Rhodium(I) Mixed CO/Phosphine/Amine Complexes: Synthesis, Structure, and Reactivity

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A series of new complexes of the general formula $Rh(CO)(Cl)(PPh_3)(NRR'R'')$ have been prepared via the bridge-splitting reactions of $[Rh(\mu\text{-}Cl)(CO)(PPh_3)]_2$ with primary, secondary, and tertiary amine ligands. The Rh(I) complexes, $Rh(CO)(Cl)(PPh_3)(H_2NCy)$ (**3**) and $Rh(CO)(Cl)(PPh_3)(HNEt_2)$ (**6**) were crystallographically characterized and were found to possess a local square-planar geometry with a triphenylphosphine ligand trans to the amine. There is evidence for inter- and intramolecular hydrogen bonding between the amine hydrogen and the chloride ligand in **3** and **6**. Complex **6** adds CX_4 (X = Cl, Br, I) resulting in the formation of Rh(III) anionic complexes of the type $[RhCl_nX_{4-n}(PPh_3)(CO)]^-(NH_2R_2)^+$. The complex $[RhCl_4(PPh_3)(CO)]^-(NH_2Et_2)^+ \cdot {}^1/_2\ C_6H_6$ (**19**) was characterized by X-ray diffraction and was found to crystallize in the monoclinic *C*2/*c* space group. The crystal structure of complex **20**, which is synthesized from the reaction of **6** with CBr_4, indicates that the compound corresponds to the formula $[RhBr_{2.85}Cl_{1.15}(CO)(PPh_3)]^-(H_2NEt_2)^+ \cdot {}^1/_2\ C_6H_6$. $Rh(CO)(Cl)(PPh_3)(HNEt_2)$ catalyzes hydrosilation of 1-hexene and polymerization of styrene and methyl methacrylate in the presence of perhaloalkanes.

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Introduction

Rh(I) complexes of the type $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ are probably among the oldest and most extensively studied homogeneous catalysts and are known to promote a variety of organic transformations.[1] In these sterically crowded molecules with 16 electrons at the metal center, ligand dissociation is an important first step in the catalytic cycle leading to coordinatively unsaturated active species.[1] We were intrigued by the possibility of having a weakly coordinating ligand such as an amine in a position directly opposite that of PPh_3, a ligand with a strong σ-donor trans effect.[2] The latter is expected to enhance the lability of the amine ligand and may offer rich and intriguing chemistry of these complexes. We report herein synthesis and a detailed study of Rh(I) complexes containing Cl, CO, PPh_3, and a primary, secondary, or tertiary amine ligand. Such stable d^8-Rh(I) complexes, $RhCl(CO)(PPh_3)(NRR'R'')$, are easily accessible via bridge-splitting reactions of $[Rh(CO)(PPh_3)(\mu\text{-}Cl)]_2$ with amines. A single-crystal structure determination of $RhCl(CO)(PPh_3)(NEt_2H)$ and $RhCl(CO)(PPh_3)(NCyH_2)$ showed that the Rh(I) centers in these complexes have square-planar geometry with the amine ligand trans to a phosphine. The bound amine in $RhCl(CO)(PPh_3)(NEt_2H)$ is sufficiently labile and undergoes ligand displacement reactions under mild reaction conditions. The complex $RhCl(CO)(PPh_3)(NEt_2H)$ is an efficient catalyst for (i) hydrosilation of 1-hexene and (ii) polymerization of styrene and methyl methacrylate in the presence of haloalkanes such as CCl_4. The hydrosilation reaction with $RhCl(CO)(PPh_3)(NEt_2H)$ is complete in 30 min at 60 °C, while a similar reaction with $RhCl(CO)(PPh_3)_2$ requires refluxing for 6 days and gives a lower yield of the hydrosilated product. The polymerization of methyl methacrylate proceeds in a living fashion.

The Rh(I) complexes such as $RhCl(CO)(PMe_3)_2$ are known to oxidatively add a $X-CX_3$ (X = Cl, Br) bond that is subsequently added across the double bond of alkenes (the Kharasch reaction).[3] A similar reaction of $RhCl(CO)(PPh_3)(NEt_2H)$ with CX_4 (X = Cl, Br, I) does not lead to the oxidative addition product and, instead, produces Rh(III) anionic complexes of the type $[RhCl_4(CO)(PPh_3)]^-[NR_2H_2]^+$ and $[RhCl_nX_{4-n}(CO)(PPh_3)]^-[NR_2H_2]^+$. The anionic complexes $[RhCl_4(CO)(PPh_3)]^-[NEt_2H_2]^+ \cdot {}^1/_2 C_6H_6$ and $[RhCl_{1.15}Br_{2.85}(CO)(PPh_3)]^-[NEt_2H_2]^+$ have been structurally characterized.

Results and Discussion

Synthesis and Characterization of Rh(I) Mixed CO/PPh_3/Amine Complexes. The Rh(I) complexes employed in this study were synthesized by the bridge-splitting reactions[4] of the appropriate rhodium halide dimer, $[Rh(\mu\text{-}Cl)(CO)(PPh_3)]_2$, with 2 equiv of either primary, secondary, or tertiary amine ligand (Scheme 1).

Using this methodology, the monoamine adducts containing primary amines $RhCl(CO)(PPh_3)(H_2NR)$ [R

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Scheme 1

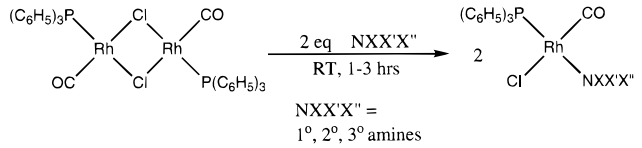

Table 1. $^{31}P\{^1H\}$ NMR and FT-IR Spectral Data for Rh(I) Amine Complexes

complexes	$^{31}P\{^1H\}$ δ (ppm)	$J(^{103}Rh-^{31}P)$ (Hz)	ν_{CO} cm^{-1} (KBr)
$RhCl(CO)(PPh_3)[NH_2Et]$ (**1**)	46.0 (d)	156	1967
$RhCl(CO)(PPh_3)[NH_2(CH_2)_5CH_3]$ (**2**)	45.2 (d)	154	1969
$RhCl(CO)(PPh_3)[NH_2Cy]$ (**3**)	44.5 (d)	155	1969
$RhCl(CO)(PPh_3)[NH_2C(Me_2)CH_2CMe_3]$ (**4**)	45.8 (d)	157	1971
$RhCl(CO)(PPh_3)[HN(CH_3)_2]$ (**5**)	45.3 (d)	151	1964
$RhCl(CO)(PPh_3)[HNEt_2]$ (**6**)	45.3 (d)	153	1954
$RhCl(CO)(PPh_3)[NHPr_2]$ (**7**)	44.8 (d)	153	1962
$RhCl(CO)(PPh_3)[HN(CH(CH_3)_2)_2]$ (**8**)	45.1 (d)	158	1961
$RhCl(CO)(PPh_3)[NHBu_2]$ (**9**)	44.3 (d)	153	1965
$RhCl(CO)(PPh_3)[HN(CH_2CH(CH_3)_2)_2]$ (**10**)	44.4 (d)	155	1968
$RhCl(CO)(PPh_3)[HN(CH_2C_6H_5)_2]$ (**11**)	46.0 (d)	157	1956
$RhCl(CO)(PPh_3)[HN(C_5H_{10})]$ (**12**)	46.2 (d)	150	1960
$RhCl(CO)(PPh_3)[NH(C_4H_8O)]$ (**13**)	46.4 (d)	152	1962
$RhCl(CO)(PPh_3)[HN(C_5H_9)NC_5H_{10}]$ (**14**)	46.1 (d)	150	1957
$RhCl(CO)(PPh_3)[HNEt(CH_3)]$ (**15**)	45.1 (d)	162	1956
$RhCl(CO)(PPh_3)[HN(CH_3)(CH_2C_6H_5)]$ (**16**)	45.7 (d)	154	1965
$RhCl(CO)(PPh_3)[HN(CH_3)(CH_2(C_{14}H_9))]$ (**17**)	46.2 (d)	152	1966
$RhCl(CO)(PPh_3)[NEt_3]$ (**18**)	47.8 (d)	176	1971

$= C_2H_5$ (**1**), $(CH_2)_5CH_3$ (**2**), C_6H_{11} (**3**), $C(CH_3)_2CH_2C(CH_3)_3$ (**4**)], secondary amines $RhCl(CO)(PPh_3)(NRR'H)$ [$R = R' = CH_3$ (**5**), C_2H_5 (**6**), C_3H_7 (**7**), $CH(CH_3)_2$ (**8**), C_4H_9 (**9**), $CH_2CH(CH_3)_2$ (**10**), $CH_2(C_6H_5)$ (**11**), C_5H_{10} (**12**), C_4H_8O (**13**), $C_5H_9NC_5H_{10}$ (**14**); $R = CH_3$, $R' = C_2H_5$ (**15**), $R = CH_3$, $R' = CH_2(C_6H_5)$ (**16**), $R = CH_3$, $R' = CH_2(C_{14}H_9)$ (**17**)], and tertiary amine $RhCl(CO)(PPh_3)(N(C_2H_5)_3)$ (**18**) were isolated in very good yields. These yellow-colored complexes were found to be soluble in a wide range of organic solvents and were characterized by routine spectroscopic and analytical techniques.

The $^{31}P\{^1H\}$ NMR and infrared spectral data for these complexes are presented in Table 1. These complexes typically displayed a doublet in their $^{31}P\{^1H\}$ NMR spectra at ~46 ppm with the Rh−P coupling constant of ~155 Hz, with the exception of the tertiary amine complex **18**, which gave a J_{Rh-P} value of 176 Hz. Their FT-IR spectra showed ν_{CO} stretching frequencies in the range 1954−1971 cm^{-1}. The lowest value was observed for the diethylamine complex **6**, and the highest one for the *tert*-octylamine (**4**) and triethylamine (**18**) complexes.

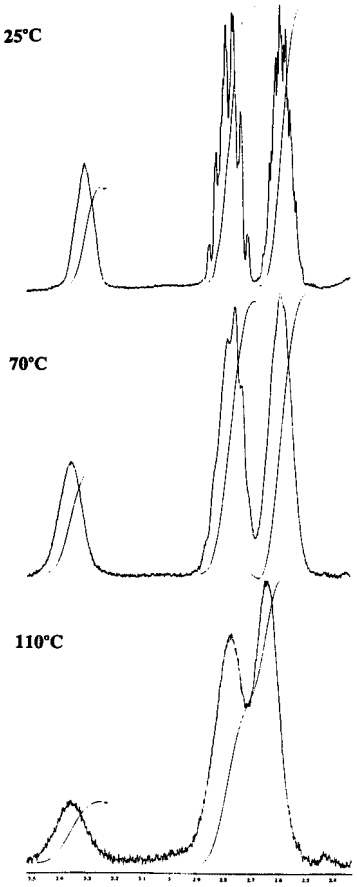

Figure 1. Variable-temperature ^1H NMR spectra (270 MHz, toluene-d_8, CH_2 region) of compound **6**.

The ^1H NMR spectrum of $RhCl(CO)(PPh_3)(NEt_2H)$ (**6**) in C_6D_6 at room temperature showed two broad multiplets at 2.39 and 2.63 ppm in a 1:1 ratio for the CH_2 protons on the ethyl substituents of the amine ligand. The latter indicates that the two CH_2 groups are diastereotopic. Complex **6** has C_s symmetry, and we were intrigued by the possibility of making these methylene hydrogens' chemical shift equivalent at higher temperatures. Heating the sample in toluene-d_8 from 25 to 110 °C resulted in the peaks for the two CH_2 groups merging together (Figure 1). The complete collapsing of the peaks, however, may require higher temperatures, and finding a solvent that has a sufficiently high boiling point and that does not react with the Rh(I) complexes proved to be difficult. A similar pattern was observed for the other complexes containing secondary amine ligands such as **7**, **8**, **9**, **10**, and **11**.

Single-Crystal Structural Characterization of $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ (6) and $RhCl(CO)(PPh_3)(H_2NC_6H_{11})\cdot{}^1/_2C_6H_6$ (3). Yellow sticks of compounds **3** and **6** that were suitable for single-crystal X-ray diffraction studies were obtained from crystallization using a mixture of benzene/hexanes solutions. An ORTEP drawing of **6** is shown in Figure **2**, and the relevant bond lengths and angles are shown in Table 3. The compound crystallizes in a *Pbca* space group with eight molecules in an orthorhombic unit cell. The molecule has a square-planar geometry about rhodium, with the diethylamine ligand trans to triphenylphosphine. The carbonyl ligand is close to linear about the carbon atom, with a Rh−C(1)−O angle of 175.2(8)°. The

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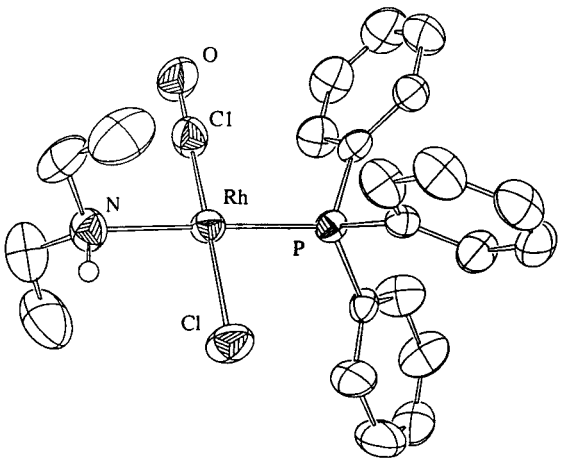

Figure 2. ORTEP drawing of **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms with the exception of N−H have been omitted for clarity.

Table 2. Experimental Data for the X-ray Diffraction Studies of the Rh(I) Amine Complexes

	$RhCl(CO)PPh_3(NEt_2H)$ (**6**)	$RhCl(CO)PPh_3(NCyH_2)$[a] (**3**)
mol formula	$C_{23}H_{26}ClNOPRh$	$C_{28}H_{31}ClNOPRh$
mol wt	501.78	566.87
color	yellow	yellow
cryst system	orthorhombic	monoclinic
space group	Pbca	*C*2/*c*
a, Å	15.805(3)	33.6292(10)
b, Å	26.006(3)	9.07880(10)
c, Å	11.150(2)	24.03910(10)
α, deg	90	90
β, deg	90	134.3054(6)
γ, deg	90	90
V, Å^3	4582.9(13)	5252.29(6)
Z	8	8
D_{calcd}, g cm^{-1}	1.454	1.434
F(000)	2048	2328
μ, mm^{-1}	0.252	0.822
transmission factors: max., min.	0.81, 0.69	0.93, 0.66
temp, K	293(2)	293(2)
cryst size, mm	0.45 × 0.32 × 0.20	0.38 × 0.20 × 0.12
diffractometer	Rigaku AFC6−S	Siemens P4, CCD
radiation	Mo Kα	Mo Kα
θ range, deg	2−25	1.69−26.39
no. of measured rflns	30 368	21 249
no. of independent rflns (R_{int})	4039 (0.073)	5304 (0.0274)
no. of refined params	258	356
no. of restraints	0	39
R1 (obs/all data)	0.056/0.085	0.024/0.060
wR2 (obs/all data)	0.133/0.121	0.033/0.066
GOF	1.156	1.027
largest diff peak, e/Å^3	+0.578, −0.510	+0.401, −0.546

[a] Compound crystallizes with 1/2 molecule of benzene.

N−Rh−P angle of 174.6(2)° reveals a slight shift from an idealized square-planar geometry. The angles between N−Rh−C(1)O, P−Rh−C(1)O, and P−Rh−Cl approach 90°; however, the largest discrepancy is found in the N−Rh−Cl angle that has a value of 84.8(2)°. A comparison of the Rh−P and Rh−C(1) distances in **6** to those in *trans*-$RhCl(CO)(PPh_3)_2$ (Table 3) indicates that the Rh−P bond distance of 2.257(2) Å in **6** is much shorter than that of 2.328(1) Å in *trans*-$RhCl(CO)(PPh_3)_2$.[5] Similarly, the Rh−C(1) bond length (1.783(8) Å) in **6** is slightly longer than that in the bis(phosphine) complex (1.759(1) Å). These results suggest, as expected, that the amine ligand is a weaker donor than a phosphine, which forces the metal center to withdraw more electron density from the bound phosphine, and there is less *π*-back-donation to the CO ligand.

Table 3. Selected Bond Distances and Angles for $RhCl(CO)PPh_3(NEt_2H)$, 6, $RhCl(CO)PPh_3(NCyH_2)$, 3, and $Rh(CO)(Cl)(PPh_3)_2$

	$Rh(CO)(Cl)(PPh_3)(HNEt_2)$ (**6**)	$Rh(CO)(Cl)(PPh_3)(H_2NCy)$ (**3**)	$Rh(CO)(Cl)(PPh_3)_2$[a]
	Distances (Å)[b]		
Rh−C(1)	1.783(8)	1.802(2)	1.759 (1)
Rh−N	2.183(6)	2.173(5)	
Rh−P	2.257(2)	2.264(5)	2.328(1)
Rh−Cl	2.364(2)	2.384(6)	2.380(2)
P−C(31)	1.825(7)	1.835(2)	1.826(4)
P−C(21)	1.831(7)	1.829(2)	1.821(4)
P−C(11)	1.836(6)	1.838(2)	1.826(4)
O−C(1)	1.148(8)	1.144(3)	1.14(1)
N−C(2)	1.470(9)	1.485(5)	
N−C(4)	1.478(11)		
N−H	0.91	0.90	
	Angles (deg)[b]		
C(1)−Rh−N	92.3(3)	85.8(3)	
C(1)−Rh−P	91.0(2)	91.6(7)	92.1(2)
N−Rh−P	174.6(2)	172.8(12)	
C(1)−Rh−Cl	174.3(3)	176.7(7)	179.7(3)
N−Rh−Cl	84.8(2)	91.1(3)	
P−Rh−Cl	91.7(7)	92.7(2)	87.8(5)
Rh−C(1)−O	175.2(8)	178.4(2)	177.2(9)

[a] Reference 2. [b] Estimated standard deviations in the least significant figure are given in parentheses.

The solid-state FT-IR spectrum of **6** displayed a sharp N−H stretching vibration at 3247 cm^{-1} with a shoulder at 3439 cm^{-1}, in addition to the ν_{CO} stretch at 1954 cm^{-1}. This suggests that there may be two types of amine groups, free and hydrogen bonded.[6] A number of possibilities for the formation of the R−*H*−*X*−R′ bonds can be considered:[7] (i) intermolecular hydrogen bonding (a) between the nitrogen atom of a bound amine ligand and the amine ligand of another complex (type I, Scheme 2); and (b) with the chloride ligand of another complex (type II, Scheme 2); (ii) intramolecular hydrogen bonding between the hydrogen atom of the amine ligand and the chloride ligand (type III, Scheme 2); with the rhodium center (type IV, Scheme 2) or with the oxygen atom of the carbonyl ligand (type V, Scheme 2). An examination of the packing diagram and of interatomic contacts of **6** suggests that intramolecular hydrogen bonding of type III and intermolecular hydrogen bonding of type V are involved in the formation of hydrogen bonds in which the hydrogen atom on the bound amine ligand interacts with the chloride and the carbonyl oxygen of a neighboring complex. The hydrogen-to-Cl and -O distances in this complex were found to be 2.636 and 2.392 Å, respectively. A typical hydrogen bond distance in NH···O systems is in the range

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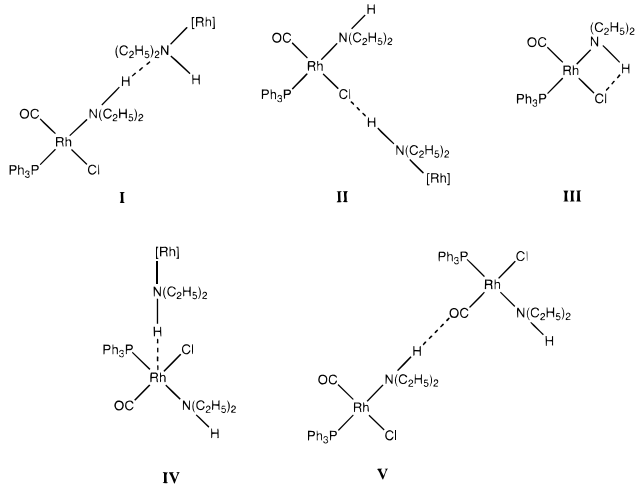
Scheme 2. Potential Hydrogen Bonding Modes for $Rh(CO)(Cl)(PPh_3)(NEt_2H)$



1.60−2.40 Å.[8] Taking into account the difference in van der Waals radii of transition metals relative to oxygen[7a,9] should result in an additional increase of 0.6−0.85 Å with an expected hydrogen bond distance in the range 2.20−3.25 Å. The hydrogen-to-acceptor distances at 2.636 Å for H···Cl and 2.392 Å for H···O≡C fall within this range.

Intermolecular hydrogen bonding between the bound amine and CO ligands in **6** may be responsible for the lower CO stretching frequency in this compound compared to the other mixed CO/PPh_3/amine complexes (Table 1) and with the bisphosphine complex *trans*-$RhCl(CO)(PPh_3)_2$ (1960 cm^{-1}).[5]

Compound **3** containing a primary amine ligand, $RhCl(CO)(PPh_3)(H_2NCy)$, crystallizes in a *C*2/*c* (monoclinic) space group with eight molecules in the unit cell. The complex displays a local geometry (Figure 4) that is similar to that described above for **6**. The Rh−C(1)O bond distance of 1.802(2) Å is longer than that in the bis(phosphine)complex (1.759(1) Å) and even that in complex **6** (1.783(8) Å) (Table 3). As in **6**, the Rh−P distance of 2.264(5) Å is shorter than that in *trans*-$RhCl(CO)(PPh_3)_2$ (2.328(1) Å). The bond angles in **3** are similar to those for **6**.

The packing diagram of **3** (Figure 5) also suggests intramolecular hydrogen bonding of type III similar to complex **6** with a H−Cl bond length of 2.532 Å. There may also be some intermolecular hydrogen bonding between the amine hydrogen and a ligated chloride of a neighboring molecule (2.561 Å) in the solid-state structure.

Amine Exchange in Rh(I) Mixed CO/Phosphine/Amine Complexes. The amine ligand in the abovementioned Rh(I) complexes can be easily displaced with strong donor phosphine ligands. For example, the reaction of 1 equiv of $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ (**6**) with 1 equiv of triphenylphosphine (PPh_3) in benzene led to an immediate and exclusive formation of *trans*-$RhCl(CO)(PPh_3)_2$ with the liberation of diethylamine. When equimolar amounts of **6** and trimethylphosphine (PMe_3) were reacted, it resulted in the formation of a mixture of $RhCl(CO)(PMe_3)_2$ and $RhCl(CO)(PPh_3)(PMe_3)$. A similar reaction with 2 equiv of PMe_3 yielded $RhCl(CO)(PMe_3)_2$ as the only product. The latter can be explained by taking into account the stronger electron-donating ability of PMe_3 than both amine and PPh_3 ligands, and it exchanges with both of these ligands in **6**.

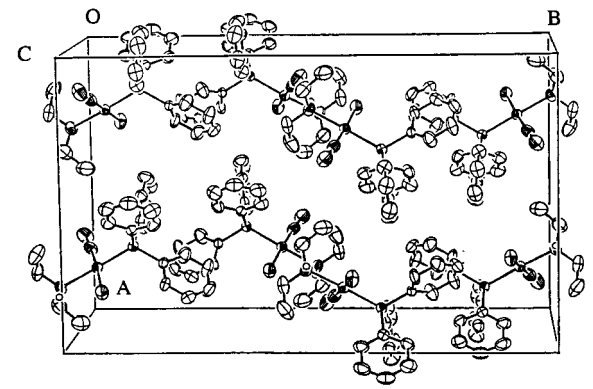


Figure 3. Packing diagram of **6** drawn at the 30% probability level. Hydrogen atoms with the exception of N−H have been omitted for clarity.

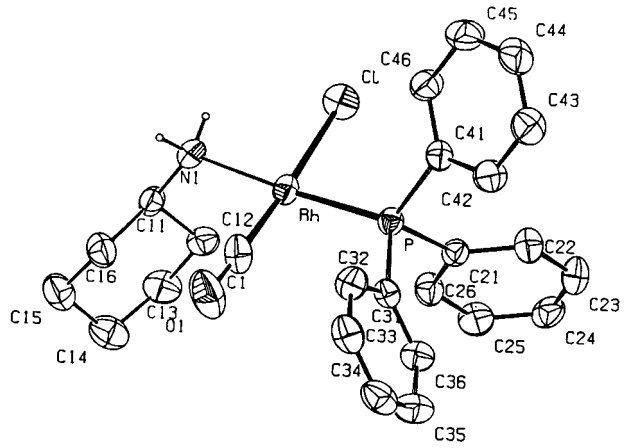


Figure 4. PLATON drawing of the structure **3**. Thermal ellipsoids are drawn at the 40% probability level. The asymmetric unit also contains 1/2 molecule of benzene. Hydrogen atoms with the exception of N−H have been omitted for clarity.

Reactivity of Rh(I) Amine Complexes toward Haloalkanes. It is known that perhaloalkanes can be added to alkenes (the Kharasch reaction)[10] in the presence of Rh(I) complexes and may proceed via initial oxidative addition of the haloalkane to rhodium followed by a rapid transfer to the coordinated alkene.[11] It has been shown that $RhCl(CO)(PMe_3)_2$ oxidatively adds $Br-CCl_3$, and the resulting product, $RhClBr(CCl_3)(CO)(PMe_3)_2$, has been structurally characterized.[3] A similar reaction of $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ (**6**) and CX_4 (X = Cl, Br, I) in benzene did not lead to the formation of

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Table 4. Inter- and Intramolecular Hydrogen[a] Bond Distances (Å) and Angles (deg) for $RhCl(CO)(PPh_3)(H_2NCy)$ (3) and $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ (6)

	donor−H···acceptor	D···A	D−H	H···A	D−H···A	H−bonding
6	N−H···O_a	3.251(9)	0.910	2.392	157.4(6)	intermolecular
	N−H···Cl	3.067(8)	0.910	2.636	109.9(5)	intramolecular
3	N−H···Cl	2.950(5)	0.900	2.532	108.97(7)	intermolecular
	N−H···Cl_a	3.346(5)	0.900	2.561	146.12(10)	intramolecular

[a] Distances involving H atoms have no error associated since the H position is calculated and not refined. O_a: $0.5 - x$, $1 - y$, $0.5 + z$. Cl_a: $0.5 - x$, $0.5 + y$, $0.5 - z$.

Table 5. Experimental Data for the X-ray Diffraction Studies of Rh(III) Amine Complexes

	$[RhCl_4(CO)PPh_3]^-(NEt_2H_2)^+$ (**19**)[a]	$[RhBr_{2.85}Cl_{1.15}(CO)PPh_3]^-(NEt_2H_2)^+$ (**20**)[a]
mol formula	$C_{26}H_{30}Cl_{14}NOPRh$	$C_{26}H_{30}Br_{2.85}Cl_{1.15}NOPRh$
mol wt	648.22	774.91
color	yellow	red
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
a, Å	21.343(4)	21.5826(3)
b, Å	9.793(2)	9.93590(10)
c, Å	29.547(4)	29.39560 (10)
α, deg	90	90
β, deg	110.85(2)	111.3868(8)
γ, deg	90	90
V, Å^3	5771(2)	5869.59(10)
Z	8	8
D_{calcd}, g cm^{-1}	1.492	1.754
F(000)	2632	3042 3192
μ, mm^{-1}	1.030	4.602
transmission factor: max., min.	0.99, 0.89	1.00, 0.98
temp, K	293(2)	293(2)
cryst size, mm	0.32 × 0.32 × 0.09	0.17 × 0.14 × 0.10
diffractometer	Rigaku AFC6-S	Siemens Smart CCD
radiation	Mo Kα	Mo Kα
θ range, deg	2.04−24.97	1.48−28.65
no. of measured rflns	19 666	33 346
independent rflns (R_{int})	5081 (0.138)	7559 (0.0553)
no. of refined params	308	325
no. of restraints	16	3
R1 (obs/all data)	0.0881/0.0959	0.0376/0.0630
wR2 (obs/all data)	0.1887/0.1192	0.0670/0.0715
GOF	1.088	1.047
largest diff peak, e/Å^3	+0.712, −0.524	+0.547, −0.496

[a] Compound crystallizes with 1/2 molecule of benzene.

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the oxidative-addition product, but instead yielded air-stable Rh(III) anionic salts, $[RhCl_4(CO)(PPh_3)]^-(H_2NEt_2)^+$, **19**, $[RhBr_3Cl(CO)(PPh_3)]^-(H_2NEt_2)^+$, **20**, and $[RhI_3Cl(CO)(PPh_3)]^-(H_2NEt_2)^+$, **21**, respectively. Complexes **19** and **20** have been structurally characterized.

Single-Crystal Structure Characterization of $[RhCl_4(CO)(PPh_3)]^-(H_2NEt_2)^+ \cdot {}^1/_2C_6H_6$ (19) and $[RhBr_{2.85}Cl_{1.15}(CO)(PPh_3)]^-(H_2NEt_2)^+ \cdot {}^1/_2C_6H_6$ (20). Yellow crystals of $[RhCl_4(CO)(PPh_3)]^-(H_2NEt_2)^+ \cdot {}^1/_2C_6H_6$ (**19**) suitable for analysis were grown from C_6H_6 at 50 °C. The ORTEP diagram of **19** is shown in Figure 6, the crystal data are presented in Table 5, and selected bond lengths and angles are given in Table 6. Complex **19** crystallizes in a *C*2/*c* space group with eight molecules in a monoclinic unit cell. The core geometry of the anion is octahedral with the triphenylphosphine and carbonyl ligands positioned in a cis orientation, and the protonated amine acts as the counterion. The carbonyl ligand is slightly bent about the carbon atom with a Rh−C(1)−O angle of 174.0(9)°. The large bond angle of 96.0(3)° for P−Rh−C(1)O is probably due to the steric repulsion of the triphenylphosphine ligand, resulting in a marked decrease for the OC(1)−Rh−Cl(4) (83.5(3)°) and OC(1)−Rh−Cl(2) (172.3(3)°) angles. The angles between OC(1)−Rh−Cl(1), OC(1)−Rh−Cl(3), P−Rh−Cl(1), P−Rh−Cl(2), P−Rh−Cl(3), and P−Rh−Cl(4) approach those expected for an idealized octahedral geometry. A comparison of the Rh−C(1) distance in **19** to that of **6** indicates that the Rh−C(1) bond length of 1.851(11) Å in **19** is slightly longer than that in **6** (1.783(8) Å). Similarly, the Rh−P bond distance in **19** (2.323(2) Å) is significantly longer than that found in the Rh(I) complex **6** (2.257(2) Å). As expected, the presence of four bound chloride ligands decreases the metal's ability to back-donate to the CO ligand, thus lengthening the Rh−

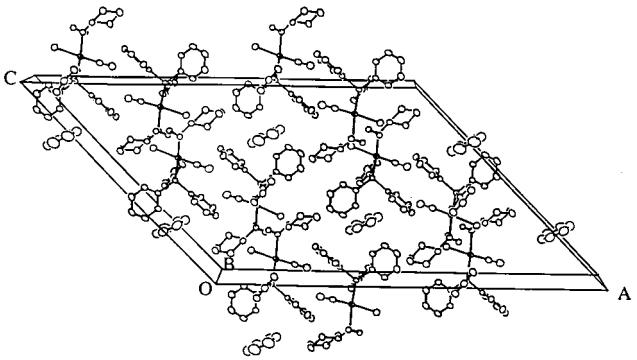

Figure 5. Packing diagram (solvent omitted) of **3**.

Table 6. Selected Bond Distances and Angles for Rh(III) Anionic Complexes[a]

	$[RhCl_4(CO)(PPh_3)]^-$ $(NEt_2H_2)^+$ (**19**)[b]	$[RhBr_{2.85}Cl_{1.15}(CO)(PPh_3)]^-$ $(NEt_2H_2)^+$ (**20**)[b]
	Distances (Å)	
Rh−C(1)O	1.851(11)	1.905(4)
Rh−P	2.323(2)	2.3308(9)
P−C(31)	1.827(8)	1.834(3)
P−C(21)	1.835(9)	1.825(3)
P−C(11)	1.815(8)	1.829(3)
O−C(1)	1.062(4)	1.132(10)
Rh−Cl(1)	2.345(2)	2.35(2)
Rh−Cl(2)	2.357(2)	2.34(2)
Rh−Cl(3)	2.348(3)	2.36(2)
Rh−Cl(4)	2.409(3)	2.411(11)
Rh−Br(1)		2.498(2)
Rh−Br(2)		2.4974(14)
Rh−Br(3)		2.483(3)
Rh−Br(4)		2.520(3)
	Angles (deg)	
C(1)−Rh−P	96.0(3)	96.11(1)
C(1)−Rh-Cl(1)	87.1(3)	88.0(10)
C(1)−Rh−Cl(2)	172.3(3)	171.1(7)
C(1)−Rh−Cl(3)	88.3(3)	88.4970
C(1)−Rh−Cl(4)	83.5(3)	76.5(2)
Rh−C(1)−O	174.0(9)	175.6(4)
C(1)−Rh−Br(1)		88.0(2)
C(1)−Rh−Br(2)		171.30(13)
C(1)−Rh−Br(3)		86.0(2)
C(1)−Rh−Br(4)		83.10(12)
P−Rh−Cl(1)	92.54(9)	89.6(10)
P−Rh−Cl(2)	91.57(9)	91.5(7)
P−Rh−Cl(3)	89.4(9)	92.9(8)
P−Rh−Cl(4)	178.41(10)	171.9(2)
P−Rh−Br(1)		89.04(13)
P−Rh−Br(2)		92.44(7)
P−Rh−Br(3)		93.16(13)
P−Rh−Br(4)		178.30(6)

[a] Estimated standard deviations in the least significant figure are given in parentheses. [b] Compound crystallizes with 1/2 molecule of benzene.

C(1) bond length. This also has a pronounced effect on the C(1)−O bond distance (1.062(4) Å), which is shorter than that in **6** (1.148(8) Å). The Rh−Cl bond distances decrease on going from the Rh(I) to the Rh(III) complex, with the exception of the chloride ligand trans to a carbonyl that has a bond length of 2.357(2) Å, similar to the Rh−Cl bond distance in $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ (2.364(2) Å).

Red prisms of **20** suitable for X-ray analysis crystallized directly out of benzene after 24 h at ambient temperature. Compound **20** crystallizes ($[RhBr_{2.85}Cl_{1.15}(CO)(PPh_3)]^-(H_2NEt_2)^+ \cdot {}^1/_2C_6H_6$, Figure 7, Tables 5 and 6) in a *C*2/*c* space group with eight molecules in the monoclinic unit cell. The geometry of the molecule is similar to **19**; however, the halogen atoms bound to rhodium show disorder, each site being occupied by a mixture of chlorine and bromine atoms. The final occupancy factors for the Cl/Br sites indicate a nonstoichiometric compound with average positions of Br 2.85 and Cl 1.15. Imposing occupancies of Br atoms to a total of 3.00 and 1.00 for Cl led to a significantly higher disagreement factor as well as negative residues near the Br sites. Complex **20** ($[RhBr_{2.85}Cl_{1.15}(CO)(PPh_3)]^-(H_2NEt_2)^+ \cdot {}^1/_2C_6H_6$) is a mixture mainly of the $[RhBr_3Cl(CO)(PPh_3)]^-(H_2NEt_2)^+$ and $[RhBr_2Cl_2(CO)(PPh_3)]^-(H_2NEt_2)^+$, but may also contain other compositions such as $[RhBr_4(CO)(PPh_3)]^-(H_2NEt_2)^+$ and $[RhCl_4(CO)(PPh_3)]^-(H_2NEt_2)^+$.

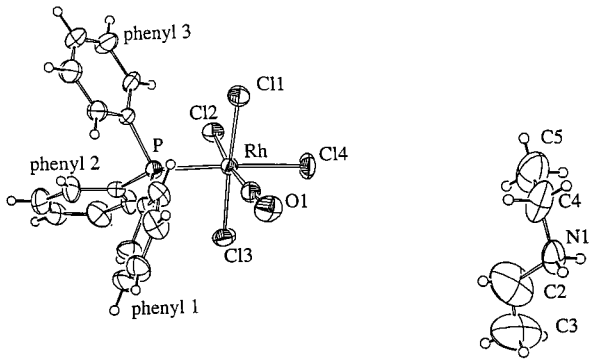

Figure 6. ORTEP view of the anion and cation of $[RhCl_4(CO)(PPh_3)]^-(H_2NEt_2)^+ \cdot {}^1/_2C_6H_6$ (**19**). The asymmetric unit also contains 1/2 molecule of benzene. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are represented as spheres of arbitrary size.

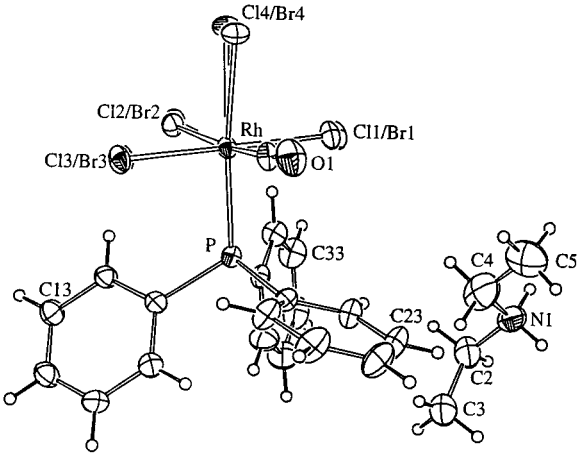

Figure 7. ORTEP view of the anion and cation of $[RhBr_{2.85}Cl_{1.15}(CO)(PPh_3)]^-(H_2NEt_2)^+ \cdot {}^1/_2C_6H_6$ (**20**). The asymmetric unit also contains 1/2 molecule of benzene. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are represented as spheres of arbitrary size.

The carbonyl ligand is close to linear about the carbon atom with a Rh−C(1)O angle of 175.6(4)°. The Rh−P, Rh−C(1)O, and C(1)−O bond distances are longer than for compound **19** (Table 6). The bond angles between C(1)−Rh−Cl(1)/C(1)−Rh−Br(1), C(1)−Rh−Cl(3)/C(1)−Rh−Br(3), P−Rh−Cl(1)/P−Rh−Br(1), P−Rh−Cl(2)/P−Rh−Br(2), and P−Rh−Cl(3)/P−Rh−Br(3) approach idealized octahedral geometry. The C(1)−Rh−Cl(2)/C(1)−Rh−Br(2) and C(1)−Rh−Cl(4)/C(1)−Rh−Br(4) bond angles at 171.1(7)°/171.3(13)° and 76.5(2)°/83.1(12)° are shorter than those present in **19**. The Cl/Br ligands trans to triphenylphosphine exhibit longer Rh−X bond lengths than all other halogens. This trend is also present in compound **19**.

The lability of the diethylamine ligand in **6** may be responsible for the formation of the Rh(III) anionic salts. For example, the displacement of the diethylamine ligand by a chlorine in CCl_4 may lead to the formation of the Rh(I) complex $RhCl(CO)(PPh_3)(Cl-CCl_3)$, which might rearrange to give the Rh(III) complex, $RhCl_2(CCl_3)(CO)(PPh_3)$. The latter may undergo a reaction with another molecule of CCl_4, yielding $RhCl_3(CO)(PPh_3)$, which reacts further with CCl_4 and diethylamine to yield the Rh(III) salt $[RhCl_4(CO)(PPh_3)]^-(H_2NEt_2)^+$.

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Hydrosilylation of 1-Hexene. Rh(I) complexes have been studied as catalysts for the hydrosilylation of olefins[11] and give rise to relatively little isomerization in the product distribution. In view of the similarities of the $RhCl(CO)(PPh_3)_2$ complex to $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ (**6**), an investigation was undertaken of some of the possible differences between these two catalysts. The hydrosilation of 1-hexene with triphenylsilane or phenyldimethylsilane in the presence of catalytic amounts of **6** and refluxing at 60 °C for 30 min in benzene led to the formation of the terminal *n*-hexyl product in 85−89% yield as determined by ^{1}H NMR and GC−MS. It has been demonstrated that the hydrosilation of 1-hexene with triphenylsilane can be catalyzed using $RhCl(CO)(PPh_3)_2$ upon refluxing at 60 °C for 6 days with a 75% yield of the product silane.[11b] The turnover efficiency of this reaction is 1.81 h^{-1}, which is significantly lower than with complex **6** at 86.5 h^{-1} for triphenylsilane and 155.8 h^{-1} for phenyldimethylsilane. There is no difference in catalyst selectivity between $RhCl(CO)(PPh_3)_2$ and complex **6**; however, in terms of activity, **6** is significantly more active, producing a greater amount of the *n*-hexyl product in a shorter reaction time. The hydrosilation of 1-pentene with phenyldimethylsilane in the presence of Wilkinson's catalyst[11a] ($RhCl(PPh_3)_3$) resulted in a turnover efficiency of 22.2 h^{-1}. The silane and olefin concentrations, reaction conditions, and yields for the latter reaction were similar to those with complex **6** for the hydrosilation of 1-hexene. The first step in the hydrosilation of olefins involves ligand dissociation followed by the oxidative addition of the silane and coordination of the alkene.[11] In the reaction with **6**, the initial step may involve dissociation of the diethylamine ligand since it is more labile than the phosphine ligand and may be responsible for an overall increase in the reaction rate.

Polymerization of Styrene and Methyl Methacrylate Using Rh(I) Amine Complexes. Metal carbonyls in the presence of organohalides are known to initiate the free radical polymerization of styrene and methyl methacrylate (MMA).[12] Low-valent metal complexes such as *trans*-$PtHCl(PPh_3)_2$, *trans*-$Rh(CO)Cl(PPh_3)_2$, $Pd(PPh_3)_4$, $RuCl_2(PPh_3)_3$, and $NiBr_2(PPh_3)_2$, in the presence of alkyl halides, have also been shown to act as radical initiators in the polymerization of MMA and styrene.[13,14] We were intrigued by the possibility of polymerizing MMA and styrene by Rh(I) mixed CO/amine/phosphine complexes in the presence of perhaloalkanes. It was found that $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ (**6**) in the presence of CCl_4 was a very good catalyst for the polymerization of MMA ($M_n = 6.6 \times 10^4$) and styrene ($M_n = 6.1 \times 10^3$). The polymerization could not be initiated with either **6** or $[RhCl_4(CO)(PPh_3)]^-(H_2NEt_2)^+$ alone under similar conditions. These results suggest that the polymerization may proceed via a free radical pathway in which the complex catalyzes the activation of one of the carbon−chlorine bonds in carbon tetrachloride to generate the trichloromethyl radical ($CCl_3^\bullet$), which then adds to the carbon−carbon double bond of the olefin, followed by the formation of the olefin−CCl_4 adduct with a terminal C−Cl bond.[12,14]

To examine the living nature of the methyl methacrylate polymerization process,[14c] a fresh feed of MMA was added to the reaction mixture when the initial charge of the monomer had been consumed. The added monomer was smoothly polymerized, and the M_n of the polymer increased with each monomer addition. The molecular weight distributions were not narrow initially; however, they became narrower as conversion increased. This suggests that the polymerization of MMA catalyzed by $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ in the presence of CCl_4 proceeds in a living fashion where the Rh(I) complex acts as a redox initiator, reversibly activating the covalent carbon−halogen bond in CCl_4.

Conclusions

Stable d^8-Rh(I) complexes containing mixed CO/phosphine/amine ligands can be easily prepared form the Rh(I) dimer, $[Rh(\mu\text{-}Cl)(CO)(PPh_3)]_2$, and primary, secondary, and tertiary amines via bridge-splitting reactions. These complexes depict a typical square-planar geometry at the rhodium center with the amine ligand trans to triphenylphosphine, as evidenced by the single-crystal structure determinations of $RhCl(CO)(PPh_3)(H_2NCy)$ and $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$. There is evidence for intramolecular hydrogen bonding between the amine hydrogen and a bound chloride ligand. The crystal structure of $RhCl(CO)(PPh_3)(H_2NCy)$ also suggests intermolecular hydrogen bonding between the amine hydrogen and chloride ligand of another molecule, while that of the complex $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ suggests intermolecular hydrogen bonding between the amine hydrogen and the carbonyl oxygen of a neighboring molecule. The compound $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ does not yield an oxidative addition product upon reacting with perhaloalkanes such as CX_4, but generates the Rh(III) anionic salt of the type $[RhCl_4(CO)(PPh_3)]^-(H_2NEt_2)^+$, which has been structurally characterized. $RhCl(CO)(PPh_3)(HN(C_2H_5)_2)$ catalyzes hydrosilation of 1-hexene and free radical polymerization of styrene and methyl methacrylate. The preliminary results suggest that the polymerization of methyl methacrylate by this complex in the presence of CCl_4 is a living polymerization.

Experimental Section

Materials and Measurements. All manipulations and reactions were carried out under a nitrogen atmosphere either using standard Schlenk techniques or in an Innovative Technology (Braun) Labmaster MB-150 drybox. Toluene, benzene, and hexanes were stored under nitrogen after being distilled over sodium. Amines used were dried and distilled over KOH and degassed prior to use. Carbon tetrachloride was dried and distilled over P_2O_5 before use. μ-Chloro(carbonyltriphenylphosphine)rhodium (I) dimer (**1a**) was prepared and purified according to literature methods.[4a] Unless otherwise specified, all other reagents were obtained from the usual commercial suppliers and used as received. NMR spectra were measured on a JEOL 270 MHz spectrometer at ambient temperatures unless otherwise specified. All NMR samples were prepared under a nitrogen atmosphere in either C_6D_6 or $CDCl_3$. Chemical shifts (ppm) reported are relative to tetramethylsilane as

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an internal standard for ^{1}H NMR spectra and to H_3PO_4 for $^{31}P\{^1H\}$ NMR spectra. Coupling constants (J) are given in hertz. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were obtained using a low-resolution KRATOS MS25RSA spectrometer with xenon as the ionizing gas and nitrobenzyl alcohol as the matrix. MALDI-TOF mass spectra were obtained on a Kratos Kompact Maldi 3 v.4.0.0 spectrometer using LiBr/didronel as the matrix. Infrared spectra were recorded on a Bruker IFS-48 Fourier transform infrared spectrometer using a standard resolution of 4 cm^{-1} for transmission. Molecular weights of the polymers were obtained on a Waters 441 Millipore GPC using polystyrene as the internal standard. Elemental analyses were performed by either Microanalytical Service Ltd. (Chemical Engineering), Montreal, Quebec, or Guelph Chemical Laboratory, Guelph, Ontario.

RhCl(CO)(PPh$_3$)[NH$_2$(CH$_2$CH$_3$)] (1): General Procedure. A solution of μ-chloro(carbonyltriphenylphosphine)-rhodium (I) dimer (**1a**) (40 mg, 0.0467 mmol) and ethylamine (0.027 mL, 0.093 mmol) in toluene (10 mL) was stirred at room temperature for 1 h. The resulting pale yellow solution was evaporated under vacuum and washed with hexanes. A microcrystalline solid was recrystallized from benzene and dried under vacuum to give (**1**) (42.5 mg, 96%). ^{1}H NMR (270 MHz, C_6D_6): δ 1.70 (3H, t, J_{H-H} = 6.9 Hz, CH_3), 2.45 (2H, q, J_{H-H} = 5.6 Hz, CH_2N), 3.57 (2H, br s, H_2N), 7.05, 7.95 (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 46.0 (d, J_{Rh-P} = 155.8 Hz). IR (KBr): ν_{CO} 1967.5 cm^{-1}. FAB-MS: m/z 474.75. Anal. Calcd for $C_{21}H_{22}$PONClRh (473.73): C, 53.24; H, 4.68; N, 2.96. Found: C, 53.35; H, 4.91; N, 2.45.

RhCl(CO)(PPh$_3$)[NH$_2$(CH$_2$)$_5$CH$_3$] (2). Reaction of hexylamine (7.69 μL, 2.94 mg, 0.0583 mmol) and **1a** (25 mg, 0.0292 mmol) using a procedure analogous to the preparation of **1** led to the isolation of **2** (26.5 mg, 86%) as an orange solid. ^{1}H NMR (270 MHz, C_6D_6): δ 0.85 (3H, t, J_{H-H} = 6.9 Hz, CH_3), 0.98 (4H, m, CH_2CH_2), 1.17 (4H, m, CH_2CH_2), 2.52 (2H, t, J_{H-H} = 5.2 Hz, CH_2N), 2.69 (2H, s, H_2N), 7.08, 7.96 (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 45.2 (d, J_{Rh-P} = 154.4 Hz). IR (KBr): ν_{CO} 1969.5 cm^{-1}. FAB-MS: m/z 529.08. Anal. Calcd for $C_{25}H_{30}$PONClRh (529.85): C, 56.67; H, 5.71; N, 2.64. Found: C, 56.36; H, 5.74; N, 2.76.

RhCl(CO)(PPh$_3$)[NH$_2$(C$_6$H$_{11}$)] (3). Reaction of cyclohexylamine (4.81 μL, 4.17 mg, 0.084 mmol) and [Rh(CO)(Cl)(PPh$_3$)]$_2$ (36 mg, 0.042 mmol) using a procedure analogous to the preparation of **1** led to the isolation of **3** (42.7 mg, 96%) as a yellow microcrystalline solid. ^{1}H NMR (270 MHz, C_6D_6): δ 0.90 (6H, m, CH_2), 1.89 (4H, m, CH_2), 2.61 (1H, m, CHN), 2.83 (2H, s, H_2N), 7.05, 8.00 (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 44.5 (d, J_{Rh-P} = 154.6 Hz). IR (KBr): ν_{CO} 1968.9 cm^{-1}. FAB-MS: m/z 527.5. Anal. Calcd for $C_{25}H_{28}$PONClRh (527.83): C, 56.89; H, 5.35; N, 2.65. Found: C, 56.19; H, 5.61; N, 2.80.

RhCl(CO)(PPh$_3$)[NH$_2$C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$] (4). Reaction of *tert*-octylamine (7.5 μL, 6.02 mg, 0.047 mmol) and **1a** (20 mg, 0.0233 mmol) using a procedure analogous to the preparation of **1** led to the isolation of **4** (23.9 mg, 88%) as a yellow/orange solid. ^{1}H NMR (270 MHz, C_6D_6): δ 0.82 (9H, s, (CH_3)$_3$C), 1.03 (2H, s, CH_2), 1.25 (6H, s, (CH_3)$_2$C), 3.17 (2H, s, H_2N), 7.04, 7.98 (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 45.8 (d, J_{Rh-P} = 156.7 Hz). IR (KBr): ν_{CO} 1971.0 cm^{-1}. FAB-MS: m/z 557.15. Anal. Calcd for $C_{27}H_{34}$PONClRh (557.89): C, 58.13; H, 6.14; N, 2.51. Found: C, 57.82; H, 6.07; N, 2.55.

RhCl(CO)(PPh$_3$)[HN(CH$_3$)$_2$] (5). A mixture of dimethylamine (0.050 mL, 0.064 mmol) and **1a** in THF (27.6 mg, 0.0322 mmol) was stirred at ambient temperature for 3 h, followed by extraction of the product and drying the residue in vacuo. Recrystallizing from THF/hexanes mixture led to the isolation of **5** (28.6 mg, 94%) as a pale yellow solid. ^{1}H NMR (270 MHz, C_6D_6): δ 2.23 (6H, d, J_{H-H} = 6.3 Hz, CH_3N), 3.10 (1H, br s, NH), 7.01, 7.92 (15H, m, P(C_6H_5)$_3$). ^{31}P$\{^1H\}$ NMR (109 MHz, C_6D_6): δ 45.3 (d, J_{Rh-P} = 151 Hz). IR (KBr): ν_{CO} 1963.9 cm^{-1}. FAB-MS: m/z 473.6. Anal. Calcd for $C_{21}H_{22}$PONClRh (473.74): C, 53.24; H, 4.68; N, 2.96. Found: C, 53.11; H, 4.61; N, 2.67.

RhCl(CO)(PPh$_3$)[HN(CH$_2$CH$_3$)$_2$] (6). A solution of **1a** (25 mg, 0.029 mmol) and diethylamine (6.04 μL, 0.058 mmol) in toluene (10 mL) was stirred at room temperature for 1 h. The resulting pale yellow solution was evaporated under vacuum and washed with hexanes. A microcrystalline solid was recrystallized from benzene and dried under vacuum to give **6** (28.3 mg, 97%). ^{1}H NMR (270 MHz, C_6D_6): δ 1.34 (6H, t, J_{H-H} = 7.2 Hz, CH$_2$CH_3), 2.39 (2H, m, J_{H-H} = 4.6 Hz, CH_2-CH$_3$), 2.63 (2H, m, J_{H-H} = 4.6 Hz, CH_2CH$_3$), 3.31 (1H, br s, NH), 7.01, 7.91, (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 45.3 (d, J_{Rh-P} = 153.4 Hz). IR (KBr): ν_{CO} 1954.4 cm^{-1}. FAB-MS: m/z 501.82. Anal. Calcd for $C_{23}H_{26}$PONClRh (501.79): C, 55.05; H, 5.22; N, 2.79. Found: C, 55.16; H, 5.30; N, 2.75.

RhCl(CO)(PPh$_3$)[NH(CH$_2$CH$_2$CH$_3$)$_2$] (7). Reaction of dipropylamine (6.38 μL, 4.71 mg, 0.047 mmol) and **1a** (20 mg, 0.0233 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **7** (23.2 mg, 94%) as a pale yellow microcrystalline solid. ^{1}H NMR (270 MHz, C_6D_6): δ 0.81 (3H, t, J_{H-H} = 7.2 Hz, CH_3), 1.87 (2H, m, J_{H-H} = 4.8 Hz CH_2CH$_3$), 2.14 (2H, m, J_{H-H} = 5.3 Hz, CH_2CH$_3$), 2.41 (2H, m, J_{H-H} = 6.9 Hz, CH_2N), 2.76 (2H, m, J_{H-H} = 6.8 Hz, CH_2N), 3.55 (1H, br s, HN), 7.13, 7.98 (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 44.8 (d, J_{Rh-P} = 153.5 Hz). IR (KBr): ν_{CO} 1962.0 cm^{-1}. FAB-MS: m/z 529.03. Anal. Calcd for $C_{25}H_{30}$-PONClRh (529.85): C, 56.67; H, 5.71; N, 2.64. Found: C, 56.90; H, 5.85; N, 2.81.

RhCl(CO)(PPh$_3$)[HN(CH(CH$_3$)$_2$)$_2$] (8). Reaction of diisopropylamine (0.0119 mL, 8.64 mg, 0.085 mmol) and **1a** (36.6 mg, 0.0427 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **8** (43.9 mg, 97%) as a yellow solid. ^{1}H NMR (270 MHz, C_6D_6): δ 1.13 (6H, d, J_{H-H} = 6.3 Hz, CH(CH_3)$_2$), 1.42 (6H, d, J_{H-H} = 6.6 Hz, CH(CH_3)$_2$), 2.77 (2H, h, J_{H-H} = 6.3 Hz, CH(CH$_3$)$_2$), 3.82 (1H, br s, NH), 7.02, 7.90 (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 45.1 (d, J_{Rh-P} = 158 Hz). IR (KBr): ν_{CO} 1961.0 cm^{-1}. FAB-MS: m/z 529.03. Anal. Calcd for $C_{25}H_{30}$PONClRh (529.85): C, 56.67; H, 5.71; N, 2.64. Found: C, 56.52; H, 5.74; N, 2.58.

RhCl(CO)(PPh$_3$)[NH(CH$_2$CH$_2$CH$_2$CH$_3$)$_2$] (9). Reaction of dibutylamine (8.24 μL, 6.32 mg, 0.049 mmol) and **1a** (21 mg, 0.0245 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **9** (25.8 mg, 94%) as a pale yellow solid. ^{1}H NMR (270 MHz, C_6D_6): δ 0.88 (3H, t, J_{H-H} = 7.3 Hz, CH_3), 1.27 (4H, m, CH_2CH$_3$), 1.89 (2H, m, J_{H-H} = 5.6 Hz, CH_2CH$_2$CH$_3$), 2.14 (2H, m, J_{H-H} = 5.6 Hz, CH_2CH$_2$CH$_3$), 2.51 (2H, m, J_{H-H} = 5.5 Hz, CH_2N), 2.82 (2H, m, J_{H-H} = 5.3 Hz, CH_2N), 3.58 (1H, br s, HN), 7.02, 7.91 (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 44.3 (d, J_{Rh-P} = 153.3 Hz). IR (KBr): ν_{CO} 1965.0 cm^{-1}. FAB-MS: m/z 557.02. Anal. Calcd for $C_{27}H_{34}$PONClRh (557.9): C, 58.13; H, 6.14; N, 2.51. Found: C, 57.92; H, 6.32; N, 2.38.

RhCl(CO)(PPh$_3$)[HN(CH$_2$CH(CH$_3$)$_2$)$_2$] (10). Reaction of diisobutylamine (16.2 μL, 11.9 mg, 0.0926 mmol) and **1a** (39.7 mg, 0.046 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **10** (47.2 mg, 91%) as a pale yellow solid. ^{1}H NMR (270 MHz, C_6D_6): δ 0.89 (12H, d, J_{H-H} = 6.6 Hz, CH_3), 1.59 (2H, m, J_{H-H} = 6.6 Hz, CH(CH$_3$)$_2$), 2.64 (2H, m, J_{H-H} = 7.9 Hz, CH_2N), 2.92 (2H, m, J_{H-H} = 7.6 Hz, CH_2N), 3.84 (1H, br s, NH), 7.01, 7.90 (15H, m, P(C_6H_5)$_3$). ^{31}P $\{^1H\}$ NMR (109 MHz, C_6D_6): δ 44.4 (d, J_{Rh-P} = 154.7 Hz). IR (KBr): ν_{CO} 1968.0 cm^{-1}. FAB-MS: m/z 556.93. Anal. Calcd for $C_{27}H_{34}$PONClRh (556.93): C, 58.13; H, 5.42; N, 2.51. Found: C, 57.95; H, 5.46; N, 2.53.

RhCl(CO)(PPh$_3$)[HN(CH$_2$C$_6$H$_5$)$_2$] (11). Reaction of dibenzylamine (8.97 μL, 9.21 mg, 0.0467 mmol) and **1a** (20 mg, 0.023 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **11** (26.2 mg, 90%) as a yellow solid. ^{1}H

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NMR (270 MHz, C_6D_6): δ 4.18 (4H, dd, J_{H-H} = 7.2 Hz, CH_2N), 4.50 (1H, br s, NH), 7.01, 7.77 (15H, m, P(C_6H_5)$_3$), 7.32 (5H, m, C_6H_5). ^{31}P {^{1}H} NMR (109 MHz, C_6D_6): δ 46.0 (d, J_{Rh-P} = 156.9 Hz). IR (KBr): ν_{CO} 1955.9 cm^{-1}. FAB-MS: *m*/*z* 625.07. Anal. Calcd for $C_{33}H_{30}PONClRh$ (625.94): C, 63.32; H, 4.83; N, 2.24. Found: C, 63.76; H, 4.95; N, 2.21.

RhCl(CO)(PPh$_3$)[HN(C$_5$H$_{10}$)] (12). Reaction of piperidine (9.14 μL, 7.87 mg, 0.085 mmol) and **1a** (39.6 mg, 0.0462 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **12** (45.1 mg, 95%) as a pale yellow solid. ^{1}H NMR (270 MHz, C_6D_6): δ 1.38 (6H, s, CH_2), 2.66 (4H, s, CH_2), 3.39 (1H, s, *H*N), 7.04, 7.95 (15H, m, P(C_6H_5)$_3$). ^{31}P {^{1}H} NMR (109 MHz, C_6D_6): δ 46.2 (d, J_{Rh-P} = 149.9 Hz). IR (KBr): ν_{CO} 1960.5.0 cm^{-1}. FAB-MS: *m*/*z* 512.82. Anal. Calcd for $C_{24}H_{26}$-PONClRh (513.81): C, 56.10; H, 5.10; N, 2.73. Found: C, 55.76; H, 5.18; N, 2.94.

RhCl(CO)(PPh$_3$)[NH(C$_4$H$_8$O)] (13). Reaction of morpholine (6.92 μL, 6.91 mg, 0.079 mmol) and **1a** (34 mg, 0.0396 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **13** (37.8 mg, 82%) as a pale yellow powder. ^{1}H NMR (270 MHz, C_6D_6): δ 2.84 (4H, t, J_{H-H} = 6.9 Hz, (CH_2)$_2$N), 2.96 (4H, t, J_{H-H} = 6.3 Hz, (CH_2)$_2$O), 3.46 (1H, s, NH), 7.06, 7.92 (15H, m, P(C_6H_5)$_3$). ^{31}P {^{1}H} NMR (109 MHz, C_6D_6): δ 46.4 (d, J_{Rh-P} = 152.1 Hz). IR (KBr): ν_{CO} 1962.0 cm^{-1}. FAB-MS: *m*/*z* 515.45. Anal. Calcd for $C_{23}H_{24}$-PONClRh (515.77): C, 53.56; H, 4.96; N, 2.72. Found: C, 53.25; H, 4.72; N, 2.64.

RhCl(CO)(PPh$_3$)[HN(C$_5$H$_9$(NC$_5$H$_{10}$))] (14). Reaction of 4-piperidinopiperidine (15.3 mg, 0.091 mmol) and **1a** (39 mg,0.046 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **14** (52.1 mg, 86%) as an orange solid. ^{1}H NMR (270 MHz, C_6D_6): δ 0.87 (6H, t, J_{H-H} = 6.9 Hz, (CH_2)$_3$), 1.44 (4H, q, J_{H-H} = 5.3 Hz, CH_2), 2.07 (4H, t, J_{H-H} = 5.6 Hz, CH_2), 2.21 (1H, m, (CH)N), 3.51 (4H, t, J_{H-H} = 6.3 Hz, CH_2NRh), 3.51 (1H, s, NH(C_5H_{10})), 3.56 (1H, s, *H*NRh), 7.06, 7.95 (15H, m, P(C_6H_5)$_3$). ^{31}P {^{1}H} NMR (109 MHz, C_6D_6): δ 46.1 (d, J_{Rh-P} = 149.8 Hz). IR (KBr): ν_{CO} 1957.0 cm^{-1}. FAB-MS: *m*/*z* 596.88. Anal. Calcd for $C_{29}H_{36}PON_2ClRh$ (597.94): C, 58.25; H, 6.07; N, 4.69. Found: C, 57.93; H, 6.15; N, 4.72.

RhCl(CO)(PPh$_3$)[HN(CH$_3$)(CH$_2$CH$_3$)] (15). Reaction of *N*-ethylmethylamine (0.01 mL, 6.89 mg, 0.116 mmol) and **1a** (50 mg, 0.0583 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **15** (54.2 mg, 95%) as a yellow solid. ^{1}H NMR (270 MHz, C_6D_6): δ 1.21 (3H, t, J_{H-H} = 6.9 Hz, CH_3), 3.37 (3H, d, J_{H-H} = 5.3 Hz, CH_3N), 2.57 (2H, m, J_{H-H} = 6.2 Hz, CH_2N), 3.22 (1H, br s, NH), 7.03, 7.90 (15H, m, P(C_6H_5)$_3$). ^{31}P {^{1}H} NMR (109 MHz, C_6D_6): δ 45.1 (d, J_{Rh-P} = 162.4 Hz). IR (KBr): ν_{CO} 1956.3 cm^{-1}. FAB-MS: *m*/*z* 486.9. Anal. Calcd for $C_{22}H_{24}PONClRh$ (487.8): C, 54.17; H, 4.96; N, 2.87. Found: C, 54.56; H, 4.71; N, 2.70.

RhCl(CO)(PPh$_3$)[HN(CH$_3$)(CH$_2$C$_6$H$_5$)] (16). Reaction of *N*-benzylmethylamine (10.5 μL, 9.89 mg, 0.0817 mmol) and (**1a**) (35 mg, 0.0408 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **16** (41 mg, 91%) as a yellow solid. ^{1}H NMR (270 MHz, C_6D_6): δ 2.36 (3H, d, J_{H-H} = 5.6 Hz, CH_3), 3.79 (1H, s, NH), 4.22 (2H, dd, J_{H-H} = 5.9 Hz, CH_2N), 7.03, 7.88 (15H, m, P(C_6H_5)$_3$), 7.28, 7.71 (5H, m, (C_6H_5). ^{31}P {^{1}H} NMR (109 MHz, C_6D_6): δ 45.7 (d, J_{Rh-P} = 154.4 Hz). IR (KBr): ν_{CO} 1965.0 cm^{-1}. FAB-MS: *m*/*z* 549.08. Anal. Calcd for $C_{27}H_{26}PONClRh$ (549.842): C, 58.98; H, 4.77; N, 2.55. Found: C, 58.62; H, 4.79; N, 2.48.

RhCl(CO)(PPh$_3$)[HN(CH$_3$)(CH$_2$(C$_{14}$H$_9$))] (17). Reaction of 9-(methylaminemethyl)anthracene (19.2 mg, 0.0868 mmol) and **1a** (37.2 mg, 0.0434 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **17** (54.8 mg, 97%) as an orange solid. ^{1}H NMR (270 MHz, C_6D_6): δ 2.26 (3H, dd, J_{H-H} = 5.6 Hz, CH_3), 4.42 (1H, br s, NH), 5.54 (2H, dd, J_{H-H} = 3.3 Hz, CH_2), 7.31, 7.76, 8.15, 8.55 (9H, m, $C_{14}H_9$), 7.06, 7.95 (15H, m, P(C_6H_5)$_3$). ^{31}P {^{1}H} NMR (109 MHz, C_6D_6): δ 46.2 (d, J_{Rh-P} = 152.3 Hz). IR (KBr): ν_{CO} 1966.0 cm^{-1}. FAB-MS: *m*/*z* 648.72. Anal. Calcd for $C_{35}H_{30}PONClRh$ (649.96): C, 64.68; H, 4.65; N, 2.16. Found: C, 64.82; H, 4.57; N, 2.25.

RhCl(CO)(PPh$_3$)[N(CH$_2$CH$_3$)$_3$] (18). Reaction of triethylamine (8.13 μL, 5.90 mg, 0.0582 mmol) and **1a** (25 mg, 0.0291 mmol) using a procedure analogous to the preparation of **6** led to the isolation of **18** (27.5 mg, 89%) as an orange microcrystalline solid. ^{1}H NMR (270 MHz, C_6D_6): δ 1.36 (9H, t, J_{H-H} = 7.2 Hz, CH_3CH$_2$), 2.66 (6H, q, J_{H-H} = 7.2 Hz, CH$_3$CH_2), 7.04, 7.93 (15H, m, P(C_6H_5)$_3$). ^{31}P {^{1}H} NMR (109 MHz, C_6D_6): δ 47.8 (d, J_{Rh-P} = 176.3 Hz). IR (KBr): ν_{CO} 1971.0 cm^{-1}. FAB-MS: *m*/*z* 530.13. Anal. Calcd for $C_{25}H_{30}$-PONClRh (529.85): C, 56.67; H, 5.71; N, 2.64. Found: C, 56.23; H, 5.75; N, 2.57.

[RhCl$_4$(CO)(PPh$_3$)]$^-$(H$_2$N(CH$_2$CH$_3$)$_2$)$^+$ (19). A solution of **6** (40 mg, 0.08 mmol) and carbon tetrachloride (36.8 mg, 23 μl, 0.24 mmol) in benzene was set to reflux for 48 h. A color change from pale yellow to orange occurred within 1 h. Orange crystals began to precipitate out of the red/orange solution. The solution was decanted, and the orange crystals were washed with hexanes and dried in vacuo: yield, 30.84 mg, 63%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.33 (6H, t, J_{H-H} = 7.2 Hz, CH_3-CH$_2$), 3.12 (4H, q, J_{H-H} = 6.6 Hz, CH$_3$CH_2), 7.37, 8.00 (15H, m, P(C_6H_5)$_3$), 7.88 (2H, br s, NH_2). ^{31}P {^{1}H} NMR (109 MHz, $CDCl_3$): δ 27.9 (d, J_{Rh-P} = 102.3 Hz). IR (KBr): ν_{CO} 2103.7 cm^{-1}. (−)FAB-MS: *m*/*z* 609.96. Anal. Calcd for $C_{23}H_{27}$-PONCl$_4$Rh (609.17): C, 45.35; H, 4.47; N, 2.29. Found: C, 45.62; H, 4.57; N, 2.04.

[RhClBr$_3$(CO)(PPh$_3$)]$^-$(H$_2$N(CH$_2$CH$_3$)$_2$)$^+$ (20). Carbon tetrabromide (25.5 mg, 0.78 mmol) was added to a solution of **6** (12.8 mg, 0.026 mmol) in benzene-d_6, resulting in an immediate color change from pale yellow to bright red with the evolution of a red precipitate. The reaction was complete within 1 h, and crystal formation occurred within 14 h. The clear red solution was decanted, and the solvent removed in vacuo to result in a red microcrystalline product: yield, 17.3 mg, 86%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.44 (6H, t, J_{H-H} = 6.9 Hz, CH_3CH$_2$), 3.32 (4H, q, J_{H-H} = 7 Hz, CH$_3$CH_2), 7.39, 8.07 (15H, m, P(C_6H_5)$_3$), 7.71 (2H, br s, NH_2). ^{31}P {^{1}H} NMR (109 MHz, $CDCl_3$): δ 8.5 (d, J_{Rh-P} = 77.2 Hz). IR (KBr): ν_{CO} 2090 cm^{-1}. MALDI-TOF: 742.7. Anal. Calcd for $C_{23}H_{27}$-PONClBr$_3$Rh (742.52): C, 37.20; H, 3.66; N, 1.89. Found: C, 37.88; H, 3.53; N, 1.85.

[RhClI$_3$(CO)(PPh$_3$)]$^-$(H$_2$N(CH$_2$CH$_3$)$_2$)$^+$ (21). Carbon tetraiodide (62.2 mg, 0.12 mmol) was added to a solution of **6** (20 mg, 0.04 mmol) in C_6D_6, resulting in the immediate formation of a dark red precipitate. The reaction was complete after 15 min. The solid was filtered, washed with hexanes (5 mL), and recrystallized from a chloroform/benzene solution: yield, 30.1 mg, 77.4%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.16 (6H, t, J_{H-H} = 7.3 Hz, CH_3CH$_2$), 2.81 (4H, q, J_{H-H} = 5.9 Hz, CH$_3$CH_2), 6.94, 8.33 (15H, m, P(C_6H_5)$_3$), 7.63 (2H, br s, NH_2). ^{31}P {^{1}H} NMR (109 MHz, $CDCl_3$): δ −0.59 (d, J_{Rh-P} = 78.3 Hz). IR (KBr): ν_{CO} 2076 cm^{-1}. (−)FAB-MS: *m*/*z* 973.45. Anal. Calcd for $C_{23}H_{27}PONClI_3Rh$ (883.52): C, 31.27; H, 3.08; N, 1.58; $C_{23}H_{27}$-PONI$_4$Rh (975.03): C, 28.33; H, 2.79; N, 1.44. Found: C, 29.11; H, 2.84; N, 1.32.

Hydrosilation of 1-Hexene Using 6. (a) A 5.0 g (3.6 × 10^{-2} mol) sample of phenyldimethylsilane and 5.1 g of 1-hexene (6.1 × 10^{-2} mol) were added to 200 mg of RhCl(CO)(PPh$_3$)-(NEt$_2$H) (3.99 × 10^{-4} mol) dissolved in 10 mL of benzene, and the mixture were refluxed at 60 °C for 30 min. The unconverted olefin was separated by distillation (1.98 g), and the remaining liquid was distilled under vacuum to yield 6.84 g of phenyldimethylhexylsilane (84.7%): ^{1}H NMR (270 MHz, C_6D_6): δ 0.24 (6H, s, SiCH_3), 0.72 (2H, t, J_{H-H} = 8.6 Hz, SiCH_2), 0.88 (3H, t, J_{H-H} = 6.3 Hz, CH_3), 1.28 (8H, m, CH_2), 7.21, 7.47 (5H, m, Si(C_6H_5)) ppm. IR (KBr/neat): ν 699, 728, 815.3, 1112.8, 1180.2, 1383.6, 2854.6, 2955.9, 3021, 3068.5 cm^{-1}. GC−MS (C_6H_6): 20.693 min., *m*/*z* 220. Turnover no.: (mol$_{prod}$/mol$_{cat}$) 77.9. Turnover efficiency: (mol$_{prod}$/mol$_{cat}$/h) 155.8 h^{-1}.

(b) A 5.0 g (1.92 × 10^{-2} mol) sample of triphenylsilane and

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5.0 g of 1-hexene (5.95×10^{-2} mol) were added to 200 mg of $RhCl(CO)(PPh_3)(NEt_2H)$ (3.99×10^{-4} mol) dissolved in 10 mL of benzene, and the mixture was refluxed at 60 °C for 30 min. Excess 1-hexene was separated by distillation (2.5 g). The product was distilled under vacuum to yield 5.95 g of triphenylhexylsilane (89%): ^{1}H NMR (270 MHz, C_6D_6): δ 0.84 (3H, t, $J_{H-H} = 6.3$ Hz, CH_3), 1.14−1.39 (8H, m, CH_2), 1.54 (2H, m, $J_{Si-H} = 9.88$, CH_2Si), 7.15, 7.59 (15H, m, Si(C_6H_5)$_3$) ppm. IR (KBr/neat): ν 699, 731, 804, 998, 1113, 1428, 1588, 2856, 2924, 3020, 3049, 3068 cm^{-1}. GC−MS (C_6H_6): 22.158 min., m/z 344. Turnover no.: (mol_{prod}/mol_{cat}) 43.3. Turnover efficiency: (mol_{prod}/mol_{cat}/h) 86.5 h^{-1}.

Polymerization of Styrene Using [Rh(Cl)(CO)(PPh$_3$)(HNEt$_2$)] (6). A 25 mg sample of **6** (0.05 mmol) was dissolved in 5 mL of benzene. Styrene (5 mL, 0.0435 mol) was added via syringe followed by the addition of CCl_4 (3 mL, 0.0311 mol). The mixture was allowed to reflux for 14 h at 60 °C. The solvent was removed in vacuo, resulting in a viscous orange residue. Polystyrene was recrystallized from chloroform/methanol, resulting in a white solid: yield, 2.105 g, 91%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.33 (2H, d, CH_2), 1.85 (1H, s, Ar−CH), 6.57, 7.07 (5H, m, C_6H_5). ^{13}C {^{1}H} NMR (270 MHz, $CDCl_3$): δ 40.61 (d, $CHCH_2$), 127.9 (d, C_5H_5−C), 145.5 (m, C_5H_5-C). IR (KBr): ν 3024, 2921, 1600, 1492, 1451, 1028, 906, 758, 699, 538 cm^{-1}. GCP ($CHCl_3$): no. average 2921 units/chain; wt average 6076 g/mol; polydispersity 2.08; turnover rate 56.8 h^{-1}.

Polymerization of Methyl Methacrylate Using [Rh(Cl)(CO)(PPh$_3$)(HNEt$_2$)] (6). Poly(methyl methacrylate) was prepared and isolated as was polystyrene using **6** (25 mg, 0.05 mmol), methyl methacrylate (5 mL, 0.047 mol), and CCl_4 (3 mL, 0.031 mol) and refluxing the mixture for 14 h at 60 °C: yield, 3.31 g, 89.7%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.73 (3H, s, CH_3), 1.70 (2H, s, CH_2), 3.49 (3H, s, O−CH_3). ^{13}C {^{1}H} NMR (270 MHz, $CDCl_3$): δ 16.47 (m, CH_3), 18.71 (m, CH_2), 44.5 (s, O−CH_3), 51.78 (m, −CH_2C(COOCH_3), 177.82 (m, COOCH$_3$). IR (KBr): ν 2950, 1733, 1456, 1241, 1148, 988, 841, 750 cm^{-1}. GCP ($CHCl_3$): no. average 65 545 units/chain; wt average: 93 814 g/mol; polydispersity 1.43.; turnover rate 76.2 h^{-1}.

X-ray Diffraction Study. X-ray-quality crystals of **3** and **6** were grown from a mixture of benzene/hexanes by the slow evaporation of the solvent. The crystals were cut from the grown needles, mounted on a glass fiber, and transferred to the diffractometer. All of the samples were stable in air. Crystallographic data are summarized in Table 2. X-ray data for **3** were collected on a P4 diffractometer equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector. Processing was carried out using the program SAINT,[15a] which applied Lorenz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS[15b] was utilized for the scaling of the diffraction data, the decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by direct method using SHELXS-86[16a] and was refined using SHELXL-93.[16b] Hydrogen atoms were calculated at idealized positions using a riding model with different C−H distances for the type of hydrogen. The isotropic displacement factors, U_{iso}, were adjusted to a 20% higher value than the bonded carbon or nitrogen atom. The cyclohexylamine group is disordered over two orientations with occupancies of 0.70 and 0.30, respectively. The minor geometry was restrained to be similar to that of the major orientation. For atoms closer than 0.5 Å, the thermal parameters were restrained to be similar. Major orientation is numbered N1 and C11−C16, and minor orientation is denoted as N2 and C61−C66.

X-ray data for **6** were collected on a Rigaku AFC6-S diffractometer. Cell constants were obtained from 24 reflections with $32° < 2\theta < 40°$. Data reduction was done using the NRCVAX package.[17] Structure was solved by a direct method using SHELXS-86 and was refined using SHELXL-93.[16a,b] All atoms except hydrogen were refined anisotropically. Hydrogen atoms were introduced at idealized geometries. Hydrogen atoms on the methyl groups were located at the position of maximum electron density, and a common isotropic thermal parameter was refined for each methyl group.

Small yellow crystals of **19** were mounted on a glass rod and examined on a Rigaku AFC6-S diffractometer using Mo Kα radiation. Data were collected in ω scan mode on the reduced cell, and crystallographic data are collected in Table 5. The cell was transformed to monoclinic $C2/c$ after data collection. Data reduction and absorption corrections were done with TEXSAN.[19] Structure refinement was performed using SHELXL-96.[16c] All non-hydrogen atoms are anisotropic, and hydrogen atoms are isotropic. Hydrogen atoms were constrained to the parent site using a riding model; SHELXL-96[16c] defaults, C−H 0.93−0.98, N−H 0.86 Å. The isotropic factors, U_{iso}, were adjusted to a 50% higher value of the parent site (methyl) and 20% higher for the others. A final verification for possible missed solvent areas was performed using the VOID routine of the PLATON program.[18]

A red crystal of **20** mounted on a glass fiber was examined by a P4 Siemens diffractometer equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector using graphite-monochromatic Mo Kα radiation. Data reduction processing, absorption correction, and structure solution and refinement were carried out as described for compound **3**.

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Supporting Information Available: Tables of experimental parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, torsion angles, hydrogen coordinates, anisotropic parameters, least-squares planes in crystal coordinates and deviations (64 pages). Ordering information is given on any current masthead page.

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