Rhodium Arylimido/Arylamido Ring Reactions: Electrophilic Additions[1]

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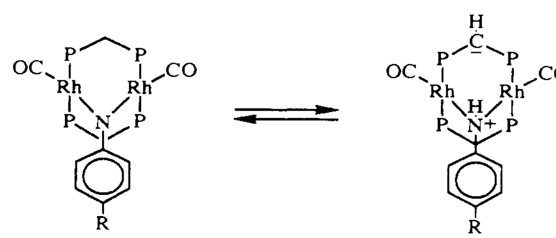
Tautomeric mixtures of the arylimido/arylamido complexes $Rh_2(\mu\text{-}N(4\text{-}R\text{-}C_6H_4)(CO)_2(\mu\text{-dppm})_2$/$Rh_2(\mu\text{-}NH(4\text{-}R\text{-}C_6H_4))(CO)_2(\mu\text{-dppm-H})(\mu\text{-dppm})$ (**1/2**) (dppm = bis(diphenylphosphino)methane, dppm-H = bis(diphenylphosphino)methanide) react with carbon-based electrophiles, R′X, to give the arylimido ring addition products $[Rh_2(\mu\text{-}N(4,4\text{-}R,R'\text{-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+X^-$ (**3** (R, R′ = Me, Me; H, Me; Me, CH_2Ph; Me, CH_2Cl; F, CH_2Ph) (X = Cl, I, OTf)). Crystals of **3** (R, R′ = Me, Me; X = Cl)·CH_2Cl_2 from CH_2Cl_2/ether are monoclinic (*C*2/*c*) with $a = 37.20$ (1) Å, $b = 12.827$ (3) Å, $c = 26.497$ (6) Å, $\beta = 97.35$ (2)°, $V = 12538$ Å^3, $d_{calc} = 1.38$ g·cm^{-3}, and $Z = 8$. The structure reveals an A-frame cationic complex with a quinoid-like group bridging the Rh atoms via the nitrogen atom. Weaker electrophiles with the less nucleophilic **1/2** (R = H) allow other reactions to predominate, giving products resulting from loss of the imido/amido group. Attack of the electrophile at the nitrogen atom of imido tautomer **1** or at the dppm-H ligand of amido tautomer **2** is prevented by the sterically demanding dppm ligand directing the attack to the ring. An interesting ring-to-nitrogen rearrangement of **3** (R, R′ = H, Me) is catalyzed by **1/2** via deprotonation to $Rh_2(\mu\text{-}N(4\text{-}Me\text{-}C_6H_4))(CO)_2(\mu\text{-dppm})_2$ followed by protonation to the cationic amido complex $[Rh_2(\mu\text{-}NH(4\text{-}Me\text{-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+X^-$. This rearrangement occurs in the synthesis of **3** (R, R′ = H, Me; X = OTf) if a deficiency of MeOTf is used, and high yields of **3** are only obtained with 1 equiv or more of MeOTf. A similar rearrangement occurs with MeI, but the intermediate $Rh_2(\mu\text{-}N(4\text{-}Me\text{-}C_6H_4))(CO)_2(\mu\text{-dppm})_2$ is trapped by MeI to give its ring addition product **3** (R, R′ = Me, Me; X = I).

Introduction

The structure, bonding, and reactivity of metal imido (RN^{2-}) complexes have been widely investigated.[2] Despite the potential for high nucleophilicity expected from the high formal charge and the possible presence of a lone pair, for the most part, imido groups are poor nucleophiles. For terminal imido complexes, this is commonly due to multiple-bonding interactions and the donation of the lone pair to an electron-deficient metal center. For bridging imido complexes, a μ_3 interaction is usually observed and the lone pair is used in the bonding to the three metal centers.[3]

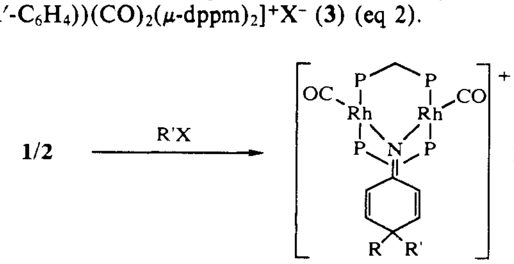
In recent years, imido complexes with electron-rich metal centers and/or with little or no metal–lone pair interaction have been synthesized, resulting in complexes with nucleophilic imido ligands with novel properties.[4] Here, we describe the full details[5] of such a case where the high electron density on the imido nitrogen atom is donated not to the metal but rather to an attached aryl group, activating the ring to electrophilic attack. The imido complexes are the dppm (dppm = bis(diphenylphosphino)methane) Rh A-frame complexes **1**, which are in tautomeric equilibrium with the amido–methanide complexes **2** (eq 1). These equilibrium mixtures are designated as **1/2**.[4a]



1 **2** (1)

Results

Treating **1/2** with the electrophilic carbon reagents R′X gives, in most cases, the ring addition products $[Rh_2(\mu\text{-}N(4,4\text{-}R,R'\text{-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+X^-$ (**3**) (eq 2).



(2)

3

R,R′ = Me,CH_2Cl; X = Cl
= Me,Me; X = I or OTf
= Me,CH_2Ph; X = Cl
= H,Me; X = OTf
= F,CH_2Ph; X = Cl

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(2) (a) Nugent, W. A.; Haymore, B. A. *Coord. Chem. Rev.* **1980**, *31*, 123. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds: The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidene, or Alkylidyne Ligands*; Wiley: New York, 1988.

(3) Conversion of a μ_3- to a μ_2-imido group by displacement of the lone pair has been observed to enhance nucleophilic reactivity: Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3426–3428. Han, S.-H.; Song, J.-S.; Macklin, P. D.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2127–2138.

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Table I. Spectroscopic Data (IR; ^1H[a] and $^{31}P\{^1H\}$ NMR) for the Ring Addition Salts **3**

R, R′, X	ν_{CO}[b]	$\delta(C_6H_4)$[c]	$\delta(PCH_2P)$	$\delta(CH_3)$	$\delta(Ph)$	$\delta(P)$[d]
Me, CH_2Cl, Cl	1989 sh	5.53 (d)	3.06 (m)	1.09 (s)	7.1–7.9	22.7
	1975 vs	5.73 (d)	3.22 (m)			
Me, Me, I	1988 sh	5.47 (d)	3.10 (m)	0.99 (s)	7.2–7.6	22.1
	1973 vs	5.54 (d)				
Me, Me, OTf	1985 sh	5.58 (m)[g]	2.99 (m)	1.00 (s)	7.1–7.8	22.1
	1974 vs		3.13 (m)			
H, Me, OTf	1987 sh	5.72 (m)	3.01 (m)	1.04 (d)[h]	7.1–7.9	22.0
	1974 vs		3.16 (m)			
Me, CH_2Ph,[e] Cl	1988 sh	5.57 (d)	2.82 (m)	1.10 (s)	6.9–7.8	22.3
	1974 vs	5.69 (d)	3.04 (m)			
F, CH_2Ph,[f] Cl		5.69 (m)	2.03 (m)			21.9
			3.11 (m)			

[a] 300 MHz and CD_2Cl_2, except for R, R′ = Me, Me and X = I, where $CDCl_3$ was used. [b] cm^{-1}; CH_2Cl_2. [c] J_{HH} = 10 Hz for all AB doublets. [d] In CH_2Cl_2 or CD_2Cl_2 at 36 MHz. $J = {}^1J_{RhP} + {}^xJ_{RhP} = 138 \pm 1$ Hz for all complexes; see ref 6. [e] $\delta(PhCH_2) = 2.66$ (s). [f] $\delta(PhCH_2) = 2.91$ (d, J_{HF} = 18 Hz). [g] Resolves to an AB quartet in $CDCl_3$: δ 5.54; 5.48; J_{HH} = 10.2 Hz. [h] Coupled to R = H at 2.75 ppm with J_{HH} = 7.5 Hz.

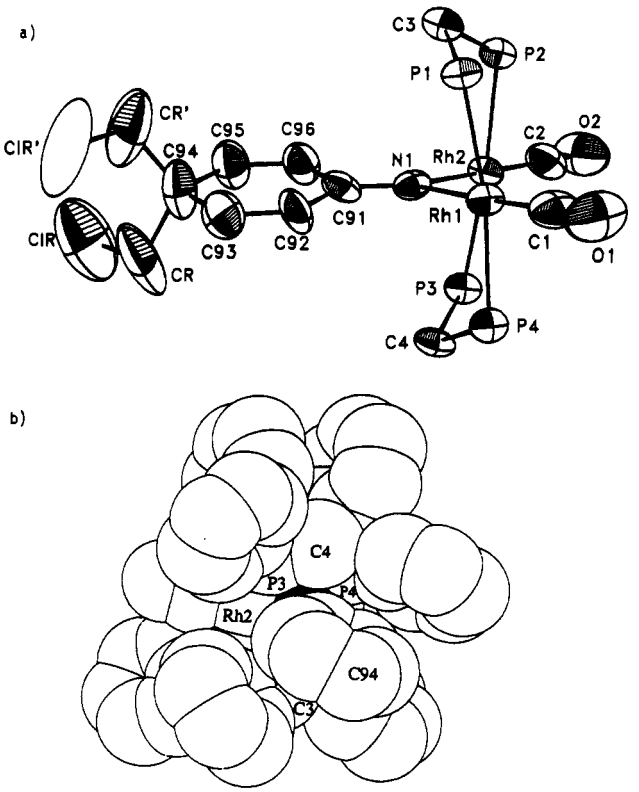


Figure 1. Drawings of the cationic portion of $[Rh_2(\mu\text{-}N(4,4\text{-}CH_3,CH_2Cl\text{-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+Cl^-$ (**3** (R, R′ = Me, CH_2Cl; X = Cl)): (a) ORTEP, 50% probability ellipsoids (phenyl rings omitted; the open ellipsoid of ClR′ represents the minor position for the CH_2Cl group (see text)); (b) PLUTO, van der Waals radii (substituents CR, CR′, Cl, and Cl′ omitted from C94; darkened area is N1).

The spectroscopic data for the ring addition products are summarized in Table I. The common structure (see eq 2) results in similar IR and ^{31}P and ^1H NMR spectra for all **3**. The carbonyl stretching vibrations are found at ca. 1988 and 1975 cm^{-1}. These higher frequency values, as compared to those of the parent neutral imido/amido complexes, are consistent with the formation of cationic complexes. Their ^{31}P NMR spectra are AA′A″A‴XX′ patterns typical of symmetric Rh dppm A-frame complexes.[6] This is true even when R ≠ R′ (down to −80 °C), indicating either that the ring substituents are too far removed from the core region for the phosphorus centers to develop inequivalency or that the cations are fluxional. The ^1H NMR spectra are more distinctive and clearly show the loss of aromaticity as an upfield shift (from the aromatic region) of the resonances for the ring protons (A_2B_2 pattern). Alkyl ring substituents are also shifted upfield from their aromatic positions.

The X-ray crystal structure of $[Rh_2(\mu\text{-}N(4,4\text{-}CH_3,CH_2\text{-}Cl\text{-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+Cl^-$ (**3**) (R, R′= Me, CH_2Cl; X = Cl)) is consistent with the solution spectroscopic data. An ORTEP diagram of the cationic portion (without dppm phenyl rings) is shown in Figure 1. Full crystallographic and structural data are included as supplementary material. Selected data are given in Tables II–IV. The complex cation possesses a typical *trans,trans*-dppm A-frame geometry and closely resembles the structure found for the imido complex $Rh_2(\mu\text{-}N(4\text{-}NO_2\text{-}C_6H_4)(CO)_2(\mu\text{-dppm})_2$.[4a]

Table II. Crystallographic Data for $[Rh_2(\mu\text{-}N(4,4\text{-}CH_3,CH_2Cl\text{-}C_6H_4)(CO)_2(\mu\text{-dppm})_2]^+Cl^-\cdot CH_2Cl_2$ (**3** (R, R′ = Me, $CH_2Cl)\cdot CH_2Cl_2$)

formula	$C_{60}H_{53}Cl_2NO_2P_4Rh_2\cdot CH_2Cl_2$	space group	$C2/c$ (No. 15)
fw	1306.64	T, °C	22
a, Å	37.20 (1)	λ, Å	0.710 69
b, Å	12.827 (3)	d_{calc}, $g\cdot cm^{-3}$	1.38
c, Å	26.497 (6)	μ(Mo Kα), cm^{-1}	8.30
β, deg	97.35 (2)	$R(F_o)$[a]	0.065
V, Å^3	12538	$R_w(F_o)$[b]	0.087
Z	8		

[a] $R(F_o) = (\Sigma\|\|F_o\|-\|F_c\|\|)/\Sigma F_o$. [b] $R_w(F_o) = [(\Sigma w(\|\|F_o\|-\|F_c\|\|)^2/\Sigma wF_o^2]^{1/2}$; $w = 4F_o^2/(\Sigma F_o^2)^2$. Weights based on counting statistics were used with an instrument instability factor of 0.06.

Table III. Selected Coordinates for **3** (R, R′ = Me, $CH_2Cl)\cdot CH_2Cl_2$

	x	y	z	B,[a] Å^2
Rh1	0.59296 (3)	−0.01496 (8)	0.31360 (4)	2.96 (2)
Rh2	0.67290 (3)	−0.01207 (8)	0.35973 (4)	2.94 (2)
ClR	0.6090 (3)	0.051 (1)	0.6215 (4)	14.7 (4)
ClR′	0.5368 (7)	−0.124 (2)	0.5687 (8)	16.2 (9)
Cl1	0.3781 (1)	0.5107 (3)	0.5942 (2)	5.6 (1)
P1	0.5894 (1)	−0.1945 (3)	0.3227 (1)	3.18 (9)
P2	0.6718 (1)	−0.1892 (3)	0.3449 (1)	3.21 (9)
P3	0.6701 (1)	0.1641 (3)	0.3807 (1)	3.12 (9)
P4	0.5948 (1)	0.1665 (3)	0.3178 (1)	3.16 (9)
O1	0.5464 (4)	−0.0183 (9)	0.2132 (4)	7.2 (3)
O2	0.7458 (3)	−0.0004 (9)	0.3270 (5)	7.2 (3)
N1	0.6231 (3)	−0.0199 (8)	0.3839 (4)	2.9 (2)
CR	0.5874 (6)	0.067 (2)	0.5626 (7)	11.3 (7)
CR′	0.5732 (6)	−0.133 (2)	0.5522 (8)	10.8 (7)
C1	0.5661 (4)	−0.016 (1)	0.2512 (6)	4.7 (4)
C2	0.7164 (4)	−0.004 (1)	0.3385 (6)	4.7 (4)
C3	0.6306 (3)	−0.249 (1)	0.3591 (5)	3.1 (3)
C4	0.6236 (4)	0.213 (1)	0.3753 (5)	3.3 (3)
C91	0.6122 (4)	−0.024 (1)	0.4282 (5)	3.2 (3)
C92	0.5745 (4)	−0.010 (1)	0.4360 (5)	4.3 (4)
C93	0.5648 (4)	−0.011 (1)	0.4819 (7)	6.4 (5)
C94	0.5875 (5)	−0.036 (2)	0.5297 (6)	6.3 (5)
C95	0.6268 (5)	−0.050 (1)	0.5199 (6)	5.6 (4)
C96	0.6377 (4)	−0.045 (1)	0.4742 (5)	4.4 (4)

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

(6) (a) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *12*, 1632–1638 and references cited therein. (b) Jenkins, J. A.; Ennett, J. P.; Cowie, M. *Organometallics* **1988**, *7*, 1845–1853.

Table IV. Intramolecular Distances (Å) and Angles (deg) for $[Rh_2(\mu\text{-}N(4,4\text{-}CH_3,CH_2ClC_6H_4))(CO)_2(\mu\text{-dppm})_2]^+Cl^-\cdot CH_2Cl_2$ (**3** (R, R′ = Me, CH_2Cl)·CH_2Cl_2)

Rh(1)–P1	2.321 (4)	O2–C2	1.17 (2)
Rh1–P4	2.330 (4)	N1–C91	1.29 (2)
Rh1–N1	2.05 (1)	C91–C92	1.46 (2)
Rh1–C1	1.82 (1)	C91–C96	1.47 (2)
Rh2–P2	2.306 (4)	C92–C93	1.31 (2)
Rh2–P3	2.332 (4)	C93–C94	1.47 (2)
Rh2–N1	2.04 (1)	C94–C95	1.53 (2)
Rh2–C2	1.78 (2)	C95–C96	1.33 (2)
P1–C3	1.84 (1)	CR–C94	1.58 (3)
P2–C3	1.79 (1)	CR′–C94	1.51 (3)
P3–C4	1.83 (1)	ClR–CR	1.67 (2)
P4–C4	1.85 (1)	ClR′–CR′	1.48 (4)
O1–C1	1.17 (2)	Rh1–Rh2	3.067 (2)
P1–Rh1–P4	171.0 (1)	Rh2–P3–C4	112.7 (4)
P1–Rh1–N1	84.6 (3)	Rh1–P4–C4	111.9 (4)
P1–Rh1–C1	93.0 (5)	Rh1–N1–Rh2	97.2 (4)
P4–Rh1–N1	88.8 (3)	Rh1–N1–C91	129.1 (9)
P4–Rh1–C1	93.6 (4)	Rh2–N1–C91	133.7 (9)
N1–Rh1–C1	177.6 (5)	ClR–CR–C94	112 (2)
P2–Rh2–P3	174.3 (2)	ClR′–CR′–C94	116 (2)
P2–Rh2–N1	90.5 (3)	N1–C91–C92	123 (1)
P2–Rh2–C2	89.9 (5)	N1–C91–C96	121 (1)
P3–Rh2–N1	84.4 (3)	C92–C91–C96	116 (1)
P3–Rh2–C2	95.2 (5)	C91–C92–C93	121 (1)
N1–Rh2–C2	179.6 (6)	C92–C93–C94	127 (2)
Rh1–P1–C3	112.1 (4)	CR–C94–CR′	117 (2)
Rh2–P2–C3	112.4 (4)	CR–C94–C93	105 (2)
CR–C94–C95	105 (1)	C91–C96–C95	122 (1)
CR′–C94–C93	109 (1)	Rh1–C1–O1	174 (1)
CR′–C94–C95	111 (2)	Rh2–C2–O2	177 (1)
C93–C94–C95	110 (1)	P1–C3–P2	113.8 (7)
C94–C95–C96	124 (1)	P3–C4–P4	113.3 (7)

The ring methyl and CH_2Cl groups are disordered by a 2-fold rotation of the ring about the N1–C91 bond. This results in full occupancy of both carbon atom positions CR and CR′ but only partial occupancy of the chlorine atom positions. Occupancy refinement of chlorine atom positions ClR and ClR′ suggests a 70% and 30% distribution, with ClR being the major position. The distances and angles of the N–C and C–C bonds clearly show a quinoid-like structure. The short N1–C91 distance (1.29 Å) indicates extensive nitrogen lone pair interaction with the ring system and a bond order of 2. The loss of aromaticity is shown by the alternating bond lengths within the ring, with short, C92–C93 (1.31 Å) and C95–C96 (1.33 Å), and long bonds, C91–C92 (1.46 Å), C91–C96 (1.47 Å), C93–C94 (1.47 Å), and C95–C94 (1.53 Å). The ring is planar (largest deviation is 0.03 (2) Å) and slightly tilted (11.9 (5)°) out of the Rh1–N1–Rh2 plane.

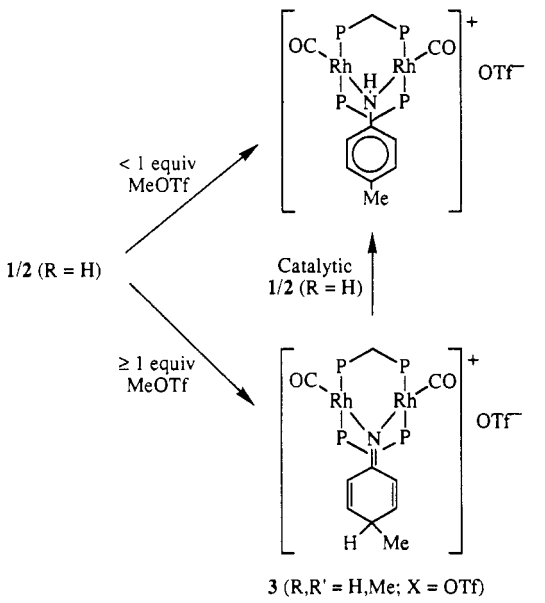
While the ring addition products **3** are the major products for **1/2** (R = Me), with **1/2** (R = H), ring-to-N hydrogen shifts may occur and with weak electrophiles and the less electron-rich complexes other reactions compete with the ring addition. The details of each system follow.

R = Me. The presence of the 4-methyl group results in relatively uncomplicated reaction chemistry with simple addition of the electrophile to the ring. In general, the rate of the reaction depends on the electrophilicity of the reagent. Thus, the reaction of **1/2** (R = Me) with neat CH_2Cl_2 requires several days. The major product is the orange ring addition salt **3** (R, R′ = Me, CH_2Cl; X = Cl). A minor product, $Rh_2(\mu\text{-OHCl})(CO)_2(\mu\text{-dppm})_2$,[7] presumably results from a competitive reaction of **1/2** with traces of water in the reaction system.

The CH_3I (10-fold) and MeOTf reactions with **1/2** (R = Me) are much faster and are complete in minutes. The ring addition products **3** (R, R′ = Me, Me; X = I, OTf) are obtained in high yield with only traces of side products. A somewhat slower but still rapid reaction occurs with $PhCH_2Cl$ (2 equiv), and **3** (R, R′ = Me, CH_2Ph; X = Cl) is obtained in a 68% isolated yield.

(7) Deraniyagala, S. P.; Grundy, K. R. *Inorg. Chem.* **1985**, *24*, 50–56.

Scheme I



R = H. As might be expected, the absence of the electron-donating methyl group leads to decreased nucleophilicity and slower reactions for **1/2** (R = H) relative to **1/2** (R = Me). This allows other reactions to compete with ring addition. Thus, with CH_2Cl_2, complete consumption of **1/2** (R = H) requires many days and a ring addition product is not obtained. Instead, the imido/amido group is replaced with chlorides and the major product is a yellow precipitate of $Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2$.[8] Small amounts of $Rh_2(\mu\text{-OHCl})(CO)_2(dppm)_2$[7] also form.

With 1 equiv or more of the more powerful electrophile MeOTf, **1/2** (R = H) does give the anticipated ring addition product, **3** (R, R′ = H, Me; X = OTf). Interestingly, a different product (a tautomer of **3**), $[Rh_2(\mu\text{-NH(4-Me-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+OTf^-$,[4a] is obtained if less than 1 equiv of MeOTf is used (Scheme I). The difference is that, with less than 1 equiv of MeOTf, excess **1/2** is present. That this is critical for the formation of $[Rh_2(\mu\text{-NH(4-Me-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+OTf^-$ is shown by the observation that a solution of **3** (R, R′ = Me, H) is slowly converted to a solution of $[Rh_2(\mu\text{-NH(4-Me-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+OTf^-$ in the presence of a catalytic amount of **1/2** (Scheme I). A deuterium-labeling experiment was performed to investigate the ring-to-nitrogen hydrogen shift.

$Rh_2(\mu\text{-NC}_6D_5)(CO)_2(\mu\text{-dppm})_2/Rh_2(\mu\text{-NHC}_6D_5)(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$ was treated with less than 1 equiv of MeOTf. The ^1H NMR spectrum of the resulting amido salt showed complete deuterium scrambling over the NH and the dppm methylene groups (both endo and exo). The ^2D NMR spectrum confirmed this result and showed by integration (relative to the ring deuteriums) that a total of one deuterium was incorporated into the NH and the dppm methylene positions.

The reaction of **1/2** (R = H) with excess MeI is slower and more complicated. The expected ring addition product **3** (R, R′ = H, Me; X = I) is not observed. Instead, the "double" ring addition product **3** (R, R′ = Me, Me; X = I) is formed along with $[Rh_2(\mu\text{-NH(4-Me-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+I^-$ and $[Rh_2(\mu\text{-NHPh})(CO)_2(\mu\text{-dppm})_2]^+I^-$. Small amounts of $[Rh_2(\mu\text{-CO})(CO)I(\mu\text{-dppm})_2]^+I^-$[9] and $Rh_2I_3(\mu\text{-H})(\mu\text{-CO})(\mu\text{-dppm})_2$ were also detected.

The reaction of **1/2** (R = H) with excess $PhCH_2Cl$ is slow and complicated. Among the major products are $Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2$,[8] $Rh_2(OHCl)(CO)_2(dppm)_2$,[7] and what appears to be a

(8) (a) Mague, J. T. *Inorg. Chem.* **1969**, *8*, 1975. (b) Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1969**, *8*, 119. (c) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1981**, 228–231.

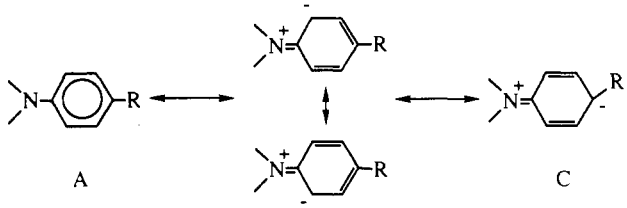
(9) Cowie, M.; Dwight, S. T. *Inorg. Chem.* **1980**, *19*, 2500.

ring addition product (by NMR). No attempt was made to separate the mixture.

R = F. The reaction of $Rh_2(\mu\text{-}N(4\text{-}F\text{-}C_6H_4))(CO)_2(\mu\text{-}dppm)_2$/$Rh_2(\mu\text{-}NH(4\text{-}F\text{-}C_6H_4))(CO)_2(\mu\text{-}dppm)(\mu\text{-}dppm\text{-}H)$ (**1/2** (R = F)) with $PhCH_2Cl$ is slow. Two equivalents of $PhCH_2Cl$ does not give a detectable change after 1 h. With more $PhCH_2Cl$ and a longer reaction time, partial conversion to the ring addition product **3** (R, R′ = F, CH_2Ph; X = Cl) is possible. The ^1H NMR spectrum shows the two magnetically equivalent CH_2 protons of the $PhCH_2$ group coupled with the ring fluorine (J_{HF} = 18 Hz).

Discussion

Our previous work on the imido/amido complexes **1/2** has shown a high negative charge density on the imido nitrogen atom.[4a] Indeed, the complexes are readily protonated by a number of compounds with active hydrogens either at the nitrogen atom of **1** or at the methanide of **2**. It was therefore surprising to us to find these ring addition reactions with carbon-based electrophiles. The possibility of charge delocalization out into the ring is apparent from an examination of resonance forms A–C. In fact, these



A B C

resonance forms were invoked in the analysis of the crystal structure of **1** (R = NO_2) and in the explanation for the much higher than expected charge density on the nitrogen atom of **1** when the aryl ring was methyl substituted at the 2-position.[4a] But why the difference between H^+ and the carbon-based electrophiles?

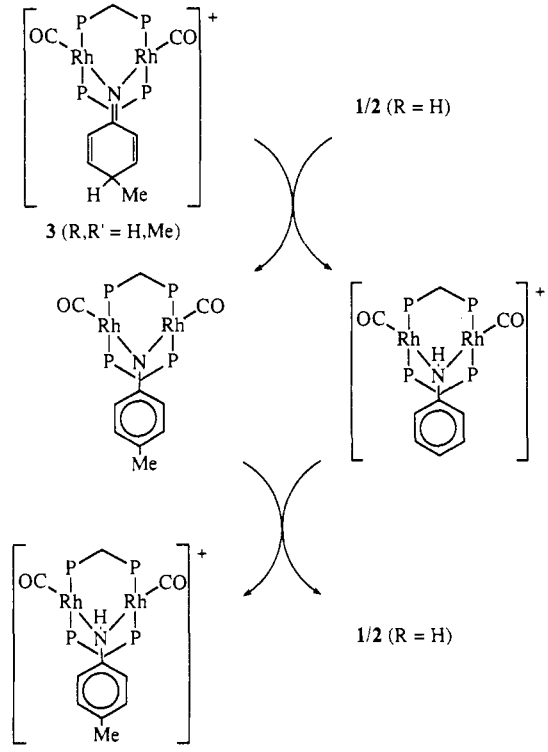
The absence of carbon-based electrophilic attack at the nitrogen atom is explained by an examination of the space-filling PLUTO diagram of **3** (R, R′ = Me, CH_2Cl; Figure 2, ring substituents removed). As can be seen, the nitrogen atom is not readily accessible, being well sheltered by a "pocket" formed by the dppm methylene and phenyl groups. Even if attack at the nitrogen atom were possible, the resulting N(Ar)(R′) bridging amide wold be too large for the A-frame structure to be retained.

Attack at the methanide (CH^-) of tautomer **2** is also possible but presents problems as well. The stability of dppm type A-frame structures is quite sensitive to substituents on the dppm methylene groups. Even with a single methyl substituent ($Ph_2PCH(Me)PPh_2$), the A-frame structure no longer seems to be accessible.[10] Thus, attack at the methanide would require a structural rearrangement with an activation energy that is not attainable.

We are left with electrophilic attack on the ring. As shown by the resonance forms, attack at both the 2- and the 4-positions is possible. Again, steric factors are directing with the 2-position shielded by the dppm phenyl groups and probably also the Rh. This leaves the 4-position, where there are no steric problems, as shown by the fact that methyl substitution is not only tolerated but even accelerates the reaction.

Alternative reactions to ring addition appear as the rate of the ring attack drops. This is most clearly illustrated in the CH_2Cl_2 reaction of unsubstituted **1/2** (R = H). The product, $Rh_2Cl_2(CO)_2(dppm)_2$, most likely results from dehydrohalogenation of CH_2Cl_2, probably initiated by deprotonation of CH_2Cl_2 by **1/2**. A similar reaction occurs in competition with ring addition

Scheme II



reactions in the reaction of MeI with **1/2** (R = H). There is also some evidence in this reaction for attack at the metal centers with the formation of the Rh(II) complex $Rh_2I_3(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)_2$, although how this low-yield product is formed is not clear.

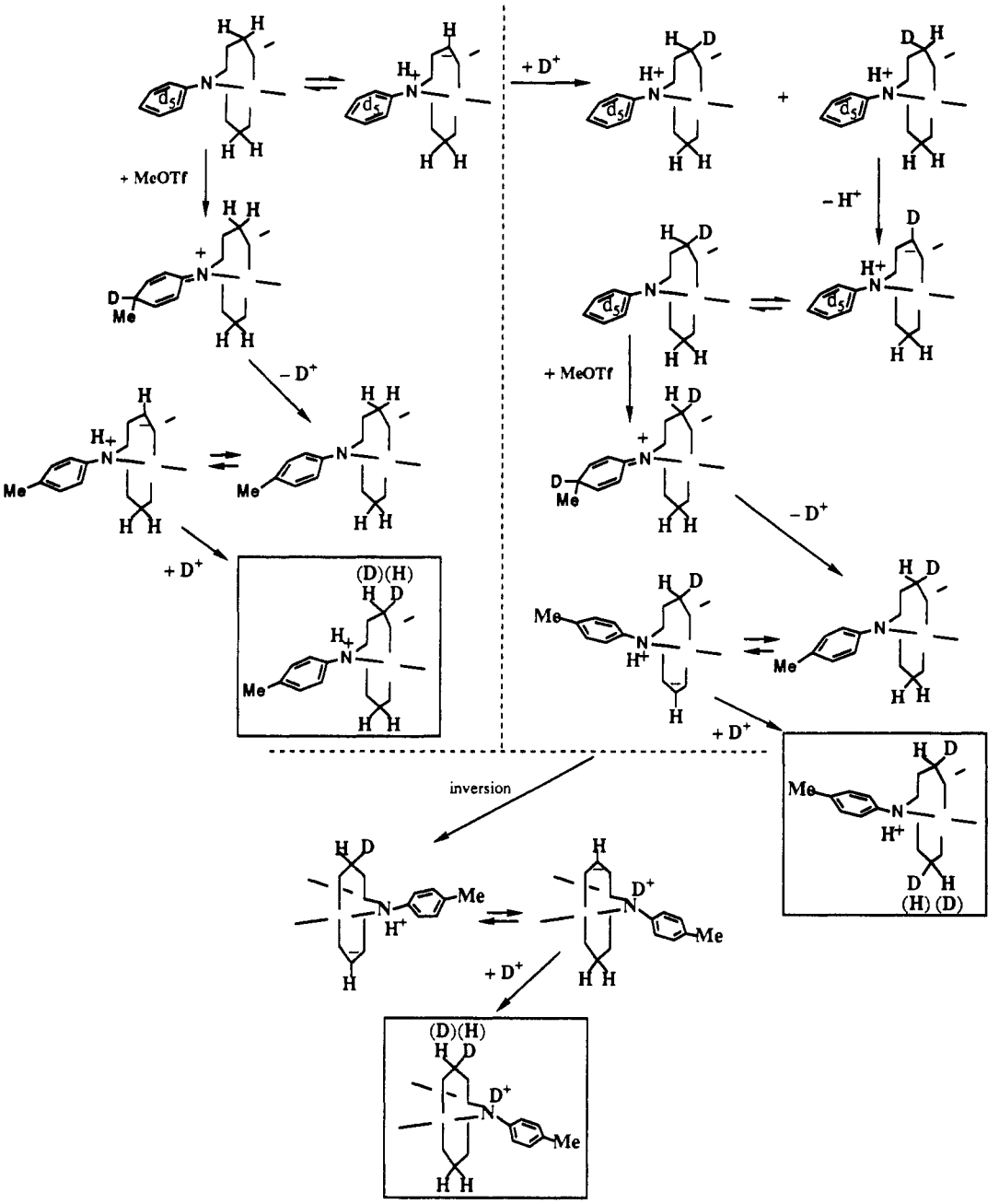
A rather interesting slower secondary reaction can occur with the ring addition products of **1/2** (R = H) due to the presence of the acidic ring hydrogen at the 4-position. This is evident in the rearrangement of **3** (R, R′ = H, Me; X = OTf) to $[Rh_2(\mu\text{-}NH(4\text{-}Me\text{-}C_6H_4))(CO)_2(\mu\text{-}dppm)_2]^+OTf^-$ when **1/2** (R = H) remains in the reaction mixture or is added to isolated **3** (R, R′ = H, Me; X = OTf). The important property of **1/2** that promotes this proton shift is its basicity. As shown in Scheme II, a reasonable first step is deprotonation of **3** by **1/2** (R = H) to generate **1/2** (R = Me) and $[Rh_2(\mu\text{-}NH(Ph))(CO)_2(\mu\text{-}dppm)_2]^+$. Since **1/2** (R = Me) is more basic than **1/2** (R = H),[4a] the proton is transferred back from $[Rh_2(\mu\text{-}NH(Ph))(CO)_2(\mu\text{-}dppm)_2]^+$ to **1/2** (R = Me) to give the final product, $[Rh_2(\mu\text{-}NH(4\text{-}Me\text{-}C_6H_4))(CO)_2(\mu\text{-}dppm)_2]^+$, and to regenerate the catalyst, **1/2** (R = H).

Because of the steric factors discussed above, we believe that the exposed methanide of the dppm-H ligand in amido tautomer **2** is the functional base in the rearrangement reactions. Attempting to confirm this, we treated the ring-deuterated **1/2**, $Rh_2(\mu\text{-}NC_6D_5)(CO)_2(\mu\text{-}dppm)_2$/$Rh_2(\mu\text{-}NH(C_6D_5))(CO)_2(\mu\text{-}dppm)(\mu\text{-}dppm\text{-}H)$, with MeOTf. We had hoped that the resulting amido product would have the deuterium on only one of the dppm ligands, perhaps in either the endo or the exo position, as a result of the dedeuteronation by the dppm-H of **2**. However, we observed complete scrambling of the deuterium over the N and both of the methylene carbons (exo and endo positions) of the dppm ligands. The scrambling over the dppm ligand is readily explained by a series of deuteron transfers (Scheme III). The scrambling onto the N is somewhat more difficult to explain and requires either direct deuteronation of the sterically protected N or inversion of the A-frame structure[11] probably by Rh–N bond rupture of the amido tautomer and inversion at the N.

(10) Lee, C.-L.; Yang, Y.-P.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Organometallics* **1986**, *5*, 2220–2228.

(11) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Grossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642–5646.

Scheme III



Hydrogen shifts also take place in the reaction of **1/2** (R = H) with MeI. However, the situation is more complex than with MeOTf because of the slower ring addition reaction (Scheme IV). Even in the presence of excess MeI, the deprotonation of the initial ring addition product **3** (R, R′ = H, Me; X = I) by **1/2** (R = H) is competitive. The resulting **1/2** (R = Me) is much more reactive and some is trapped before being protonated at the nitrogen atom by the excess MeI, giving the unexpected "double" ring addition product **3** (R, R′ = Me, Me; X = I). Additionally, if protonation occurs before **1/2** (R = Me) is trapped, the larger amount of **1/2** (R = H) present in the first stage of the reaction allows significant amounts to be deprotonated even though **1/2** (R = H) is less basic than **1/2** (R = Me). This scheme predicts equal amounts of **3** (R, R′ = Me, Me; X = I) and $[Rh_2(\mu\text{-NHPh})(CO)_2(\mu\text{-dppm})_2]^+$, as is observed.

As with many electrophile/nucleophile reactions, the mechanistic details of the ring addition reactions may involve a single-electron transfer (SET). SET in reactions of alkyl halides with nucleophiles, including metal complexes, is a well-established process.[12,13] Although we have not probed this question in any detail, we can probably say that free radicals are not involved in most or all of the reactions. This is supported by the absence of products expected from the formation of free radicals (coupling etc.) and by the insensitivity of the reaction to the addition of 1,4-cyclohexadiene as a radical trap (**1/2** (R = H) and Me_3OBF_4). However, this does not exclude the formation of caged radical pairs[11a] with rapid collapse to the ring addition products (eq 3).

We have studied the electrochemical and chemical oxidation of the imido/amido complexes **1/2** and found that **1/2** (R = Me, H) undergo oxidation in THF at very low potentials (−1.04 and −1.00 V vs Cp_2Fe, respectively) to produce radical cations and, subsequently, radical products (coupling etc).[14] This suggests a

(12) (a) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987. (b) Rossi, R. A.; Pierini, A. B.; Palacios, S. M. *J. Chem. Educ.* **1989**, *66*, 720–722. (c) Ashby, E. C.; Argyropoulos, J. N. *J. Org. Chem.* **1985**, *50*, 3274–3283. (d) Pierini, A. B.; Penenory, A. B.; Rossi, R. A. *J. Org. Chem.* **1985**, *50*, 2739–2742.

(13) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (b) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; Chapter 5.

$$1/2 + R'X \longrightarrow [1/2^{\bullet+}, R'X^{\bullet-}] \longrightarrow 3 \quad (3)$$

low single-electron-transfer barrier for our imido/amido complexes and reinforces the possibility of a SET step in the ring addition reactions. The steric directing effects discussed above should hold for a radical coupling process.

Conclusions

The proper combination of high basicity and steric protection of an arylimido nitrogen atom results in selective electrophilic attack at the 4-position of the aryl ring. Decreasing the basicity of the imido complex or the strength of the electrophile allows other reactions (protonation, metal attack, etc.) to compete or dominate. Ring addition reactions may be expected in related arylamido and aryloxo systems,[15] where major contributions from resonance forms similar to B and C are possible and where there is steric protection of the heteroatom.

Experimental Section

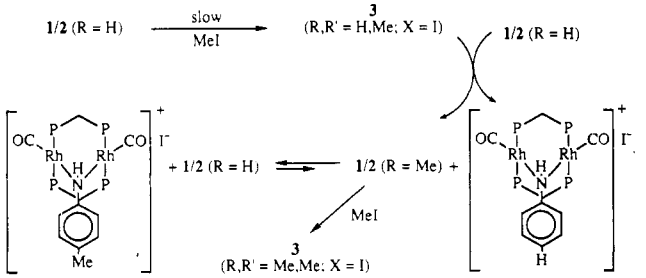
General Procedures. All experiments were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corp. drybox or by Schlenk techniques. Solvents were carefully dried under dinitrogen.[16] $Rh_2(\mu\text{-}N(4\text{-}R\text{-}C_6H_4))(CO)_2(\mu\text{-dppm})_2$/$Rh_2(\mu\text{-}NH(4\text{-}R\text{-}C_6H_4))(CO)_2(\mu\text{-dppm-H})(\mu\text{-dppm})$ (**1/2**) were prepared according to literature procedures.[4a] Methyl iodide, MeOTf, and $PhCH_2Cl$ were used as received (Aldrich). NMR shifts are reported in ppm referenced to TMS for ^1H and ^{13}C, to external H_3PO_4 for ^{31}P, and to $BF_3\cdot Et_2O$ for ^{19}F. Microanalyses were performed by Oneida Research Services, Inc. (air-sensitive handling); however, as noted by Balch,[17] poor analyses are common for dppm A-frame complexes due to solvent occlusion and incomplete combustion of the dppm ligand.

Preparation of 3 (R, R′ = Me, CH_2Cl; X = Cl). One hundred milligrams of **1/2** (R = Me) was stirred in CH_2Cl_2 (2 mL) for 5 days. The orange solution was reduced to half of the original volume and layered under Et_2O at −40 °C to give orange crystals. Filtering, washing with cold Et_2O/CH_2Cl_2 (~3/1) and then Et_2O, and drying in vacuo gave 65 mg (60%) of **3** (R, R′ = Me, CH_2Cl; X = Cl). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 194.5 (d, CO), 168.0 (s, N=C), 52.0 (s, CH_2Cl), 42.0 (s, C in C_6H_4), 25.0 (s, CH_3), 21.3 (m, PCH_2P). Assignments were confirmed by DEPT experiments. See Table I for other spectroscopic data. X-ray-quality crystals were obtained by layering a CD_2Cl_2 solution with CH_2Cl_2 and then Et_2O.

Preparation of 3 (R, R′ = Me, Me; X = I). CH_3I (10 μL, *d* = 2.28, 0.16 mmol) was added to a stirred solution of **1/2** (R = Me) (18 mg, 0.016 mmol) in DME (1 mL). After a few minutes, a yellow-orange precipitate formed. After 0.5 h, the solid was filtered off, washed with DME and Et_2O, and dried in vacuo to give 15 mg of yellow-orange product **3** (R, R′ = Me, Me; X = I) in 74% yield. The ^1H NMR spectrum (90 MHz, CD_3Cl) revealed a multiplet for the ring protons at δ 5.51, which separated into two doublets at 300 MHz. See Table I for other spectroscopic data.

Preparation of 3 (R, R′ = Me, Me; X = OTf). MeOTf (4 μL, *d* = 1.45, 0.036 mmol) was added to a brown-orange solution of **1/2** (R = Me) (20 mg, 0.018 mmol) in CH_2Cl_2 (1 mL). The solution immediately turned orange. After 1 h, the volume of the reaction mixture was reduced in vacuo to about one-third and 1 mL of Et_2O was added to induce precipitation. The precipitate was filtered off, washed, and dried in vacuo to give 19 mg (83%) of orange product **3** (R, R′ = Me, Me; X = OTf). The same results were obtained with 1 equiv of MeOTf. ^{19}F NMR (85 MHz, CD_2Cl_2): δ 74.7. Anal. Calcd (found) for $C_{61}H_{54}F_3NO_5P_4Rh_2S\cdot 0.67CH_2Cl_2$: C, 54.47 (54.53); H, 4.12 (3.93); N, 1.04 (1.03). The presence of the CH_2Cl_2 of crystallization was confirmed by ^1H NMR spectroscopy in $CDCl_3$.

Scheme IV



Preparation of 3 (R, R′ = Me, CH_2Ph; X = Cl). $PhCH_2Cl$ (4 μL, *d* = 1.1, 0.035 mmol) was added to a stirred solution of **1/2** (R = Me) (20 mg, 0.018 mmol) in CH_2Cl_2 (1 mL). The color of the solution did not change significantly. After 1 h, a ^{31}P NMR spectrum showed a reaction had occurred. The solution was concentrated to about one-third of its original volume, and an orange solid was precipitated with Et_2O. Product **3** (R, R′ = Me, CH_2Ph; X = Cl) was isolated by filtration (15 mg, 68%). Analyses were variable from sample to sample and consistently low for carbon. Anal. Calcd (found) for $C_{66}H_{58}ClNO_2P_4Rh_2$: C, 62.8 (60.5, 54.7, 59.5); H, 4.6 (4.5, 4.0, 4.2); N, 1.1 (1.1, 0.9, 0.9).

Reaction of 1/2 (R = H) with CH_2Cl_2. A solution of **1/2** (R = H) (35 mg) in CH_2Cl_2 (0.7 mL) was stirred for 9 days to give a yellow precipitate and a green-brown solution. After filtering, washing with toluene and Et_2O, and drying in vacuo, 18 mg of yellow $Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2$,[8] was isolated (53% yield). The IR spectrum of the green-brown mother liquor was complex. The volatiles were removed in vacuo from the mother liquor, and the residue was extracted with toluene to give a brown solution and 10 mg of a green solid. The green solid contained some $Rh_2(\mu\text{-OHCl})(CO)_2(\mu\text{-dppm})_2$[7] along with other unidentified products.

Reaction of 1/2 (R = H) with CH_3I. **1/2** (R = H) (36 mg, 0.032 mmol) was partially dissolved in DME (2 mL). After CH_3I (20 μL, 0.32 mmol) was added, the suspension changed gradually from brown to orange. After 0.5 h of stirring, the suspension was filtered to give 20 mg of yellow-orange solid and a brown solution. The yellow-orange solid was a mixture of three products identified by their spectral properties as **3** (R, R′ = Me, Me; X = I), $[Rh_2(\mu\text{-}NH(4\text{-Me-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+I^-$, and $[Rh_2(\mu\text{-NHPh})(CO)_2(\mu\text{-dppm})_2]^+I^-$.

At −40 °C, brown needles and a few red needles crystallized from the brown solution. The brown needles were identified as $[Rh_2(\mu\text{-CO})(CO)I(\mu\text{-dppm})_2]^+I^-$ (NMR and IR)[9] and the red needles as $Rh_2I_3(\mu\text{-H})(\mu\text{-CO})(\mu\text{-dppm})_2$ (X-ray crystal structure determination;[18] see supplementary material).

When the reaction was carried out in THF using 1.2 equiv of CH_3I, a small amount of pure **3** (R, R′ = Me, Me; X = I) was isolated.

Reaction of 1/2 (R = H) with MeOTf. A. Excess MeOTf. MeOTf (4 μL, 0.036 mmol) was added to a brown solution of **1/2** (R = H) (20 mg, 0.018 mmol) in CH_2Cl_2 (0.5 mL). The solution lightened and then gradually turned orange. After being stirred for 1 h, the solution was reduced to about one-third of its original volume and 1 mL of Et_2O was added to induce precipitation. Product **3** (R, R′ = H, Me; X = OTf) was isolated by filtration (21 mg, 92%). ^{19}F NMR (85 MHz, CD_2Cl_2): δ 74.7.

B. Excess 1b/2b. MeOTf (3.5 μL, 0.031 mmol) was added to a brown solution of **1/2** (R = H) (40 mg, 0.036 mmol) in CH_2Cl_2 (1 mL). The solution gradually turned orange, and after 1 h, the solvent was removed in vacuo. The residue was washed with toluene to remove the excess **1/2**; then it was dissolved in 1 mL of CH_2Cl_2, and the solution was layered with Et_2O at −40 °C. The resulting crystals were removed by filtration, washed with cold Et_2O/CH_2Cl_2 (3/1) and Et_2O, and then dried in vacuo to give 33 mg (85%) of orange $[Rh_2(\mu\text{-}NH(4\text{-Me-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+OTf^-$.

C. Excess Ring-Deuterated 1/2 (R = D). As in the above procedure (B), excess $Rh_2(\mu\text{-}NC_6D_5)(CO)_2(\mu\text{-dppm})_2$/$Rh_2(\mu\text{-}NH(C_6D_5))(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$ was treated with MeOTf to give a deuterated analogue of $[Rh_2(\mu\text{-}NH(4\text{-Me-}C_6H_4))(CO)_2(\mu\text{-dppm})_2]^+OTf^-$. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.8–7.0 (m, 40 H, Ph), 4.19 (br, 0.8 H, NH),

(14) Ge, Y.-W.; Sharp, P. R. Manuscript in preparation.
(15) An exactly opposite reactivity pattern is observed for an Os tolyl–carbyne complex where hydride adds at the 4-position to give a vinylidene complex. Interestingly, HCl induces a ring-to-α-carbon hydrogen shift again, exactly opposite to our base-induced shift: Roper, W. R.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1980**, *201*, C27–C30.
(16) Burfield, D. R.; Lee, K.-H.; Smithers, R. H. *J. Org. Chem.* **1977**, *42*, 3060–3065.
(17) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996–3003.
(18) Crystals of $Rh_2I_3(\mu\text{-H})(\mu\text{-CO})(\mu\text{-dppm})_2\cdot 2CH_2Cl_2$ are monoclinic ($P2_1/c$) with a = 17.441 (5) Å, b = 12.248 (6) Å, c = 27.13 (1) Å, and β = 95.64 (3)°.

3.93, 3.82, 3.00, and 2.83 (4 m, 4 × 0.8 H, PCH_2P), 2.20 (s, 3 H, CH_3). ^2D NMR (46 MHz, CH_2Cl_2): δ 7.2–6.5 (m, 4 D, C_6D_4), 4.2–2.8 (m, 1 D, ND and PCHDP).

Catalytic Transformation of 3 (R, R′ = H, Me; X = OTf) to $[Rh_2(\mu\text{-NH(4-Me-C}_6H_4))(CO)_2(\mu\text{-dppm})_2]^+OTf^-$. One milligram of **1/2** (R = H) was added to a solution of **3** (R, R′ = H, Me; X = OTf) (13 mg) in CH_2Cl_2. After 0.5 h, the ^{31}P NMR spectrum showed complete conversion to $[Rh_2(\mu\text{-NH(4-Me-C}_6H_4))(CO)_2(\mu\text{-dppm})_2]^+OTf^-$.

Reaction of 1/2 (R = H) with $PhCH_2Cl$. $PhCH_2Cl$ (4 μL, d = 1.1, 0.035 mmol) was added to a stirred solution of **1/2** (R = H) (20 mg, 0.018 mmol) in CH_2Cl_2 (1 mL). After 1 h, no reaction had occurred (by NMR). The addition of more $PhCH_2Cl$ (16 μL) and stirring for 3 h more resulted in the precipitation of yellow $Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2$. The green mother liquor contained what appeared to be a ring addition product. ^{31}P NMR (36 MHz, CH_2Cl_2): δ 22.6 (dm, J_{RhP} = 139.2 Hz), and $Rh_2(\mu\text{-OHCl})(CO)_2(\mu\text{-dppm})_2$.

Preparation of 3 (R, R′ = F, CH_2Ph; X = Cl). $PhCH_2Cl$ (4 μL, d = 1.1, 0.035 mmol) was added to a stirred solution of **1/2** (R = F) (20 mg, 0.018 mmol) in CH_2Cl_2 (1 mL). After 1 h, no reaction had occurred (by NMR). More $PhCH_2Cl$ (16 μL) was added, and the solution was stirred for 3 h more. An IR spectrum indicated partial reaction. The solution volume was reduced, and Et_2O was added to cause precipitation. After filtration and washing with toluene (to remove remaining **1/2**), **3** (R, R′ = F, CH_2Ph; X = Cl) was isolated in a 45% yield.

Structure Analysis of 3 (R, R′ = Me, CH_2Cl; X = Cl)·CH_2Cl_2. Orange, prismatic crystals were grown from CH_2Cl_2. A crystal was selected in air, mounted on a glass fiber, and coated with epoxy. A summary outline of crystallographic and data collection parameters is given in Table II. Details of the data collection and reduction and the structure solution and refinement are provided as supplementary material.

Acknowledgment. We thank ARCO Chemical Co., Johnson Matthey (loan of $RhCl_3$), and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant DE-FG02-88ER13880) for support of this work. The National Science Foundation provided a portion of the funds for the purchase of the X-ray (Grant CHE-7820347) and NMR (Grant PCM-8115599) equipment.

Supplementary Material Available: A listing of detailed experimental data, a textual presentation of the structure determinations, tables of positional parameters, thermal parameters, bond distances and angles, and least-squares planes for **3** (R, R′ = Me, CH_2Cl; X = Cl) and $Rh_2I_3(\mu\text{-H})(\mu\text{-CO})(\mu\text{-dppm})_2$, and an ORTEP diagram of $Rh_2I_3(\mu\text{-H})(\mu\text{-CO})(\mu\text{-dppm})_2$ (16 pages). Ordering information is given on any current masthead page.