Transition-Metal Derivatives of the Cyclopentadienylphosphine Ligands. 11. Reactivity of the Dinuclear Bridged Rhodium(II) Complexes toward Nitrogen-Containing Ligands

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Received March 2, 1995[⊗]

We report observations on the reactivity of the dinuclear bridged metal−metal-bonded carbonyl $[Rh^{II}(CO)(\mu\text{-}CpPPh_2)]_2^{2+}$ ($\mathbf{2}^{2+}$) and of the bis(solvate) cations $[Rh^{II}(solv)(\mu\text{-}CpPPh_2)_2]_2^{2+}$ ($\mathbf{3}^{2+}$) with nitriles, amines and pyridine and in general with nitrosyl cation and nitrite anion. By reaction of nitriles and pyridine with $\mathbf{2}^{2+}$ we obtained monosubstituted $[Rh_2(CO)L(\mu\text{-}CpPPh_2)_2]^{2+}$ ($\mathbf{4}^{2+}$) and disubstituted $[Rh(L)(\mu\text{-}CpPPh_2)]_2^{2+}$ ($\mathbf{5}^{2+}$) (L = MeCN, PhCN, pyridine). These complexes ($\mathbf{5}^{2+}$) were also obtained directly from $\mathbf{3}^{2+}$. In the reactions with $\mathbf{2}^{2+}$ the difference in reactivity of the two rhodium(II) sites suggests a specific role of the metal−metal bond. With secondary and primary amines, reductions of $\mathbf{2}^{2+}$ to $[Rh^{I}(CO)(\mu\text{-}CpPPh_2)]_2$ (**1**) were also observed, and the selectivity with respect to substitution or reduction was strongly solvent dependent. Lithium diisopropylamide induces quantitatively the reduction of $\mathbf{2}^{2+}$ to **1** and apparently the substitution of the solvent in $\mathbf{3a}^{2+}$. Finally, the new compounds $[Rh^{II}(THF)(\mu\text{-}CpPh_2)]_2^{2+}$ ($\mathbf{3a}^{2+}$), $[Rh^{II}(\mu\text{-}H_2NC_5H_4N)(\mu\text{-}CpPh_2)_2]^{2+}$ ($\mathbf{6}^{2+}$) and $[Rh^{II}(NO_2)(\mu\text{-}CpPh_2)]_2$ ($\mathbf{7}^{2+}$) were obtained from $\mathbf{2}^{2+}$ and PhIO, from $\mathbf{3}^{2+}$ and aminopyridine, and from $\mathbf{2}^{2+}$ and nitrite anion, respectively. The compounds were characterized by elemental analysis and the usual spectroscopic methods including COSY NMR experiments. Reaction of $NOBF_4$ with **1** led efficiently to the compound $\mathbf{2}^{2+}$ again through a redox process, instead of a substitution.

Introduction

The chemistry of rhodium(I) and rhodium(III) compounds has been extensively studied,[1] but the chemistry of rhodium(II) has progressed less rapidly. In fact, rhodium(II) monomers are rather unstable, and hence 17-electron rhodium species produced electrochemically will couple, forming a metal−metal bond.[2] However, paramagnetic rhodium(II) monomers have been prepared using bulky phosphine ligands, as in $RhCl_2(PCy_3)_2$.[3] Dimeric rhodium(II) species are more common as they allow the formation of a metal−metal bond to stabilize the two 17-electron rhodium(II) centers.[4] A recent example, $(Cp^*RhCl)_2$, illustrates the high reactivity of this dimer which coordinates dioxygen.[5]

Cyclopentadienyl-substituted phosphines[6] offer interesting possibilities for tailoring coordination spheres, using both their cyclopentadienyl and phosphine functions. In particular, reagents such as $TlCpPR_2$ and $LiCpPR_2$ (where R may be methyl, phenyl, or tolyl and Cp is C_5H_4, C_5Me_4, ..., etc) have been used as sources of the corresponding $CpPR_2^-$. Part of the popularity of these as ligands is due to the fact that, acting as 8-electron donors, they can bridge two metalic centers.[7,8] Moreover the η^5-bound Cp still has the potential to undergo ring slippage to bind in an η^3 manner and this may allow greater reactivity than the usual diphosphine ligands such as dppm and dppe. These $CpPR_2^-$ ligands can also bind through either the cyclopentadienyl moiety (a six-electron donor) or through the phosphine atom (a two-electron donor) to form mononuclear complexes.[8f]

In our laboratory we have utilized $CpPR_2^-$ to bridge two d^8 metal centers. The reactions of the bimetallic complex $[Rh(CO)(\mu\text{-}CpPPh_2)]_2$ [**1**] with the electrophiles MeX ($X^- = I^-$ or $CF_3SO_3^-$) have been studied.[8c] The electrochemistry of **1** and its oxidized form, $[Rh(CO)(CpPPh_2)]_2^{2+}$ ($\mathbf{2}^{2+}$), has revealed a fast conformational change involving two monocationic intermediates.[8b] The study of the reactivity of $\mathbf{2}^{2+}$ toward various reagents has been undertaken and the first results[8c,9] reveal that it has a richer chemistry than its rhodium(I) counterpart.

Our interest in rhodium and iridium derivatives of the $CpPR_2$ ligands, also arises from their relationship to the mononuclear

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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0020-1669/96/1335-1266$12.00/0

Table 1. ^{31}P NMR Data for the Compounds Studied

	X	Y	solvent	$\delta(P^a)$	$^1J(P^aRh^a)$	$^2J(P^aRh^b)$	$\delta(P^b)$	$^1J(P^bRh^b)$	$^2J(P^bRh^a)$	$^3J(P^aP^b)$
$[Rh^I(CO)(\mu\text{-}CpPPh_2)]_2$ [**1**]	CO	CO	$CDCl_3$	40.5	199[a]					
$[Rh(CO)(\mu\text{-}CpPPh_2)]_2^{2+}$ [$\mathbf{2}^{2+}$]	CO	CO	$(CD_3)_2CO$	43.7	125.7					
$[Rh(solv)(\mu\text{-}CpPh_2)]_2^{2+}$ [$\mathbf{3a}^{2+}$]	THF	THF	$(CD_3)_2CO$	50.1	156.9					
$[Rh_2(CO)(MeCN)(\mu\text{-}CpPPh_2]_2(CF_3SO_3)_2$ [**4a**][CF_3SO_3]$_2$	CO	MeCN	CD_3CN	41.5	137.5	6.9	38	139.0	6.5	3.5
$[Rh_2(CO)(PhCN)(\mu\text{-}CpPPh_2]_2(CF_3SO_3)_2$ [**4b**][CF_3SO_3]$_2$	CO	PhCN	CD_3CN	41.3	136.9	6.9	37.6	137.9	6.4	3.6
$[Rh_2(CO)(py)(\mu\text{-}CpPPh_2)_2](BF_4)_2$ [**4c**][BF_4]$_2$	CO	py	$(CD_3)_2CO$	39.1	140.8	7.3	31.8	135.3	8.8	2.9
$[Rh_2(CO)(PhNH_2)(\mu\text{-}CpPPh_2)_2](CF_3SO_3)$ [**4e**][CF_3SO_3]$_2$	CO	$PhNH_2$	CD_3OD	37.4	140.4	6.9	32.6	136.8	5.9	3.4
$[Rh_2(CO[(i\text{-}Pr)_2NH](\mu\text{-}CpPPh_2)_2](PF_6)_2$ [**4f**][PF_6]$_2$	CO	$(i\text{-}Pr)_2NH$	CD_3OD	52.1	155.0	5.5	45.6	146.3	5.0	4.5
$[Rh(MeCN)(\mu\text{-}CpPPh_2)]_2(CF_3SO_3)_2$ [**5a**][CF_3SO_3]$_2$	MeCN	MeCN	CD_3CN	43.2	140.8[a]					
$[Rh(PhCN)(\mu\text{-}CpPPh_2)_2]_2(CF_3SO_3)_2$ [**5b**][CF_3SO_3]$_2$	PhCN	PhCN	CD_3CN	43.2	139.9[a]					
$[Rh(py)(\mu\text{-}CpPPh_2)]_2(CF_3SO_3)_2$ [**5c**][CF_3SO_3]$_2$	py	py	CD_3CN	38.2	145.7[a]					
$[Rh_2(H_2NC_5H_4N)(\mu\text{-}CpPPh_2)_2](PF_6)_2$ [**6**][PF_6]$_2$	H_2N	C_5H_4N	$CDCl_3$	49.7	172.6	5.17	52.8	169.2	5.45	8.70
$[Rh(NO_2)(\mu\text{-}CpPPh_2)]_2$ [**7**]	NO_2^-	NO_2^-	$(CD_3)_2CO$	53.7	163.9					

[a] This value represents the absolute value of $[^1J(P^aRh^a) + {}^2J(P^aRh^b)]$.

18-electron $CpRh^I(CO)L$ complexes.[1] The oxidative addition reactions of the latter with saturated hydrocarbons are specially interesting and have been extensively studied.[10ab] The bis(solvates) $[Rh(solv)(\mu\text{-}CpPPh_2)]_2^{2+}$ ($\mathbf{3}^{2+}$) could be useful intermediates in related reactions, by taking advantage of the adjacent positions of the two accessibles sites. Moreover the structures of the metal−metal bonded complexes $[Rh^{II}_2LL'(\mu\text{-}CpPPh_2)_2]^{n+}$ (LL′ = pyr_2, $n = 2$; L = CO, L′ = C(O)Me, $n = 1$; L = I, L′ = Me, $n = 0$)[8c] already studied, appears to be characterized by a cisoid relation of the terminal ligand sites, which could promote cooperative reactions.

To our knowledge, examples of oxidative addition to a group 8 metal center by N−H activation[11c,i] are rare[11] while the synthesis and the reactivity of amide hydride iridium(III) complexes $Cp^*Ir^{(III)}PPh_3(NHR)H$, were circumstantially studied.[10c,d]

In this paper, we report our observations on reactions of $\mathbf{2}^{2+}$ or $\mathbf{3}^{2+}$ with nitriles, amines, and pyridine. We also include results concerning the reactions of nitrogen ligands with higher oxidation levels, the nitrosyl cation, and the nitrite anion.

Results and Discussion

Previous studies performed in this laboratory revealed that $\mathbf{2}^{2+}$ could be readily converted into other complexes by the replacement of the carbonyl by various ligands (py, $P(OMe)_3$, ...).[8c] Reaction of $\mathbf{2}^{2+}$ with pyridine allows the substitution of both carbonyls, but it was more convenient to use a decarbonylation reagent to replace the carbonyls by labile ligands such as acetonitrile. Thus trimethylamine oxide (TMNO) in dichloromethane solution gave the solvated species $[Rh(solv)(CpPPh)_2]_2^{2+}$ which readily reacts with acetonitrile to give the complex $[Rh(MeCN)(CpPPh)]_2^{2+}$.

Previous work was mostly carried out using PF_6^- or BF_4^- salts of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$. However, the triflate anion $CF_3SO_3^-$ is reputed to give better yield and cleaner reactions,[11] and this was now used to continue these studies.

The use of TMNO as decarbonylation agent introduced some uncertainties concerning the nature of the coordinated solvent in $[Rh(solv)(CpPPh_2)]_2^{2+}[A^-]_2$. Not only the solvent used—acetonitrile, dichloromethane, THF—but also trimethylamine or even water (when the dehydration of TMNO· $2H_2O$ is neither optimized nor accurately controlled) are able to occupy the vacant sites in $\mathbf{3}^{2+}$. In order to achieve better control of the nature of the coordinated solvent, we have used iodosylbenzene PhIO in THF as decarbonylation reagent. Starting from [**2**]$(PF_6)_2$, the salt $[Rh(THF)(\mu\text{-}CpPPh_2)]_2(PF_6)_2$ [**3a**][PF_6]$_2$ was obtained as a green precipitate fully characterized by elemental analysis and by ^{1}H and ^{31}P NMR spectroscopies in deuteroacetone. Peaks were observed at δ 7.13 (m, 4H) and δ 6.67 (m, 4H) for the cyclopentadienyl protons, at δ 1.92 (m, 8H) and 3.76 (m, 8H) for the THF protons and at δ 50.6 (J(Rh−P) = 156.9 Hz) for the two equivalent phosphorus atoms. The THF molecules remained bound even after [**3a**][PF_6]$_2$ was kept under reduced pressure for long periods (10 h). The ^{31}P NMR spectrum of $\mathbf{3}^{2+}$ is of AA′XX′ type spectrum due to the coupling between the two phosphorus and the two rhodium atoms (see Figure 4a in the Supporting Information).

Table 1 reports the NMR data of all new compounds. In several cases the signals due to the protons of the cyclopentadienyl appear as two broad peaks. This has already been interpreted as the result of an intramolecular wagging of the molecule around a mean plane.[8f]

Substitution Reactions in $[RhL(\mu\text{-}CpPPh_2)]_2^{2+}$ $[A^-]_2$ (L = CO or Solvent; $A^- = BF_4^-, PF_6^-, CF_3SO_3^-$) with Nitriles and Pyridine. The reactivity of the various salts [**2**][PF_6]$_2$, [**2**][BF_4]$_2$, [**2**][CF_3SO_3]$_2$, and [**3a**][PF_6]$_2$ is not affected by changing the anion. We will therefore refer to the starting

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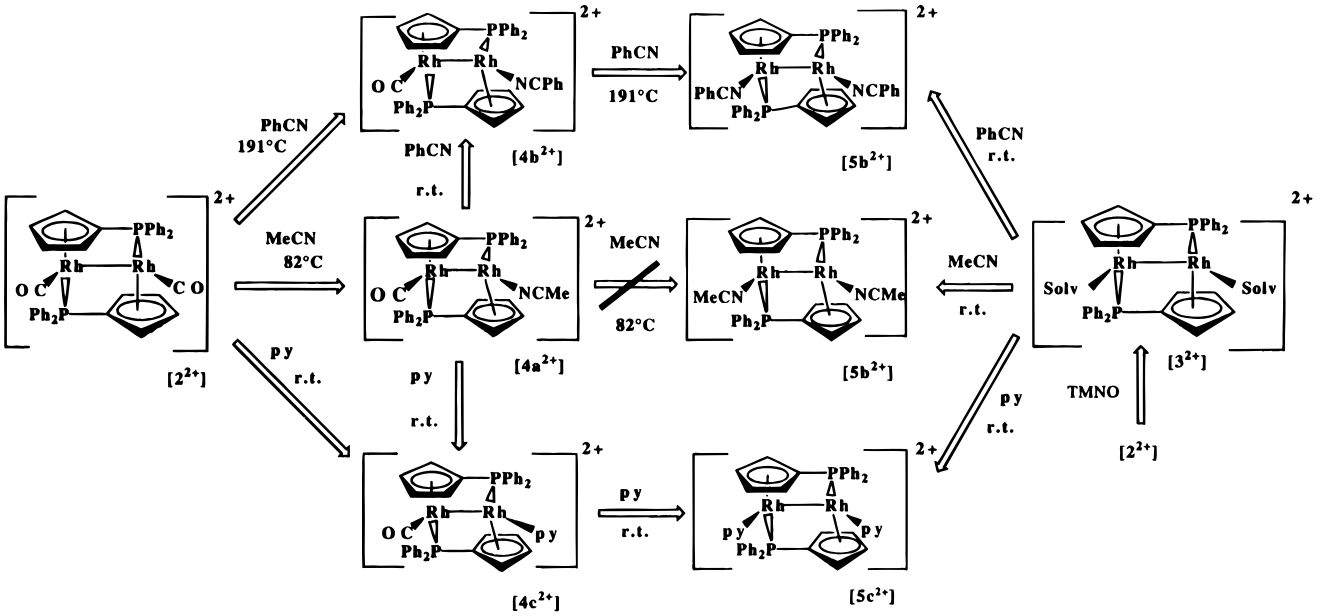
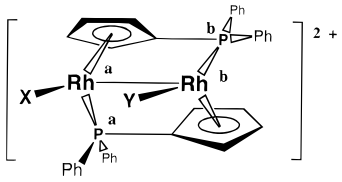


Figure 1. Pathways toward mono- and disubstituted products (the various compounds present are assumed to have structures similar to that of [**5c**$^{2+}$], previously determined by X-ray diffraction[8d]).

materials by the cationic moiety $[Rh(CO)(CpPPh_2)]_2^{2+}$ (**2**$^{2+}$) or $[Rh(solv)(CpPPh_2)]_2^{2+}$ (**3**$^{2+}$).

Figure 1 shows the reaction pathways discussed in the present paragraph. The replacement of both CO groups in **2**$^{2+}$ by acetonitrile requires a decarbonylating reagent such as TMNO or PhIO, but these are not necessary for the substitution of a single CO. There is no observable reaction at ambient temperature when **2**$^{2+}$ is stirred in acetonitrile for 12 h, but after 4 h in refluxing acetonitrile, **2**$^{2+}$ is quantitatively converted to $[Rh(CO)(MeCN)(CpPPh_2)_2]^{2+}$ (**4a**$^{2+}$). The ^{31}P NMR spectrum of the complex **4a**$^{2+}$ is a distinctive AXBY type (Figure 4c in the Supporting Information). Structure **I** shows the NMR labeling scheme generally used.



I

The spectrum of [**4a**$^{2+}$] appears as two doublets of doublets of doublets. In one signal the large coupling constant is assigned as $^1J(P^aRh^a)$, and the two smaller ones are due to $^2J(P^aRh^b)$ and $^3J(P^aP^b)$. In a similar manner, the other signal readily affords the coupling constants $^1J(P^bRh^b)$, $^2J(P^bRh^a)$, and $^3J(P^aP^b)$. Recording the ^{31}P NMR spectrum at two different frequencies removed any ambiguity in the assignment of the coupling constants. The IR spectrum reveals an absorption at 2061 cm^{-1} confirming the presence of a CO. There is no evidence in the ^{31}P NMR spectra of any starting material or of the bis(acetonitrile) product $[Rh_2(MeCN)_2(\mu\text{-}CpPPh_2)_2]^{2+}$ (**5a**$^{2+}$).[8d]

The observed clear-cut separation between the two steps of substitution of **2**$^{2+}$ implies a difference of reactivity of the two rhodium(II) sites. It suggests that the carbonyl present on one site activates the second site toward nucleophilic attack and thereafter to substitution, through a partial electron transfer. As previously described for the redox processes between **1** and **2**$^{2+}$ and for the mechanisms involved in the oxidative addition and in the methyl migration observed on **1**,[8e] this electron transfer could involve the heterolytic breaking (or at least the polarization) of the metal−metal bond changing the two 18-electron rhodium(II) centers to a 16-electron rhodium(III) center—a target for the nucleophilic attack—and a 18-electron rhodium(I) center (Figure 2a). In **4a**$^{2+}$ this cannot occur, while in the hypothesis of a CO substitution MeCN now present at the site likely to become a 18-electron rhodium(I) center is much less polarizable than CO. Figure 2 compares the proposed pathway (a) with another possible one (b) involving the η^5-to-η^3 slippage of the cyclopentadienyl moiety of one of the bridging ligands. This second hypothesis does not offer a straighforward rationaliation of the difference of reactivity between the first and the second steps of substitution. Process a, implying an electronic flow along the metal−metal axis, has some analogy with the classical *trans* effect occuring in mononuclear complexes.

The dicarbonyl dication [**2**][CF_3SO_3]$_2$was heated under *reflux* in PhCN in an effort to synthesize the benzonitrile analogs to **4a**$^{2+}$ and **5a**$^{2+}$. This higher-temperature procedure gave primarily, shown by ^{31}P NMR spectroscopy, a mixture of **2**$^{2+}$, $[Rh_2(PhCN)(CO)(\mu\text{-}CpPPh_2)_2]^{2+}$ (**4b**$^{2+}$), and $[Rh(PhCN)_2(\mu\text{-}CpPPh_2)]_2^{2+}$ (**5b**$^{2+}$). However, reflux during 12 h yielded [**5b**][CF_3SO_3]$_2$ as an isolable solid. Complex [**4b**][CF_3SO_3]$_2$ could not be purified from refluxing benzonitrile as it has a solubility similar to those of both [**2**][CF_3SO_3]$_2$ and [**5b**][CF_3SO_3]$_2$. If, however, one stirs [**4a**][CF_3SO_3]$_2$ in methanol at room temperature with an excess of PhCN then product [**4b**][CF_3SO_3]$_2$ can be isolated as a pure solid. Continued stirring of [**4b**][CF_3SO_3]$_2$ in refluxing PhCN will also replace the second carbonyl, but at room temperature this reaction is very slow and does not interfere with the isolation of [**4b**][CF_3SO_3]$_2$.

It has already been shown that pyridine will readily replace the carbonyls in **2**$^{2+}$.[8d] However the reaction of **2**$^{2+}$ in pyridine at ambient temperature can be stopped after 45 min to give the monosubstituted product **4c**$^{2+}$ in fair yield. Continued reaction for 5 h in pyridine leads to replacement of the second CO to give the product **5c**$^{2+}$. Both products are characterized by ^{31}P NMR, ^{1}H NMR, and IR spectroscopy, in addition to CHN analyses. Starting with **4a**$^{2+}$, the replacement of the acetonitrile by the pyridine is complete in 15 min.

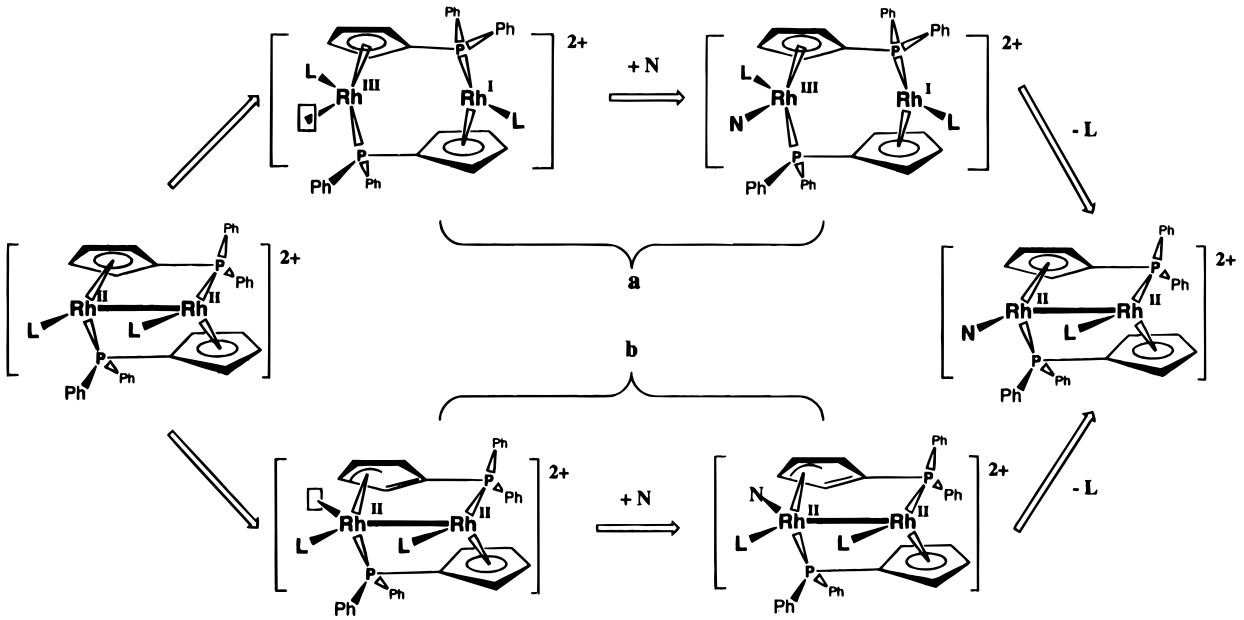


Figure 2. Two possible mechanisms of substitution at the 18-electron metal center exposed to a nucleophilic reactant: (a) via mixed-valence intermediate and (b) via η^3-cyclopentadienyl intermediate.

The reaction of aniline leads to the formation of a monosubstituted compound $[Rh_2(CO)(PhNH_2)(\mu\text{-}CpPPh_2)_2]$ (**4e**$^{2+}$), but this was not studied further.

Reactions of the Dicationic Compounds [Rh(CO)(μ-CpPPh$_2$)]$^{2+}$$_2$[A$^-$]$_2$, [2][A]$_2$ (A$^-$ = PF$_6^-$, BF$_4^-$, CF$_3$SO$_3^-$) with the Secondary Amines. The reaction of **2**$^{2+}$ with diisopropylamine on varying the solvent has been studied. The selected procedure consists of using a constant amount (around 50 mg) of [**2**][A]$_2$ dissolved in 5 mL of degassed and anhydrous solvent, to which were added different quantities of the amine. The reactions were monitored by infrared and NMR spectroscopies and stopped after 12 h of stirring at room temperature.

Using *tetrahydrofuran* as solvent, with a ratio Rh:amine = 1:2, the initial orange suspension turned to a dark-brown solution. After 12 h the reaction mixture contained the reduced compound **1** in addition to decomposition products, as shown by infrared and ^{31}P NMR spectroscopies.

In *methanol*, with ratios Rh:amine between 1:1 and 1:4, the reaction afforded a violet solution from which precipitated a small amount of a yellow powder which was identified as complex **1** (ν_{CO} = 1950 cm^{-1} in THF; NMR ($CDCl_3$) δ(^{1}H) 5.67 (m, 2H), 5.56 (m, 2H); δ(^{31}P) 40.5 (t : J(P−Rh) = 199 Hz)). The infrared spectrum of the solution shows a CO stretching vibration at 2036 cm^{-1}, indicative of a derivative in which the oxidation state of the rhodium center is greater than one. This product was isolated and fully characterized by elemental analysis and ^{1}H and ^{31}P NMR spectroscopies as the monosubstituted derivative $[Rh_2(CO)(HNPr^i_2)(\mu\text{-}CpPPh_2)]^{2+}$ (**4f**$^{2+}$). The ^{31}P NMR spectrum of this isolated compound, **4f**$^{2+}$, contains two doublets of doublets of doublets (δ(P) 52.1; J(P−Rh) = 155 Hz, and δ(P) 45.6, J(P−Rh) = 146.3 Hz) implying that the two rhodium atoms possess different environments and, from the value of the coupling constants, that they have the oxidation number II. The anion PF_6^- is easily identified in infrared spectroscopy by its P−F stretching frequency at 840 cm^{-1} and in ^{31}P NMR spectroscopy by the presence of a septet (δ(P) −147.5, J(P−F) = 708 Hz).

In *toluene*, no reaction was observed, even after 18 h stirring at room temperature, but when some distilled water (10 mL) was added to the toluene solution both **1** and **4f**$^{2+}$ formed. Separation was achieved by using their different solubilities in the ethanol.

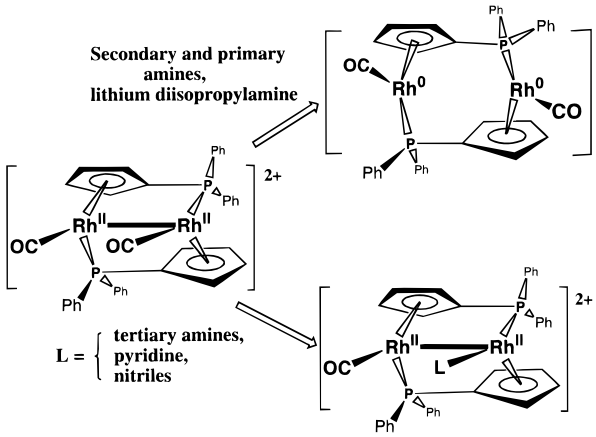


Figure 3. Redox and substitution processes during the reaction of **2a**$^{2+}$ with various nitrogen-containing ligands.

Finally *in acetone and dichloromethane*, the reaction of **2**$^{2+}$ with the amine was rapid and afforded preponderantly the reduced product **1**. In addition, small quantities of nonidentified products (resonances at δ(^{31}P) 69.3, J(P−Rh) = 142 Hz, and δ(^{31}P) 54.7, J(P−Rh) = 174 Hz) were observed.

From the above results it appears that in all the solvents tested there is a competition between the reduction of **2**$^{2+}$ to **1** and the substitution of one of its CO groups by the amine (Figure 3). The selectivity with respect to substitution or reduction is strongly solvent-dependent. Similar observations were made from the reactions of **2**$^{2+}$ with aniline and amidopyridine.

Because of these results, we considered the hypothesis that the reduction of **2**$^{2+}$ by the secondary and primary amines might involve their acid−base equilibrium of dissociation. Therefore, we also investigated the reaction of lithium diisopropylamide (LDA) with this compound. As expected, the reaction in THF under similar conditions to those above, afforded mainly the reduction product **1**, as shown by infrared and NMR spectroscopies.

In order to characterize the reduction process, we tried to reduce also the solvate species $[Rh(solv)(\mu\text{-}CpPPh_2)]^{2+}[PF_6^-]_2$ using lithium diisopropylamide.

A mixture containing [**3**][PF$_6$]$_2$ and a 2-fold excess of LDA was allowed to react during 12 h stirring at room temperature.

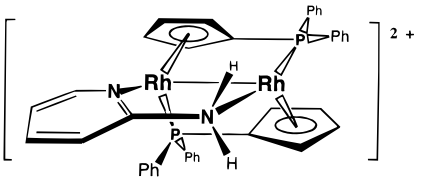
The products of the reaction were then separated by evaporation of the solvents and washed with pentane. No product of reduction were detected. Instead, in the ^{31}P NMR spectrum a doublet at $\delta(^{31}P)$ 40.6 (J(Rh−P) = 156 Hz) was observed, interpreted as due to the presence of a symmetrical rhodium(II) species, possibly a diamido neutral species but attempts to isolate this species were unsuccessful.

To sum up, it appears that the reduction of the rhodium(II) dinuclear complexes $[Rh^{(II)}L(\mu\text{-}CpPPh_2)]^{2+}$ is effective when L is carbonyl and is able to stabilize the rhodium(I) corresponding species.

Attempting to balancing the equation of reduction of $\mathbf{2}^{2+}$ to **1** by LDA leads us to study the hypothesis of the primary formation of two di-isopropylamine radicals. We have attempted to identify the derivatives of such radicals by mass spectrometry, including the substituted hydrazine which could formed by coupling. The DCI mass spectrum of the reaction mixture was quite complicated and gave no indication of such a coupling process. The formation of hexane was tentatively inferred from the presence of the most intense peak at *m*/*e* 86. The hypothesis that this fragment could form by coupling of isopropyl radicals suggests a further method of investigation of the reaction.

Addition of the Bridging 2-Aminopyridine to the Adjacent Coordination Sites of the Bis(solvate) Species 3. Further Observations on the Reduction Process. As an extension of the chemistry of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ and pyridine and RNH_2, we have examined the reaction of the rhodium(II) dimers $\mathbf{2}^{2+}$ with 2-aminopyridine, which has two possible sites of ligation.

The reaction of the solvated species $\mathbf{3}^{2+}$ with 2-aminopyridine gave $[Rh_2(\mu\text{-}H_2N\text{-}C_5H_4N)(\mu\text{-}CpPPh_2)_2]^{2+}$ ($\mathbf{6}^{2+}$) in good yield,



[$\mathbf{6}^{2+}$]

regardless of the quantity of 2-aminopyridine used (either stoichiometric, 2-fold, or an excess). This product has been well characterized by elemental analysis and by multinuclear ^1H, ^{31}P, ^{13}C NMR spectroscopy. The ^{31}P NMR spectrum contains two doublets of doublets of doublets (Figure 4b in Supporting Information), implying that the two rhodium atoms possess different donor-atom ligands. The ^{13}C NMR and the ^1H NMR spectra unequivocally show that there is only one 2-aminopyridine molecule per rhodium dimer bound to one rhodium atom via the NH_2 unit and to the other rhodium atom by the pyridine group. The characterization was completed by a 2-dimensional $^1H-^1H$ NMR COSY experiment confirmed the assignments of the cyclopentadienyl resonances. The $^1H-^1H$ spectrum clearly shows coupling between the hydrogen atoms of the Cp rings, and one can even see which four Cp signals belong to the same ligand. Thus the assignment of the protons to each Cp is unambiguous. The wide range of δ values for the Cp ring hydrogen atoms (7.0−3.0 ppm) shows the large asymmetry present in this molecule, which is typical for this type of compound. The four protons of the pyridine ring are also clearly observed and assigned. Thus, we believe the 2-aminopyridine is chelating.

As mentioned previously, pyridine can readily replace the carbonyls of the dinuclear complex $\mathbf{2}^{2+}$ without the use of TMNO. Therefore the reaction of $\mathbf{2}^{2+}$ was carried out in refluxing THF solution with 1 equiv of 2-aminopyridine. This gave a dark solution in addition to 39% of the red starting material recovered. Product **1** was present in the solution, as verified by IR and NMR spectroscopies. Thus, approximately 50% of the dimer $\mathbf{2}^{2+}$ was converted to dimer **1**, 1 molar equiv of Rh^{II} centers per molecule of 2-aminopyridine. This would imply that each rhodium reduced corresponded to one a 2-aminopyridine being oxidized. This was confirmed by reaction of $\mathbf{2}^{2+}$ with 2 molar equiv of 2-aminopyridine which led quantitatively to **1**. These results further confirm the role of the CO in influencing the capacity of rhodium(II) species to be reduced by the amines. Moreover, whereas pyridine affords only the substituted product $\mathbf{4c}^{2+}$ by reaction with the carbonyl dinuclear complex $\mathbf{2}^{2+}$, the reaction of 2-aminopyridine is entirely switched toward the redox process, consistent with the presence of the secondary amine function.

Miscellaneous Results on the Reactions of Cationic and Anionic Nitrogen-Containing Ligands. The accessibility of two adjacents coordination sites in the bis(solvate) species $[Rh(solv)(CpPPh_2)]^{2+}{}_2$ offered the opportunity to observe the reaction of nonreducing nitrogen-containing ligands.

Reaction of $\mathbf{3}^{2+}$ with $NaNO_2$ gave $[Rh(NO_2)(\mu\text{-}CpPPh_2)]_2$ ($\mathbf{7}^{2+}$) which has been fully characterized by elemental analysis and infrared and ^1H and ^{31}P NMR spectroscopies. The doublet of doublets in the ^{31}P NMR spectrum ($\delta(^{31}P)$ 53.7; J(P−Rh) = 163.9 Hz) confirms the presence of two equivalent phosphorus atoms. The four peaks in the ^1H NMR spectrum (δ 7.21; δ 7.06; δ 6.48; δ 2.49) suggests a rigid structure on the NMR time scale and a strong anisotropic influence of the nitrite. The three bands observed in the infrared spectrum at 1376, 1305, and 820 cm^{-1} are characteristic of coordination through the nitrogen atom.

Compound $\mathbf{7}^{2+}$ was also obtained in low yield from the reaction of $NaNO_2$ with $\mathbf{2}^{2+}$ in $MeOH-CH_2Cl_2$. By contrast, reaction of $\mathbf{2}^{2+}$ with other anionic ligands (Cl^-, CN^-, I^-) does not occur. This seems to be due to a labilizing effect of NO_2^- through the two metals atoms (see above).

Finally an attempt has been made to obtain some nitrosyl compounds (for instance the non-metal−metal-bonded $[Rh^{II}(NO)(\mu\text{-}CpPPh_2)]_2$) by reaction of nitrosyl tetrafluoroborate in THF with **1**, but instead of a substitution reaction, a redox process was again observed.

$$[Rh(CO)(CpPPh_2)]_2 + 2NO^+BF_4^- \rightarrow [Rh(CO)(CpPPh_2)]_2^{2+}(BF_4^-)_2 + 2NO$$

This process gives access to the valuable tetrafluoroborate salt of $\mathbf{2}^{2+}$, avoiding the use of the expensive silver tetrafluoroborate, as previously reported.[8c]

Experimental Section

All reactions were routinely carried out under argon using standard Schlenk-tube techniques. All solvents were dried and deoxygenated prior to use. Tetrahydrofuran (THF) and diethyl ether were dried over sodium/benzophenone. Acetonitrile was distilled from $CaCl_2$, methylene chloride from P_2O_5, and methanol from CaH_2. Flash chromatography used silica 230−240 mesh (0.040−0.063 mm) from Jansen. $RhCl_3 \cdot nH_2O$ was from Johnson Matthey Corp., while all other reagents were purchased from Aldrich. Pyridine, aniline, and 2-aminopyridine were used without further purification. $TlCpPPh_2$[6], $[RhCl(CO)_2]_2$,[13] $(Rh(CO)(\mu\text{-}CpPPh_2))_2$ and $[Rh(CO)(\mu\text{-}CpPPh_2)]_2^{2+}$,[8e] and $[FeCp_2](PF_6)$[14] were prepared according to literature procedures. Cyclopentadienyl thallium was sublimed prior to use. Trimethylamine oxide, TMNO, was dehydrated prior to use by vaccuum sublimation at 80 °C.

(13) Gallay, J.; de Montauzon, D.; Poilblanc, R. *J. Organomet. Chem.* **1972**, *38*, 179.
(14) Desbois, M.-H.; Astruc, D. *New J. Chem.* **1989**, *13*, 595.

Iodosylbenzene was prepared from its diacetate by hydrolysis, according to a published method.[15]

Microanalyses were performed by the Service de Microanalyses du Laboratoire de Chimie de Coordination du CNRS. Infrared spectra of solutions or KBr disks were recorded using a Perkin-Elmer 1725X FT-IR or a Perkin-Elmer 833 spectrometer. ^{1}H NMR spectra were recorded using either a Bruker WH 90 FT spectrometer (90.02 MHz), a Bruker 200 AC FT spectrometer (200.133 MHz) or a Bruker AM250 spectrometer. ^{13}C NMR spectra were obtained using a Bruker WM 250 FT spectrometer at 62.9 MHz. ^{31}P(^{1}H) NMR spectra were recorded using either a Bruker WH 90 FT spectrometer (36.43 MHz) or a Bruker AC 80 FT spectrometer (32.438 MHz). Chemical shifts for ^{1}H, ^{13}C, and ^{31}P were referenced to, respectively, tetramethylsilane and external H_3PO_4. DCI mass spectrometric measurements with ammonia were recorded on a NERMAG R10-10 instrument.

[Rh(CO)(μ-CpPPh$_2$)]$_2$(BF$_4$), [2b][BF$_4$]$_2$. A mixture of **1** (240 mg, 0.31 mmol) and $NOBF_4$ (80 mg, 0.68 mmol) was poured into THF (15 mL). NO gas was immediately evolved, the solution turned brown, and a light brown powder precipitated. After removal of the solvent, the powder was washed with methanol and dried under vacuum. This gave 255 mg of red-brown [**2b**][BF_4]$_2$ (0.27 mmol, 88% yield). Anal. Calcd for $C_{36}H_{28}B_2F_8O_2P_2Rh_2$, C, 46.29; H, 3.02; Found C, 46.48; H, 2.94. IR in (KBr): ν(CO) 2084 cm^{-1}. ^{1}H NMR (CD_3COCD_3), δ: 8.04, 6.72, 5.27 (three broad peaks for 8H of Cp).

[Rh(CO)(μ-CpPPh$_2$)]$_2$(CF$_3$SO$_3$)$_2$, [2c][CF$_3$SO$_3$]$_2$. In a Schlenk tube **1** (661.8 mg, 0.87 mmol) and $AgCF_3SO_3$ (470.0 mg, 1.83 mmol) were dissolved in acetonitrile (30 mL). After 2 h of stirring, the red-brown solution was filtered through Celite to eliminate elemental silver. The filtrate was then evacuated to dryness. The red-brown solid gave a slurry in CH_2Cl_2/ether (4 mL/15 mL) and was filtered. A black-green impurity was left in solution. The red solid was washed with cold (0 °C) CH_2Cl_2 (2 × 2 mL) and ether and then dried. This gave 684.6 mg of the red product [**2c**][CF_3SO_3]$_2$ (74% yield). IR(CH_2Cl_2): ν(CO) 2086, 2054 cm^{-1}. Anal. Calcd for $C_{38}H_{28}F_6O_8P_2Rh_2S_2$. C, 42.61; H, 2.73 Hz. Found: C, 42.40; H, 2.81. ^{1}H NMR: δ (CD_3CN) 7.19 (s, Cp, 2H), 6.10 (s, Cp, 2H), 4.29 (s, Cp, 2H).

[Rh(THF)(μ-CpPPh$_2$)]$_2$(PF$_6$)$_2$, [3a][PF$_6$]$_2$. In a Schlenk tube were placed [Rh(CO)(CpPPh$_2$)]$_2$(PF$_6$)$_2$[**2a**][PF $_6$]$_2$ (320 mg, 0.30 mmol) and freshly prepared PhIO (220 mg, 1 mmol). This was evacuated and put under argon, then THF (10 mL) was added, and after 5 min a green solution was obtained. It was stirred for an additional 30 min, and then a green precipitate formed. This precipitate was washed with THF and dried under vacuum during 8-10 h. A total of 210 mg of [**3a**]-[PF_6]$_2$ is obtained (61% yield). Anal. Calcd for $C_{42}H_{44}F_{12}O_2P_4Rh_2$, C, 44.31; H, 3.90. Found, C, 44.61; H, 4.28. ^{1}H NMR: δ (CD_3-$COCD_3$) 7.14 (s, Cp, 4H), 6.67 (m, Cp, 4H), 3.75 (m, THF, 8H), 1.92 (m, THF, 8H).

[Rh$_2$(CO)(MeCN)(μ-CpPPh$_2$)$_2$](CF$_3$SO$_3$)$_2$, [4a][CF$_3$SO$_3$]$_2$. A 2-necked 50 mL round bottom flask equipped with a reflux condenser and an argon inlet was charged with [**2c**][CF_3SO_3]$_2$ (182.6 mg, 0.173 mmol). The red solid was evacuated and put under argon, and acetonitrile (20 mL) was added. The solution was heated under reflux for 4 h, and the red solution gradually became violet. The solution was then allowed to cool and evaporated to dryness. The solid was washed with ether and pentane, giving a deep purple microcrystalline solid (155.1 mg, 84% yield). IR(CH_2Cl_2): ν(CO) 2061 cm^{-1}. Anal. Calcd for [**4a**][CF_3SO_3]$_2$·H_2O i.e. $C_{40}H_{34}F_6O_8P_2Rh_2S_2$: C, 43.02; H, 2.95; N, 1.24. Found: C, 42.99, H, 3.05, N, 1.29. ^{1}H NMR: δ (CD_2-Cl_2) 7.00 (m, Cp, 1H), 6.97 (s, Cp, 1H), 6.24 (m, Cp, 1H), 5.90 (s, Cp, 1H), 3.76 (m, Cp, 1H), 3.06 (s, Cp, 1H), 1.98 (s, CH_3CN, 3H). A similar method is used to synthesize the BF_4^- derivative of $\mathbf{4}^{2+}$ but one starts with the BF_4^- derivative of $\mathbf{2}^{2+}$. IR(KBr): ν(CO) 2046 cm^{-1}. Anal. Calcd for $C_{40}H_{34}B_2F_8O_2P_2Rh_2$: C, 46.32, H, 3.35, N, 1.68; Found, C, 46.93, H, 3.30, N, 1.48.

[Rh$_2$(CO)(PhCN)(μ-CpPPh$_2$)$_2$](CF$_3$SO$_3$)$_2$, [4b][CF$_3$SO$_3$]$_2$. Into a Schlenk tube was introduced [**4a**][CF_3SO_3]$_2$ (71.7 mg, 0.067 mmol). This was evacuated and put under argon, and then freshly distilled, degassed methanol (10 mL) was added. This gave a purple-red solution. An excess of freshly distilled benzonitrile (0.2 mL, 1.96 mmol) was added. The solution did not noticeably change color, but after 48 h the solution was concentrated and a ^{31}P NMR spectrum revealed completion of the reaction. The methanol was reduced in volume to 1 mL and diethyl ether was added to precipitate the product. The solid was washed several times with ether and dried in vacuo yielding a lavender powder (45 mg, 60% yield). IR(KBr): ν(CO) 2056 cm^{-1}; ν(CN) 2268 cm^{-1}. Anal. Calcd for $C_{44}H_{33}F_6O_7P_2Rh_2S_2$: C, 46.58; H, 2.89; N, 1.55, Found: C, 46.62; H, 2.93; N, 1.34. ^{1}H NMR: δ (CD_3OD) 7.34 (m, Cp, 1H), 7.29 (m, Cp, 1H), 6.73 (m, Cp, 1H), 6.05 (m, Cp, 1H), 4.23 (m, Cp, 1H), 3.57 (m, Cp, 1H).

[Rh$_2$(CO)(py)(μ-CpPPh$_2$)$_2$](BF$_4$)$_2$, [4c][BF$_4$]$_2$. Into a Schlenk tube was introduced [**2**][BF_4]$_2$ (72.7 mg, 0.078 mmol). This was evacuated and put under argon, then pyridine (4.8 mL) was added, and the solution was stirred for 45 min. The solution was evacuated to dryness. Methanol was added to dissolve the product and the product was precipitated by addition of ether. The dark solid was washed with ether and dried *in vacuo* (43 mg, 63% yield). IR(KBr): ν(CO) 2046 cm^{-1}. Anal. Calcd for $C_{41}H_{33}B_2F_8NOP_2Rh_2$: C, 48.84; H, 3.72; N, 1.47. Found: C, 48.77; H, 3.88; N, 1.42%. ^{1}H NMR: δ ((CD_3)$_2$CO) 6.98 (s, Cp, 2H), 6.49 (s, Cp, 1H), 4.64 (s, Cp, 1H), 3.92 (s, Cp, 1H).

[Rh$_2$(CO)(PhNH$_2$)(μ-CpPPh$_2$)$_2$](CF$_3$SO$_3$)$_2$, [4e][CF$_3$SO$_3$]$_2$. A 10 mm NMR tube was charged with 46.2 mg (0.044 mmol) of [**2**][CF_3-SO_3]$_2$. Under an atmosphere of argon 2 mL of CD_3OD was added. To this red solution was added 8 mL (0.088 mmol) of aniline (freshly distilled from NaOH) giving a blood red solution. The ^{31}P NMR spectrum (Table 1) was recorded after 2 days at room temperature revealing the conversion to [**4e**][CF_3O_3]$_2$. The solution was evaporated to dryness and washed with ether to afford a black powder. IR(CH_2-Cl_2): ν(CO) 2055 cm^{-1}. Another ^{31}P NMR spectrum recorded at the beginning of the reaction revealed the existence of some nonidentified intermediate.

[Rh$_2$(CO)[(*i*-Pr)$_2$NH](μ-CpPPh$_2$)$_2$](PF$_6$)$_2$, [4f][PF$_6$]$_2$. To a suspension of [**2**][PF_6]$_2$ (50 mg, 0.05 mmol) in methanol (5 mL) was added (*i*-Pr)$_2$NH (40 μl). While stirring during 12 h, the solution turned to purple. [Rh(CO)(μ-CpPPh$_2$)]$_2$ formed was separated by filtration and the solution reduced by evaporation. Addition of diethylether (15 mL) afforded a red precipitate of [**4f**][PF_6]$_2$ which is washed with pentane and dried under vacuum (27 mg, yield 45%). NMR (CD_3COCD_3) ^{1}H: δ 7.39 (m, 2HCp); δ 6.86 (m, 2HCp); δ 6.08 (m, 2HCp); δ 5.76 (m, 2HCp); δ 1.52 (d, 12H *i*-Pr). IR (B-KBr), ν(CO) = 2037 cm^{-1}, ν(NH) = 3223 cm^{-1}. Anal. Calcd for $C_{41}H_{43}F_{12}$ $NOPh_2$; C, 43.83; H, 3.86, N, 1.25. Found: C, 44.01; H, 3.94; N, 1.15%.

[Rh(MeCN)(μ-CpPPh$_2$)]$_2$(CF$_3$SO$_3$)$_2$, [5a][CF$_3$SO$_3$]$_2$. To a solid mixture of [**2**][CF_3SO_3]$_2$ (76.6 mg, 0.072 mmol) and Me_3NO (10.9 mg, 0.145 mmoles) under argon was added acetonitrile (5 mL). Within one minute the solution was violet and very fine bubbles of gas were observed in the Schlenk tube. After quickly renewing the atmosphere in the Schlenk tube with argon, it was left to stir for a half hour. This gave a dark violet residue when evaporated to dryness. The yield was quantitative as observed by ^{31}P NMR spectroscopy. The product was reprecipitated from CH_2Cl_2 with ether, washed with ether and dried under vacuum over P_2O_5 to afford 34 mg (43%) of an analytically pure compound. IR (KBr): no carbonyl peak; ν(CN) 2291 cm^{-1}. Anal. Calcd for $C_{38}H_{34}F_6O_8P_2Rh_2S_2$: C, 43.48; H, 3.57; N, 2.92. Found: C, 43.57; H, 3.29; N, 2.54. ^{1}H NMR: δ (CD_3CN) 7.27 (m, Cp, 2H), 6.80 (m, Cp, 2H), 5.95 (m, Cp, 2H), 2.97 (m, Cp, 2H), 1.86 (s, CH_3-CN, 6H).

[Rh(PhCN)(μ-CpPPh$_2$)]$_2$(CF$_3$SO$_3$)$_2$, [5b][CF$_3$SO$_3$]$_2$. A 3-necked 50 mL round-bottomed flask was charged with [**2**][CF_3SO_3]$_2$ (99.3 mg, 0.094 mmol) under argon. Benzonitrile (10 mL freshly distilled from CaH_2) was added, giving an orange-red solution. The reaction flask was equipped with a reflux condenser and an outlet to a mercury bubbler. The reaction flask was heated on an oil bath at 140 °C for 16 h and monitored by ^{31}P NMR spectroscopy. The dark solution was evaporated to dryness. The residue was then washed with toluene/ether and the dirty gray solution was discarded leaving a black product. The product was recrystallized from methanol/ether giving a black powder. Anal. Calcd for $C_{44}H_{38}F_6O_6P_2Rh_2S_2$: C, 43.48; H, 3.57; N, 2.92. Found: C, 43.57; H, 3.29; N, 2.54. IR(KBr): ν(CN) 2292 cm^{-1}. ^{1}H NMR: δ (CD_3OD) 7.13 (s, Cp, 2H), 6.38 (s, Cp, 2H), 3.57 (s, Cp, 2H), 3.23 (s, Cp, 2H), 6.95 (d, ^1J = 7.3 Hz, PhCN, 4H).

[Rh(py)(μ-CpPPh$_2$)]$_2$(CF$_3$SO$_3$)$_2$, [5c][CF$_3$SO$_3$]$_2$. A Schlenk tube was charged with [**2**][CF_3SO_3]$_2$ (52.2 mg, 0.049 mmol) under argon.

(15) Saltzman, H.; Sharefkin, J. G. *Org. Synth.* **1963**, *43*, 60.

Pyridine (4.5 mL freshly distilled from NaOH) was added, giving a green-blue solution. The reaction mixture was stirred for 5 h and then evaporated to dryness. The residue was then dissolved in methanol and precipitated with ether to give a dark blue powder. The ^{31}P and ^{1}H NMR spectra were consistent with that found previously for the BF_4^- derivative.[8c]

$[Rh_2(H_2NC_5H_4N)(\mu\text{-}CpPPh_2)_2](PF_6)_2$, [6]$[PF_6]_2$. Into a Schlenk tube were introduced [**2**]$[PF_6]_2$ (116 mg, 0.11 mmol), $ONMe_3$ (25 mg, 0.22 mmol), and CH_2Cl_2 (10 mL). After 15 min of stirring, the green solution was filtered. To the filtrate was added an excess of 2-aminopyridine (30 mg, 0.32 mmol). After 4 h of stirring, the red-brown solution was reduced in volume to 3 mL and then flash-chromatographed on a 20 cm column of silica (CH_2Cl_2/acetone = 9/1 as eluent). After evaporation of the solvent, the product was dried under vacuum to give a burgundy microcrystalline powder (87 mg, 80% yield). Anal. Calcd for $C_{39}H_{34}N_2P_4F_{12}Rh_2$: C, 43.01; N, 2.57; H, 3.15. Found: C, 43.50; N, 2.79; H, 3.62.

^{13}C NMR ($CDCl_3$): 2-aminopyridine carbons, δ 175.8 (s, 1C), δ 154.3 (d, ^{1}J(CH) =179.6 Hz, 1C); phenyl carbons, δ 134−129 (m, 27C); cyclopentadienyl carbons, δ 114.1 (d, ^{1}J(CH) = 165.8 Hz, 1C), δ 107.7 (d, ^{1}J(CH) = 167.1 Hz, 1C), δ 104.3 (d, ^{1}J(CH) = 180.9 Hz, 1C), δ 102.3 (d, ^{1}J(CH) = 182.1 Hz, 1C), δ 97.7 (d, ^{1}J(CH) = 181.7 Hz, 2C), δ 71.9 (d, ^{1}J(CH) = 195.7 Hz, 1C), δ 69.8 (d, ^{1}J(CH) = 174.1 Hz, 1C), δ 62.6 (d, ^{1}J(CP) = 45.9 Hz, 1C), δ 59.5 (d, ^{1}J(CP) = 46 Hz, 1C). ^{1}H NMR (CD_3CN): δ cyclopentadienyl hydrogens, 6.97 (m, 1H), 6.89 (m, 1H), 6.51 (m, 1H), 6.33 (m, 1H), 5.34 (m, 1H), 5.20 (m, 1H), 3.05 (m, 2H), 3.2 (br. s), 2-aminopyridine hydrogens, δ 7.35 (d, ^{3}J(HH) = 6.23 Hz, 1H), δ 6.58 (dd, ^{3}J(HH) = 8.65 Hz, ^{3}J(HH) = 6.75 Hz, 1H), δ 5.79 (d, ^{3}J(HH) = 8.54 Hz, 1H), δ 5.52 (dd, ^{3}J(HH) = 6.53 Hz, ^{3}J(HH) = 6.26 Hz, 1H).

Reaction of $[Rh(CO)(\mu\text{-}CpPPh_2)]_2(CF_3SO_3)_2$ with Aniline. A 10 mm NMR tube was charged with 46.2 mg (0.044 mmol) of [**2**]$[CF_3SO_3]_2$. Under an atmosphere of argon, 2 mL of CD_3OD was added. To this red solution was added 8 mL (0.088 mmol) of aniline (freshly distilled from NaOH), giving a blood red solution. The ^{31}P NMR spectrum (Table 1) was recorded after 2 days at room temperature showing the conversion to **4e**$^{2+}$. The solution was evaporated to dryness and washed with ether to afford a black powder. IR (CH_2Cl_2): ν(CO) 2055 cm^{-1}. Another ^{31}P NMR spectrum recorded at the beginning of the reaction revealed the existence of some nonidentified intermediate.

Reaction of $[Rh(CO)(\mu\text{-}CpPPh_2)]_2$ $(A)_2$ ($A^- = BF_4^-$, $CF_3SO_3^-$) with 2-Aminopyridine. A three-necked 100 mL round-bottomed flask was charged with 106.8 mg (0.114 mmol) of [**2**]$[BF_4]_2$ and 10.3 mg (0.109 mmol) of 2-aminopyridine. The reaction vessel was evacuated and put under argon. It was then equipped with a reflux condenser and THF (17 mL) was added. The solution was heated under reflux for 2 h, giving a purple solution. Upon cooling to room temperature, a red precipitate and a brown solution were observed. The red precipitate was washed with cold THF and 42.1 mg (39%) were isolated. The IR spectrum revealed that this was the unreacted starting material. The brown solution was evaporated to dryness and the IR spectrum and ^{31}P NMR spectra were recorded revealing the presence of **1**.

The reaction was repeated with [**2**]$[CF_3SO_3]_2$ (168.1 mg, 0.159 mmol) and a 2-fold excess of 2-aminopyridine (29.8 mg, 0.317 mmol). The reaction was followed by IR spectroscopy of the THF solution. After 1 h there was the formation of a strong band at 1951 cm^{-1} and medium bands at 1673 and 1624 cm^{-1}, and the characteristic two bands of the dication had shifted to lower frequency (2068 and 2045 cm^{-1}). The reflux was continued for 19 h, but there was no change in the IR spectrum. The dark violet-red solution was transferred to a Schlenk tube and evaporated to dryness. The ^{31}P NMR spectrum again indicated the neutral species **1** in addition to another species characterized by two ^{31}P NMR signals; δ 42.5 (dd, ^{1}J(RhP) = 202.2 Hz, ^{3}J(PP) = 12.2 Hz, 1P), δ 28.8 (dd, ^{1}J(RhP) = 150.5 Hz, ^{3}J(PP) = 12.3 Hz, 1P). Unfortunately, this product could not be separated from **1**.

$[Rh(NO_2)(\mu\text{-}CpPPh_2)]_2$, 7. Due to the low solubility of $NaNO_2$ in THF it appeared preferable to use the solvate species **3**$^{2+}$, prepared from TMNO in CH_2Cl_2 rather than from PhIO in THF, as starting material.

In a typical synthesis, [**2**]$[PF_6]_2$ (150 mg, 0.14 mmol) was decarbonylated by stirring with $(CH_3)_3NO{\cdot}2H_2O$ (30 mg, 0.27 mmol) in CH_2Cl_2 (10 mL) for 15 min. The green solution was filtered and poured into $NaNO_2$ (200 mg) in methanol (10 mL). After 2 h of stirring, the solution turned red. The residue obtained from the evaporation of this solution was extracted with CH_2Cl_2. This solution was flash chromatographed on a column of silica (eluent CH_2Cl_2/acetone = 1:1). The evaporation of the obtained solution afforded **7** as a red powder (72 mg, yield 64%). ^{1}H NMR (CD_3COCD_3): δ 7.21 (m, 2HCp), 7.06 (m, 2HCp), 6.48 (m, 2HCp), 2.49 (m, 2HCp). ^{31}P NMR: δ 53.7 (dd, J(Rh−P) = 163.9 Hz). IR (in KBr): $\nu(NO_2)$ = 1376, 1305, 820 cm^{-1}. Anal. Calcd for $C_{34}H_{28}N_2O_4P_2Rh_2$: C, 51.28; H, 3.52; N, 3.54. Found: C, 51.04; H, 3.37; N, 3.78.

Acknowledgment. M.C.J. and A.I. were grateful to the CNAS for Research Fellowships. The authors thank the Johnson Matthey Co. for the generous loan of rhodium chloride.

Supporting Information Available: Figure 4 showing the evolution of the ^{31}P NMR spectra along the following series of compounds: (a) the symmetric bis(solvate) cation $[Rh(THF)(\mu\text{-}CpPPh_2)]_2^{2+}$ (**3a**$^{2+}$), (b) the dissymmetric cation$[Rh_2(H_2N\text{-}C_5H_4N)(\mu\text{-}CpPPh_2)_2]^{2+}$ (**6**$^{2+}$), (c) the dissymmetric cation $[Rh_2(CO)(MeCN)(\mu\text{-}CpPPh_2)_2]^{2+}$ (**4a**$^{2+}$), and (d) the dissymmetric cation $[Rh_2(CO)(i\text{-}Pr_2NH)(\mu\text{-}CpPPh_2)_2]^{2+}$ (**4f**$^{2+}$) (1 page). Ordering information is given on any current masthead page.

IC9502335