chloride in a trans position with respect to a metal-metal bond.<sup>8</sup> The  $\nu(\text{CO})$  at 1903  $\text{cm}^{-1}$  is in agreement with  $^{13}\text{C}$  NMR spectra and rules out any structure with the carbonyl group coordinated to the palladium, as a higher value of  $\nu(\text{CO})$  is expected for a carbonyl group bonded to a palladium(II) center.<sup>9</sup>

The displacement of the COD ligand from the  $[\text{Pd}(\text{CO})\text{DCl}_2]$  moiety by the pyridine nitrogen atom of 1 gives formally an unsaturated 14-electron palladium(II) species; this transient intermediate can lead to a tetracoordinated 16-electron species either by formation of chloro-bridges, giving the tetranuclear species 5a, or by a dative  $\text{Rh}^{\text{I}} \rightarrow \text{Pd}^{\text{II}}$  bond, where the rhodium(I) 18-electron center acts as a Lewis base. In the latter case, the product can be formulated as the bimetallic species 5b. Molecular weight



determinations, in  $\text{CH}_2\text{Cl}_2$  solution at different concentrations, suggest the presence of a dimeric species. NMR spectra, at different concentrations ( $5 \times 10^{-3}$  to  $5 \times 10^{-4}$  M) and temperatures, rule out the possibility that an equilibrium between 5a and the corresponding solvato



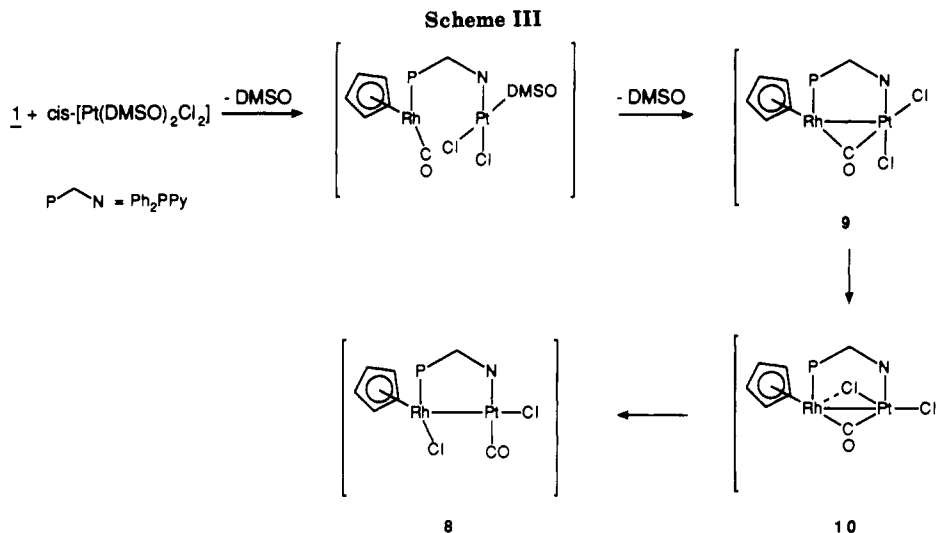
dimeric form or the species 5b can be operating in the range of temperature and concentration explored. On this basis, we are inclined to prefer structure 5b for the reaction product of 1 with  $[\text{Pd}(\text{COD})\text{Cl}_2]$ . Compound 5 reacts, in  $\text{CH}_2\text{Cl}_2$  solution, with the neutral ligands pyridine and triphenylphosphine, breaking the  $\text{Ph}_2\text{PPy}$  bridge;  $[\text{Pd}(\text{py})_2\text{Cl}_2]$  and 1 are the products of the reaction with pyridine while  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})\text{PPh}_3]$  and a mixture of uncharacterized products are formed in the reaction with  $\text{PPh}_3$ . In contrast, compound 5 reacts with  $\text{CNBu}^t$ , in the presence of  $\text{TlPF}_6$ , giving the cationic complex 2a.

The addition of  $\text{cis-}[\text{Pt}(\text{DMSO})_2(\text{CH}_3)_2]$  to a dichloromethane solution of 1 slowly gives a red violet solution from which crystals of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CH}_3)_2]$  (6) have been obtained by adding ethyl ether. The infrared spectrum of the product shows a strong  $\nu(\text{CO})$  band at 1806  $\text{cm}^{-1}$  indicating the presence of bridging carbon monoxide. The  $^1\text{H}$  NMR spectrum, in  $\text{CDCl}_3$  solution, shows two methyl resonances at  $\delta$  0.86 ( $^2J_{\text{PtH}} = 78.8$  Hz) and 1.09 ppm ( $^2J_{\text{PtH}} = 87.5$  Hz) with platinum satellites. The cyclopentadienyl protons show resonance at  $\delta$  5.13 ppm ( $^2J_{\text{RhH}} = ^3J_{\text{PH}} = 0.8$  Hz). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, in  $\text{CDCl}_3$ , shows a doublet at  $\delta$  50.0 ppm ( $^1J_{\text{RhP}} = 190.2$  Hz). The presence of the platinum satellites in the expected 1:4:1 intensity ratio ( $^2J_{\text{PtP}} = 125.6$  Hz) clearly indicates the existence of the rhodium-platinum bond and the fact that the  $\text{Ph}_2\text{PPy}$  is bound to rhodium through the phosphorus atom as in precursor 1. The formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CH}_3)_2]$  (6) by reacting 1 with  $\text{cis-}[\text{Pt}(\text{DMSO})_2(\text{CH}_3)_2]$  (DMSO = dimethyl sulfoxide) is the result of the presence in the platinum(II) substrate of the strongly trans-labilizing alkyl groups<sup>11</sup> and of the labile DMSO ligands; the alkyl groups are strongly bonded to the metal center and are not able to occupy bridging sites. No traces of products other than the starting material and 6 have been detected by monitoring the reaction with  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Thus DMSO ligand displacement and rhodium-platinum bond and bridging carbonyl group formation take place in fast steps that do not allow accumulation of intermediate 7 (Scheme II).

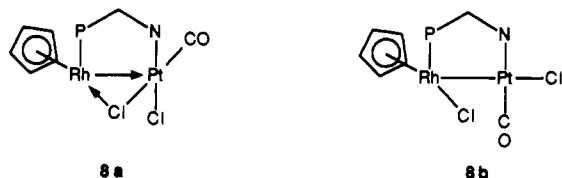
The reaction of 1 with  $\text{cis-}[\text{Pt}(\text{DMSO})_2\text{Cl}_2]$ , at room temperature, in  $\text{CH}_2\text{Cl}_2$  solution, gives the heterobimetallic complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-Cl})(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CO})\text{Cl}]$  (8) as the final product. Complex 8 was isolated in moderate yields

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as a dark red microcrystalline solid, stable in air for a few days. It was fully characterized by  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}$  NMR and IR spectroscopy and elemental analysis. Attempts to grow X-ray quality crystals have been unsuccessful. The  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  shows the cyclopentadienyl proton resonance as a doublet ( $^2J_{\text{RhH}}$  is unresolved) at  $\delta$  5.40 ppm ( $^3J_{\text{PH}} = 1.8$  Hz). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, in  $\text{CDCl}_3$ , shows a doublet at  $\delta$  40.93 ppm ( $^1J_{\text{RHP}} = 152.48$  Hz). The presence of platinum satellites ( $^2J_{\text{PtP}} = 165.9$  Hz) indicates the existence of a rhodium-platinum bond. The  $^{13}\text{C}$  NMR spectrum of a sample obtained starting from  $^{13}\text{C}$  enriched  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (1) shows the carbonyl resonance as a singlet at  $\delta$  172.36 ppm flanked by the platinum satellites ( $^1J_{\text{PtC}} = 1952$  Hz), indicating CO coordination to the platinum center. In accordance with the NMR data, the IR spectrum shows the terminal carbon monoxide stretching frequency at  $2052\text{ cm}^{-1}$ ; this value is at higher frequency than that in the precursor 1 and in neutral rhodium(I) complexes and falls in the range usually found for a CO bonded to a platinum center.<sup>9</sup> The  $\nu(\text{PdCl})$  bands at  $300$  and  $268\text{ cm}^{-1}$  indicate that one chlorine atom is terminal while the other can be either bridging or trans to the rhodium-platinum bond. The compound 8 can be regarded as containing  $\text{Rh}^{\text{I}}\text{-Pt}^{\text{II}}$  (8a) or  $\text{Rh}^{\text{II}}\text{-Pt}^{\text{I}}$  (8b) species.



In 8a, the 18-electron  $\text{Rh}^{\text{I}}$  center acts as a Lewis base, giving rise to a dative  $\text{Rh}^{\text{I}} \rightarrow \text{Pt}^{\text{II}}$  bond, while in 8b the rhodium-platinum bond would be the result of a bonding interaction between the  $\text{Rh}^{\text{II}}$  and  $\text{Pt}^{\text{I}}$  centers. The formulation 8b is supported by the magnitude of  $^3J_{\text{PH}}$  for the cyclopentadienyl proton resonance; this has been related to the oxidation state of the rhodium atom.<sup>5,10,12</sup> In bimetallic rhodium(I) complexes containing the short-bite bridging ligand  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) or  $\text{Ph}_2\text{PPy}$  the  $^3J_{\text{PH}}$  values are about 1.0 Hz [1.1 Hz in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-}$

$\text{Ph}_2\text{PPy})(\mu\text{-CO})\text{Rh}(\text{CO})\text{Cl}]$ ;<sup>5</sup> 0.8 Hz in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-dppm})(\mu\text{-CO})]^{13}$ ]; for the corresponding rhodium(II) complexes, the  $^3J_{\text{PH}}$  value is intermediate between that of the rhodium(I) precursor and that of the oxidative-addition rhodium(III) product [1.66 Hz in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-Ph}_2\text{PPy})(\mu\text{-I})\text{Rh}(\text{CO})\text{I}_2]$  and 2.19 Hz in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-Ph}_2\text{PPy})\text{Rh}(\text{CO})\text{I}_3]$ ].<sup>5</sup> Thus the  $^3J_{\text{PH}}$  value of 1.8 Hz for the cyclopentadienyl proton resonance in 8 indicates oxidation of the rhodium atom and supports 8b. The correlation of the changes of  $^1J_{\text{RHP}}$  with the rhodium formal oxidation state and the coordination geometry<sup>14</sup> appears not to be applicable to binuclear cyclopentadienyl(phosphine)rhodium complexes.<sup>15</sup>

The formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{RhCl}(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CO})\text{Cl}]$  (8), by reacting 1 with  $\text{cis-}[\text{Pt}(\text{DMSO})_2\text{Cl}_2]$ , involves transfer of carbon monoxide from rhodium to palladium and of the chloride ligand from the palladium to the rhodium atom. The reaction in some aspects resembles that of 1 with  $\text{cis-}[\text{Pd}(\text{CNBu}^t)_2\text{Cl}_2]$ ; significantly, in this case, the transfer involves the charged chloride ligand. The reaction sequence reported in Scheme III seems to be very likely for the reaction. The first step involves displacement of DMSO by the pyridine nitrogen atom of 1; the displacement of the second DMSO ligand gives the intermediate 9 in which the CO is bridging and the Rh-Pt bond is also present. This intermediate is very similar to the compound 6. The presence of the chloride ligand makes possible the formation of a new bridge and, at the same time, CO transfer to the platinum center as in 10. An intramolecular redox process with charge transfer from rhodium to platinum through the metal-metal bond could also be operating in this step. The rigid short-bite  $\text{Ph}_2\text{PPy}$  ligand, which brings the two metals in close proximity, seems to be the determining factor of this process. The formation of an anionic intermediate by initial halide transfer from palladium to rhodium, such as that observed by Balch<sup>16</sup> in the synthesis of  $[\text{RhPt}(\text{Ph}_2\text{PPy})_2(\text{CO})\text{Cl}_3]$ , can be ruled out by 1 being a 18-electron species. Oxidative addition of platinum(II) or palladium(II) complexes to a rhodium(I) center with formation of formally  $\text{Rh}^{\text{II}}\text{-Pd}^{\text{I}}$  and

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(15) See, for example, the  $^1J_{\text{RHP}}$  in  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (199.8 Hz),<sup>5</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})(\mu\text{-Ph}_2\text{PPy})\text{Rh}(\text{CO})\text{Cl}]$  (175.6 Hz)<sup>5</sup> and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-acetylene})(\mu\text{-Ph}_2\text{PPy})\text{Rh}(\text{CO})(\mu\text{-Cl})_2]$  (175.9 Hz).<sup>6</sup>

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Table I. Fractional Coordinates for Non-Hydrogen Atoms

atom	x	y	z
Pd	0.69184 (2)	0.96101 (5)	-0.08024 (3)
Rh	0.72396 (2)	0.77583 (6)	0.02212 (3)
P(2)	0.9035 (1)	0.1096 (3)	0.2201 (2)
F(1)	0.8718 (5)	0.075 (1)	0.1409 (5)
F(2)	0.8810 (6)	0.2455 (9)	0.2227 (9)
F(3)	0.8496 (6)	0.065 (1)	0.2432 (7)
F(4)	0.9233 (7)	-0.023 (1)	0.224 (1)
F(5)	0.9289 (8)	0.133 (2)	0.3002 (8)
F(6)	0.9474 (8)	0.159 (2)	0.190 (1)
Cl	0.65617 (9)	1.1410 (2)	-0.1628 (1)
P(1)	0.77331 (8)	0.7276 (2)	-0.0685 (1)
C(1)	0.6573 (3)	0.7058 (7)	-0.0417 (4)
N(1)	0.6185 (3)	0.6557 (7)	-0.0767 (4)
C(2)	0.5675 (3)	0.596 (1)	-0.1235 (5)
C(3)	0.5434 (7)	0.683 (2)	-0.184 (1)
C(4)	0.5854 (6)	0.481 (2)	-0.161 (1)
C(5)	0.5302 (5)	0.564 (2)	-0.0715 (7)
C(6)	0.6880 (3)	1.0647 (7)	0.0079 (4)
N(2)	0.6810 (3)	1.1366 (6)	0.0556 (4)
C(7)	0.6690 (4)	1.2340 (9)	0.1119 (5)
C(8)	0.7242 (5)	1.286 (1)	0.1548 (6)
C(9)	0.6371 (6)	1.343 (1)	0.0652 (7)
C(10)	0.6374 (8)	1.170 (1)	0.1655 (8)
C(11)	0.7935 (3)	0.781 (1)	0.1233 (4)
C(12)	0.7648 (4)	0.6610 (9)	0.1261 (4)
C(13)	0.7113 (4)	0.693 (1)	0.1347 (5)
C(14)	0.7061 (4)	0.831 (1)	0.1381 (4)
C(15)	0.7577 (4)	0.8835 (8)	0.1332 (4)
N(3)	0.6953 (2)	0.8379 (6)	-0.1752 (3)
C(16)	0.6609 (3)	0.8558 (8)	-0.2447 (4)
C(17)	0.6619 (4)	0.7721 (9)	-0.3062 (4)
C(18)	0.6980 (4)	0.669 (1)	-0.2974 (5)
C(19)	0.7338 (3)	0.6513 (8)	-0.2259 (4)
C(20)	0.7315 (3)	0.7357 (7)	-0.1661 (4)
C(21)	0.8351 (3)	0.8213 (7)	-0.0777 (4)
C(22)	0.8659 (4)	0.7867 (8)	-0.1331 (5)
C(23)	0.9132 (4)	0.8546 (9)	-0.1392 (5)
C(24)	0.9306 (4)	0.9558 (9)	-0.0903 (6)
C(25)	0.9014 (4)	0.9935 (8)	-0.0344 (5)
C(26)	0.8527 (3)	0.9258 (8)	-0.0284 (5)
C(27)	0.7964 (3)	0.5604 (7)	-0.0525 (4)
C(28)	0.7585 (3)	0.4581 (8)	-0.0713 (5)
C(29)	0.7722 (4)	0.3334 (8)	-0.0435 (5)
C(30)	0.8231 (5)	0.3109 (9)	0.0029 (5)
C(31)	0.8614 (4)	0.410 (1)	0.0213 (5)
C(32)	0.8490 (3)	0.5346 (8)	-0.0071 (4)
C(33)	0.5285 (6)	0.214 (1)	0.386 (1)
C(34)	0.5481 (6)	0.163 (2)	0.3279 (8)
C(35)	0.5294 (7)	0.047 (2)	0.2984 (9)
C(36)	0.4920 (7)	-0.021 (1)	0.329 (1)
C(37)	0.4712 (7)	0.029 (2)	0.386 (1)
C(38)	0.492 (1)	0.152 (3)	0.418 (1)
O(1)	0.5503 (6)	-0.062 (2)	1.006 (1)
O(2)	0.5366 (7)	0.024 (3)	0.953 (1)
C(40)	0.515 (1)	-0.093 (2)	1.059 (1)

Rh<sup>II</sup>-Pt<sup>I</sup> species have been observed in the synthesis of the complexes [RhPd(Ph<sub>2</sub>PPy)<sub>2</sub>(CO)Cl<sub>3</sub>]<sub>16-18</sub> [RhPt(Ph<sub>2</sub>PPy)<sub>2</sub>(CO)Cl<sub>3</sub>]<sub>18-19</sub> [RhPd(CNCH<sub>3</sub>)<sub>2</sub>(μ-Ph<sub>2</sub>PPy)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup><sub>18</sub> and [Rh<sub>2</sub>Pd(CO)<sub>2</sub>(μ-dpma)<sub>2</sub>Cl<sub>3</sub>]<sup>+</sup><sub>19</sub> (dpma = bis[(diphenylphosphino)methyl]phenylarsine). It was demonstrated that the formation of a metal-metal bond is a determining factor in these reactions.<sup>20</sup> The formation of M<sup>I</sup>-M<sup>I</sup> (M = Pd, Pt) complexes by reacting M<sup>II</sup> species with M<sup>0</sup> species is well-known.<sup>21</sup>

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

Bond Distances			
Pd-Cl	2.406 (2)	Pd-C(6)	1.901 (8)
Pd-Rh	2.631 (1)	Rh-P(1)	2.241 (2)
Pd-N(3)	2.112 (6)	Rh-C(11)	2.209 (7)
Rh-C(1)	1.928 (7)	Rh-C(13)	2.235 (9)
Rh-C(12)	2.241 (8)	Rh-C(15)	2.257 (8)
Rh-C(14)	2.246 (8)	C(1)-N(1)	1.147 (9)
P(1)-C(21)	1.827 (8)	C(2)-C(3)	1.43 (2)
P(1)-C(20)	1.820 (6)	C(2)-C(5)	1.45 (2)
P(1)-C(27)	1.811 (7)	N(2)-C(7)	1.48 (1)
N(1)-C(2)	1.49 (1)	C(7)-C(9)	1.51 (1)
C(2)-C(4)	1.46 (2)	C(11)-C(12)	1.42 (1)
C(6)-N(2)	1.16 (1)	C(12)-C(13)	1.39 (2)
C(7)-C(8)	1.51 (1)	C(14)-C(15)	1.39 (1)
C(7)-C(10)	1.49 (2)	N(3)-C(20)	1.362 (9)
C(11)-C(15)	1.40 (1)	C(17)-C(18)	1.37 (1)
C(13)-C(14)	1.43 (1)	N(3)-C(16)	1.355 (8)
N(3)...P(1)	2.653 (5)		
Bond Angles			
Cl-Pd-C(6)	89.6 (2)	Rh-Pd-Cl	173.0 (1)
Cl-Pd-N(3)	92.7 (2)	Rh-Pd-N(3)	93.3 (2)
C(6)-Pd-N(3)	177.3 (3)	Pd-Rh-C(15)	104.5 (2)
Rh-Pd-C(6)	84.3 (2)	Pd-Rh-C(13)	143.8 (3)
Pd-Rh-C(14)	110.8 (3)	Pd-Rh-C(11)	127.9 (5)
Pd-Rh-C(12)	164.8 (2)	Pd-Rh-P(1)	78.50 (5)
Pd-Rh-C(1)	76.4 (2)	P(1)-C(27)-C(32)	119.5 (5)
P(1)-Rh-C(1)	90.9 (2)	Rh-P(1)-C(21)	121.3 (2)
Rh-P(1)-C(27)	107.1 (2)	C(1)-N(1)-C(2)	177.6 (8)
Rh-P(1)-C(20)	112.4 (2)	N(1)-C(2)-C(4)	106.8 (8)
C(4)-C(2)-C(5)	113 (1)	P(1)-C(21)-C(26)	120.5 (6)
Rh-C(1)-N(1)	174.9 (7)	C(3)-C(2)-C(4)	106 (1)
N(1)-C(2)-C(5)	107.9 (8)	C(6)-N(2)-C(7)	175.5 (7)
N(1)-C(2)-C(3)	109.6 (9)	N(2)-C(7)-C(9)	106.5 (7)
C(3)-C(2)-C(5)	113 (1)	C(9)-C(7)-C(10)	113 (1)
Pd-C(6)-N(2)	171.8 (7)	C(8)-C(7)-C(9)	109.1 (9)
N(2)-C(7)-C(10)	108.8 (8)	C(12)-C(13)-C(14)	109.6 (9)
N(2)-C(7)-C(8)	107.3 (8)	C(11)-C(15)-C(14)	108.5 (8)
C(8)-C(7)-C(10)	111.4 (9)	C(16)-N(3)-C(20)	119.0 (6)
P(1)-C(20)-C(19)	126.6 (6)	N(3)-C(20)-C(19)	121.3 (7)
Pd-N(3)-C(20)	119.7 (4)	P(1)-C(20)-N(3)	112.2 (5)
Pd-N(3)-C(16)	121.3 (5)	N(2)-C(21)-C(22)	120.0 (6)
Cp*-Rh-C(1)	128.7 (3)	Cp*-Rh-P(1)	128.7 (1)
N(3)-C(16)-C(17)	121.3 (7)	Cp*-Rh-Pd	135.0 (1)

Other palladium(II) and platinum(II) complexes, such as [Pt(SEt<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] and [Pt(PPh<sub>3</sub>)Cl(μ-Cl)]<sub>2</sub>, failed to react with complex 1.

**Molecular Structure of [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CNBu<sup>t</sup>)Rh(μ-Ph<sub>2</sub>PPy)Pd(CNBU<sup>t</sup>)Cl]PF<sub>6</sub>·C<sub>6</sub>H<sub>6</sub>·CH<sub>3</sub>OH (2a).** The crystal structure consists of hexafluorophosphate salts of cationic heterobinuclear complexes and benzene and methanol molecules of solvation in a 1:1:1 ratio. A perspective view of the structure of the cation, giving the atom-labeling scheme, is shown in Figure 1. The molecules of solvation and the PF<sub>6</sub><sup>-</sup> ion have been omitted for clarity; there is no interaction of the solvation molecules with the cation or anion. Final atomic positional parameters are given in Table I. Selected bond distances and angles are given in Table II.

Complex 2a consists of the (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CNBu<sup>t</sup>)Rh and (CNBU<sup>t</sup>)ClPd moieties held together by the Ph<sub>2</sub>PPy bridge and the rhodium-palladium bond. The Rh-Pd distance at 2.631 (1) Å is within the range expected for a rhodium-palladium bond and is longer than that of 2.594 (1) Å reported for [RhPd(Ph<sub>2</sub>PPy)<sub>2</sub>(CO)Cl<sub>3</sub>]<sub>16-18</sub> but slightly shorter than that of 2.699 (1) Å reported for [Rh<sub>2</sub>Pd(CO)<sub>2</sub>(μ-dpma)<sub>2</sub>Cl<sub>3</sub>]<sup>+</sup><sub>19</sub> (dpma = bis[(diphenylphosphino)methyl]phenylarsine). The rhodium atom exhibits a distorted tetrahedral coordination geometry. The angles at Rh between the centroid of the cyclopentadienyl

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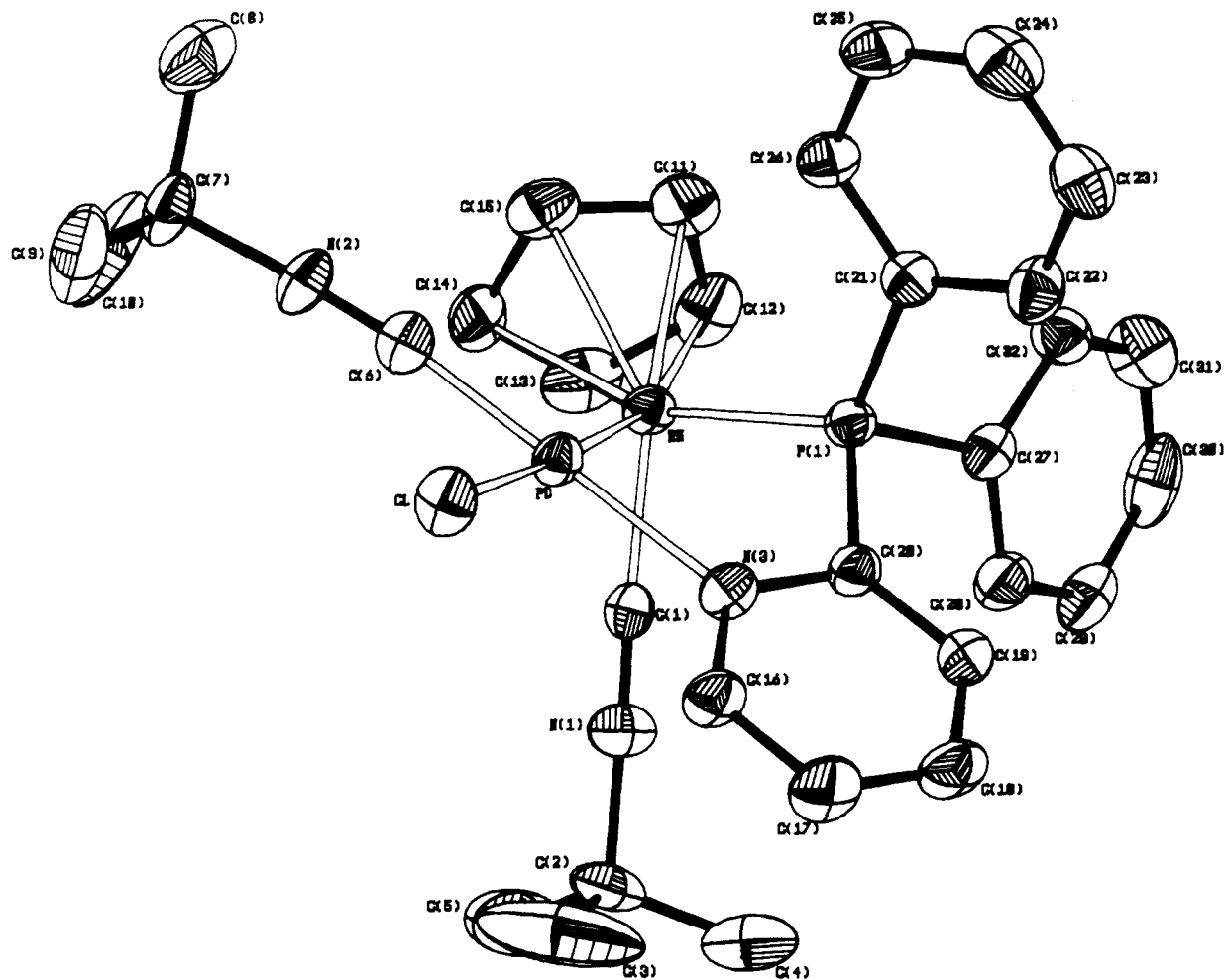


Figure 1. View of the cation  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^4)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^4)\text{C}]^+$  of **2a**.

ring Cp\* and the other ligands are larger than those expected for a tetrahedral coordination and are larger than those of the other ligands. A similar situation was found in bimetallic rhodium-cyclopentadienyl complexes in which the  $\text{C}_5\text{H}_5$  is  $\eta^5$ -coordinated.<sup>12d,13,22</sup> The carbon-carbon distances in the cyclopentadienyl ligand range from 1.39 to 1.43 Å with an average value of 1.406 Å. The average Rh-C( $\text{C}_5\text{H}_5$ ) distance [2.234 Å] and the Rh-Cp\* separation are in the range found in **1** and analogous rhodium-cyclopentadienyl systems.<sup>22,23</sup> The  $\text{Ph}_2\text{PPy}$  is twisted by 35.4 (2)° about the Rh-Pd bond such that the N on the Pd and P on the Rh metals reduce the unfavorable contacts of the pyridine ring with the CNBu<sup>4</sup> ligand and of the phenyl groups with the cyclopentadienyl ring.

The bond distances and angles are consistent with a square-planar geometry at the palladium atom. The N(3)-Pd-C(6) bond angle of 177.3 (2)° reflects the trans orientation of the pyridine ring and the isocyanide ligand. The Pd-Cl bond distance of 2.406 (2) Å is somewhat long and can be explained by the high trans influence of the rhodium-palladium bond. Several reports indicate that a metal-metal bond produces a lengthening of the trans

metal-ligand bond.<sup>8</sup> The Rh-P, Pd-N(3), Rh-C(1), and Pd-C(6) bond distances fall within the range usually found for these bonds.<sup>22</sup>

### Conclusions

The reactions of **1** with d<sup>8</sup> palladium(II) and platinum(II) complexes proceed by coordination of the pyridine nitrogen atom of **1** to palladium(II) or platinum(II) centers. These reactions appear to be strongly dependent on the presence of labile ligands (DMSO, COD) or of ligands with a strong trans-labilizing effect (alkyl group) bound to a palladium(II) or a platinum(II) center. Steric factors and the possibility that the reaction occurs with concomitant movement of terminal ligands to the bridging site are very important in determining the course of reaction and the nature of the products. The rigidity and the short bite angle of the  $\text{Ph}_2\text{PPy}$  ligand induces metal-metal bond formation. Steric interactions between the ligands coordinated to palladium(II) and platinum(II) and the ligands of the five-coordinated rhodium(I) center can give rise to bridging coordination mode of terminal ligands and, in some cases, to transfer of ligands from one metal center to another. When transfer of a charged ligand occurs, the interaction involves oxidative addition. This is what is observed in the reaction of **1** with *cis*-[Pt(DMSO)<sub>2</sub>Cl<sub>2</sub>].

### Experimental Section

Established methods were used to prepare the compounds [Rh( $\eta^5\text{-C}_5\text{H}_5$ )(CO)( $\text{Ph}_2\text{PPy}$ )],<sup>5</sup> *cis*-[Pd(CNBU<sup>4</sup>)<sub>2</sub>Cl<sub>2</sub>],<sup>24</sup> [Pd(CO-D)Cl<sub>2</sub>],<sup>25</sup> *cis*-[Pt(DMSO)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>],<sup>26</sup> and *cis*-[Pt(DMSO)<sub>2</sub>Cl<sub>2</sub>].<sup>27</sup> All

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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 by using a Perkin-Elmer FTIR 1720 spectrophotometer  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker WP80-SY or a Varian Model Gemini-300 spectrometer.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to internal tetramethylsilane and  $^{31}\text{P}$  spectra to external 85%  $\text{H}_3\text{PO}_4$ ; 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 Mikroanalytisches Laboratorium, Elbach, Germany, and by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan.

**Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^t)\text{Cl}]\text{PF}_6$  (2a).** To a dichloromethane solution (20 mL) of  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (0.150 g, 0.326 mmol), were added *cis*- $[\text{Pd}(\text{CNBu}^t)_2\text{Cl}_2]$  (0.112 g, 0.326 mmol) and  $\text{TlPF}_6$  (0.114 g, 0.326 mmol) in rapid succession. The mixture was left under stirring for ca. 20 min.; during this time the color solution turned from yellow to orange. The solution was then filtered and reduced in volume (10 mL), and on addition of diethyl ether, compound 2a was obtained as an orange microcrystalline solid (0.295 g, 0.293 mmol) in 90% yield. IR (CsI, Nujol):  $\nu(\text{CN})$  2180, 2170  $\text{cm}^{-1}$ ;  $\nu(\text{PdCl})$  276  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.16, 1.61 (s, Bu $^t$ ), 5.51 (dd,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = 1.45$  Hz,  $^2J_{\text{RH}} = 0.50$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  37.19 (d,  $^1J_{\text{RHP}} = 148.4$  Hz). Anal. Calcd for  $\text{C}_{22}\text{H}_{37}\text{ClF}_6\text{N}_3\text{P}_2\text{PdRh}$ : C, 43.46; H, 4.21; N, 4.75; Cl, 4.00; F, 12.88. Found: C, 43.49; H, 4.19; N, 4.72; Cl, 4.10; F, 12.92.

**Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^t)\text{Cl}]\text{Cl}$  (2b).** A dichloromethane solution (20 mL) containing  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (0.132 g, 0.287 mmol) and *cis*- $[\text{Pd}(\text{CNBu}^t)_2\text{Cl}_2]$  (0.098 g, 0.287 mmol) was left stirring for ca. 20 min. Then 60 mL of diethyl ether-heptane (2:1) was added. When the mixture was allowed to stand, the compound precipitated as a yellow microcrystalline solid from the solution. The analytically pure product was obtained after several recrystallizations from dichloromethane-diethyl ether as a solid (0.182 g, 0.235 mmol) in 82% yield. IR (CsI, Nujol):  $\nu(\text{CN})$  2175, 2170  $\text{cm}^{-1}$ ;  $\nu(\text{PdCl})$  272  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.16, 1.61 (s, Bu $^t$ ), 5.53 (dd,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = 1.43$  Hz,  $^2J_{\text{RH}} = 0.50$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  37.19 (d,  $^1J_{\text{RHP}} = 148.4$  Hz). Anal. Calcd for  $\text{C}_{22}\text{H}_{37}\text{Cl}_2\text{N}_3\text{PPdRh}$ : C, 49.60; H, 4.81; N, 5.42; Cl, 9.15. Found: C, 49.70; H, 4.83; N, 5.45; Cl, 9.21.

**Preparation of  $[(\eta\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^t)\text{I}]\text{I}$  (4).** **Method a.** Solid KI, in slight excess, was added to a solution of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^t)\text{Cl}]\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was left stirring for 2 h. The solution was filtered and the solvent evaporated off under reduced pressure. By crystallization from  $\text{CH}_2\text{Cl}_2$ -diethyl ether the product was obtained as a red orange solid. Anal. Calcd for  $\text{C}_{22}\text{H}_{37}\text{I}_2\text{N}_3\text{PPdRh}$ : C, 40.13; H, 3.89; N, 4.38; I, 26.49. Found: C, 40.42; H, 3.91; N, 4.40; I, 26.52.

**Method b.**  $\text{CH}_3\text{I}$  (0.5 mL) or  $\text{CH}_2\text{I}_2$  (0.5 mL) was added to a  $\text{CH}_2\text{Cl}_2$  solution of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)\text{Rh}(\mu\text{-Ph}_2\text{PPy})\text{Pd}(\text{CNBu}^t)\text{Cl}]\text{Cl}$ . The reaction mixture was left under stirring for about 4 h. The solvent was evaporated off under reduced pressure to give the product as a red orange solid. Anal. Found: C, 40.21; H, 3.92; N, 4.41; I, 26.53.

**Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\mu\text{-Ph}_2\text{PPy})\text{PdCl}_2]$  (5).** To a dichloromethane solution (20 mL) of  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (0.100 g, 0.218 mmol) was added solid  $[\text{Pd}(\text{COD})\text{Cl}_2]$  (0.062 g, 0.217 mmol) and the resulting mixture stirred for ca. 10 min. During this time, the color of the solution changed from orange to dark red. Addition of diethyl ether-heptane (3:1) (60 mL), followed by slow evaporation of the solvent, leads to the precipitation of the product as a green black microcrystalline solid (0.122 g, 0.192 mmol) in 88% yield. IR (CsI, Nujol):  $\nu(\text{CO})$  1903

$\text{cm}^{-1}$ ;  $\nu(\text{PdCl})$  270, 333  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.53 (dd,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = 1.40$  Hz,  $^2J_{\text{RH}} = 0.6$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  38.92 (d,  $^1J_{\text{RHP}} = 158.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  196.3 (dd,  $^1J_{\text{RHC}} = 74.12$ ;  $^2J_{\text{PC}} = 14.6$  Hz). Anal. Calcd for  $\text{C}_{22}\text{H}_{19}\text{Cl}_2\text{NOPPdRh}$ : C, 43.40; H, 3.01; N, 2.20; Cl, 11.14. Found: C, 43.22; H, 3.03; N, 2.18; Cl, 11.25.

**Reaction of 5 with CNBu $^t$ .** A dichloromethane solution (30 mL) containing 3 (0.100 g, 0.157 mmol) was treated with an excess of CNBu $^t$  (0.032 g, 0.386 mmol) and  $\text{TlPF}_6$ . The color of the solution turned from dark red to yellow. On addition of hexane (50 mL), a yellow solid was obtained; this was separated by filtration, washed with diethyl ether, and dried. The product was identified as 2a by IR, NMR, and analytical data.

**Reaction of 5 with Pyridine.** A few drops of pyridine were added to a stirred  $\text{CH}_2\text{Cl}_2$  solution (20 mL) of 3 (0.120 g, 0.188 mmol). Immediately a white precipitate was formed while the color of the solution turned from dark red to orange. On addition of diethyl ether (40 mL), a further white precipitate was formed. It was separated by filtration, washed with diethyl ether, and dried in vacuo. It was identified as *cis*- $[\text{Pd}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2]$  by comparison with an authentic sample. Removal of the solvent from the mother liquor gave 1.

**Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CH}_3)_2]$  (6).** To a dichloromethane solution (30 mL) of  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (0.280 g, 0.610 mmol) was added solid  $[\text{Pt}(\text{DMSO})_2(\text{CH}_3)_2]$  (0.200 g, 0.52 mmol) and the reaction mixture left stirring for 24 h. During this time the color of the solution turned from orange to red-violet. The solvent was evaporated off under reduced pressure and the solid residue washed several times with 5-mL portions of diethyl ether-pentane (1:1) to remove the unreacted  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  and then extracted with benzene (20 mL). By addition of hexane (40 mL) to the resulting violet solution, the product precipitated as a dark violet solid (0.221 g, 0.322 mmol) in 62% yield. IR (KBr, Nujol):  $\nu(\text{CO})$  1806  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.86 ( $\text{CH}_3$ ,  $^2J_{\text{PH}} = 78.8$  Hz), 1.09 ( $\text{CH}_3$ ,  $^2J_{\text{PH}} = 87.5$  Hz), 5.13 (t,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = ^2J_{\text{RH}} = 0.8$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  50.0 (d,  $^1J_{\text{RHP}} = 190.2$  Hz,  $^2J_{\text{PP}} = 125.6$  Hz). Anal. Calcd for  $\text{C}_{25}\text{H}_{25}\text{NOPPtRh}$ : C, 43.87; H, 3.68; N, 2.05. Found: C, 43.62; H, 3.70; N, 2.00.

**Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{Cl})(\mu\text{-Ph}_2\text{PPy})\text{Pt}(\text{CO})\text{Cl}]$  (8).** Solid  $[\text{Pt}(\text{DMSO})_2\text{Cl}_2]$  (0.138 g, 0.326 mmol) was added to a dichloromethane solution (30 mL) of  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PPy})]$  (0.150 g, 0.326 mmol), and the resulting mixture was left stirring for ca. 6 h. During this time, a color change from orange to rust red occurred, and formation of a very small amount of metal from decomposition was evidenced. The solution was filtered and then chromatographed on a neutral alumina column (2  $\times$  10 cm) saturated with benzene. With  $\text{CH}_2\text{Cl}_2$  used as eluting solvent, a red fraction was separated; on addition of hexane (20 mL), the product was obtained as a dark red microcrystalline solid (0.099 g, 0.137 mmol) in 42% yield. IR (CsI, Nujol):  $\nu(\text{CO})$  2052  $\text{cm}^{-1}$ ;  $\nu(\text{PtCl})$  268  $\text{cm}^{-1}$ ;  $\nu(\text{RhCl})$  300  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.40 (d,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = 1.80$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  40.93 (d,  $^1J_{\text{RHP}} = 152.48$  Hz,  $^2J_{\text{PP}} = 165.9$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  172.36 (s,  $^1J_{\text{PC}} = 1952$  Hz). Anal. Calcd for  $\text{C}_{23}\text{H}_{19}\text{Cl}_2\text{NOPPtRh}$ : C, 38.08; H, 2.64; N, 1.93; Cl, 9.77. Found: C, 37.96; H, 2.86; N, 1.89; Cl, 9.89.

**X-ray Data Collection and Structure Refinement.** Suitable orange crystals of 2a were obtained by slow evaporation of solvent from a methanol-benzene (1:1) solution. Diffraction measurements were made on a Pw 1100 four-circle diffractometer using graphite-monochromated  $\text{Mo K}\alpha$  ( $\lambda = 0.71069$  Å) radiation. Accurate unit cell dimensions and crystal orientation matrices were obtained from least-squares refinement of  $2\theta$ ,  $\chi$ , and  $\psi$  values of 25 strong reflections in the range  $16^\circ < 2\theta < 32^\circ$ . Compound 2a crystallizes in the monoclinic space group  $P2_1/n$ , with  $a = 24.485$  (3) Å,  $b = 10.262$  (2) Å,  $c = 17.626$  (3) Å,  $\beta = 101.40$  (4)°,  $V = 4341.4$  (3) Å $^3$ ,  $Z = 4$  and  $D_{\text{calc}} = 1.53$  g  $\text{cm}^{-3}$ . Lorentz and polarization corrections were applied to the intensity data, but no absorption correction was made due to the low absorption coefficient ( $\mu = 9.75$   $\text{cm}^{-1}$ ) and the fairly uniform dimensions of the crystal. Crystals and electronic stability were confirmed by the constancy of three check reflections measured every 120 min of X-ray exposure.

The structures were solved by using standard Patterson methods, successive least-squares refinements, and difference

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Fourier maps. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter ( $U = 0.08 \text{ \AA}^2$ ).

Of 8394 reflections, measured with an  $2\theta-\omega$  scan technique in the range  $3 < 2\theta < 50^\circ$ , 4630 having  $I > 3\sigma(I)$  were used to refine 518 parameters to final residuals of  $R = 0.045$  and  $R_w = 0.049$ .

The weighting scheme used in the last refinement cycles was  $w = 1.000/(\sigma^2(F_o) + 0.001163F_o^2)$ , which showed reasonable consistency in a test of  $w\Delta^2$  for data sectioned with respect to both  $F_o$  and  $(\sin \theta)/\lambda$ . Scattering factors for non-hydrogen atoms were taken from ref 28 and for hydrogen atoms from ref 29. Anomalous dispersion corrections for Rh, Pd, Cl, and P atoms were taken from ref 30.

All calculations were performed with SHELX76<sup>31</sup> and PARST<sup>32</sup> sets

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of programs on the IBM 4341 computer at the "Centro di Calcolo dell' Università di Messina". The refined structure was plotted with use of the ORTEP program (Figure 1). Full lists of bond distances and angles, hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material. Non-hydrogen coordinates are shown in Table I.

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**Supplementary Material Available:** Tables listing crystallographic parameters, anisotropic thermal parameters for non-H atoms, fractional atomic coordinates for H atoms, and complete bond lengths and angles (5 pages); a table of structure factors (26 pages). Ordering information is given on any current masthead page.

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## Rhodium(III) Biphasic and Phase-Transfer-Catalyzed Hydrogenolysis of Chloroarenes under Exceptionally Mild Conditions

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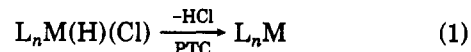
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The rhodium(III) complexes  $L_2Rh(H)Cl_2$  [ $L$  = tricyclohexylphosphine or triisopropylphosphine] are excellent catalysts for the hydrogenolysis of chloroarenes. The reaction proceeds under biphasic [40% NaOH,  $PhCH_3$ ] conditions, or to give somewhat higher product yields, under phase-transfer conditions, using benzyltriethylammonium chloride as the quaternary ammonium salt. The reaction occurs under mild conditions, and many functional groups [e.g. R, OR,  $CF_3$ , COAr, COOH,  $NH_2$ ] are compatible for the carbon-chlorine bond cleavage process.

Carbon-halogen bonds in aromatic compounds are usually quite resistant to reactions with nucleophiles and transition metal complexes. Aryl iodides, which are expensive, are able to undergo Ullmann<sup>1</sup> and  $S_{RN}1$  type<sup>2</sup> transformations. They can also participate in transition-metal-catalyzed cross-coupling reactions, olefin arylation reactions as well as some carbonylation processes.<sup>3</sup> Bromoarenes are appreciably less reactive substrates in all of these reactions. The cheapest haloarenes, chlorobenzenes, are much more inert and are usually incapable of undergoing reactions observed with iodoarenes and bromoarenes. Recently, carbonylation reactions of chloroarenes have been discovered by the use of novel palladium complexes as catalysts.<sup>4</sup> The low chemical reactivity of the aryl carbon-chlorine bond can be rationalized on the basis of kinetic and thermodynamic

( $D_{Ph-Cl} = 96 \text{ kcal/mol}$ )<sup>5</sup> factors.

Phase-transfer catalysis (PTC) has been widely used in the synthesis of organometallic complexes and for transition-metal-catalyzed organic reactions.<sup>6</sup> Recently, PTC was shown to be effective for the generation of electron-rich and coordinatively unsaturated transition-metal complexes by reductive elimination of hydrogen chloride from some hydrido transition-metal chlorides (eq 1).<sup>7</sup> For example,



the rhodium hydrides  $[(Cy_3P)_2Rh(H)Cl_2]$  ( $Cy$  = cyclohexyl; 1) and  $[(i-Pr)_3P)_2Rh(H)Cl_2]$  ( $i-Pr$  = isopropyl; 2), in the presence of KOH or NaOH, are able to catalyze H/D exchange between dihydrogen and aromatic hydrocarbons.<sup>8</sup>

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