Rhodium(III) Peroxo Complexes Containing Carbene and Phosphine Ligands

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The Rh(I) carbene precursors $[RhCl(COE)(NHC)]_2$, where the N-heterocyclic carbene is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) or 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), were used to synthesize the RhCl(NHC)(P-N) complexes **4** (NHC = IPr) and **5** (NHC = IMes), where P-N is P,N-chelated *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline, and the corresponding *cis*-$RhCl(NHC)(PPh_3)_2$ complexes **6** and **7**. The synthesis of **4** surprisingly requires the reaction to be carried out under a hydrogen atmosphere and occurs via the intermediate dihydride $RhCl(H)_2(IPr)(P\text{-}N)$ (**3**). Complexes **4**−**7** in benzene readily undergo irreversible oxidative addition of O_2 to form the corresponding Rh(III) peroxide complexes **9**−**12**. For comparative purposes, $RhCl(PPh_3)(P\text{-}N)$ (**8**) was synthesized from $RhCl(PPh_3)_3$, and this also added O_2 to form a peroxo complex (**13**). All of the complexes were generally characterized by elemental analysis and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR and IR spectroscopies and, in the cases of **9**, **10**, and **13**, by X-ray crystallography.

Introduction

Although transition-metal peroxo complexes containing ancillary tertiary phosphine ligands are well-known,[1] there have been few reports on peroxo complexes with N-heterocyclic carbene ligands (NHCs): two palladium(II) species[2] and one cobalt(III) complex[3] have been crystallographically characterized, while a nickel peroxo species has been postulated in an allylic oxidation effected at a Ni−NHC center.[4] An iridium peroxide, $IrCl(O_2)(NHC)_2$, has been reported in the Supporting Information of a recent paper, but only elemental analysis supports the peroxide formulation.[5] We now report syntheses of the Rh(I) carbene complexes RhCl(NHC)(P-N) and the known[6] *cis*-$RhCl(NHC)(PPh_3)_2$ from the $[RhCl(COE)(NHC)]_2$ precursors and their reactions with O_2 to give, respectively, the Rh(III) η^2-peroxo species $RhCl(O_2)(NHC)(P\text{-}N)$ and $RhCl(O_2)(NHC)(PPh_3)_2$, where NHC is IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) or IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), and P-N is P,N-chelated *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline. The required cyclooctene precursor complexes $[RhCl(COE)(NHC)]_2$ are of a known type,[7] although neither the IPr nor the IMes derivative has been previously reported. For purposes of comparison in reactivity between species containing either a PPh_3 or an NHC ligand, $RhCl(PPh_3)(P\text{-}N)$ was also synthesized and its reactivity toward O_2 investigated.

During a presentation of the studies described in this paper at the 89th Canadian Chemistry Conference,[8] we learned of the synthesis and characterization of peroxo complexes of the type $RhCl(O_2)(NHC)_2$, and some preliminary data on their potential for catalytic aerobic oxidation of alcohols,[9] but we are unaware of the details of this work.

Results and Discussion

$[RhCl(COE)(NHC)]_2$ Complexes 1 (NHC = IPr) and 2 (NHC = IMes). The yellow complex $[RhCl(COE)(IPr)]_2$ (**1**) was prepared by stirring $[RhCl(COE)_2]_2$ with 2 equiv of IPr in THF, hexane, or benzene for 4 h under Ar at room temperature (Scheme 1); the resulting yellow solution was concentrated, and when necessary, hexane was added to precipitate **1**, which was isolated and dried in vacuo. The use of excess IPr does not lead to a bis(carbene) complex, in contrast to the reaction using IMes, which in THF generates Rh(H)Cl(IMes′)(IMes) (**2a**), where IMes′ is the cyclometalated carbene formed from a methyl group via intramolecular C−H activation.[10] The difference is presumably caused by the more bulky IPr (vs IMes),[11] which hinders replacement of the cyclooctene ligand of **1**.

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Scheme 1. Formation of Complexes 1 and 2

$$[RhCl(COE)_2]_2 + 2IPr \xrightarrow{\text{hexane, THF, or benzene}} [RhCl(COE)(IPr)]_2 \quad \mathbf{1}$$

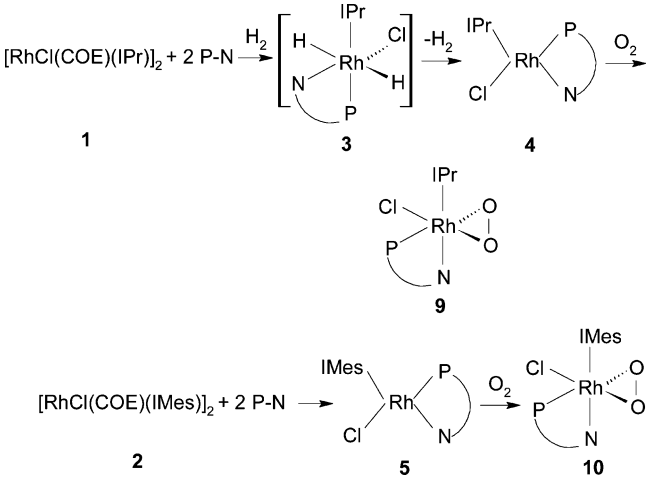
$$[RhCl(COE)_2]_2 + 2IMes \xrightarrow{\text{hexane}} [RhCl(COE)(IMes)]_2 \quad \mathbf{2} \xrightarrow[\text{benzene}]{2IMes} 2Rh(H)Cl(IMes')(IMes) \quad \mathbf{2a}$$

On investigating the reaction of $[RhCl(COE)_2]_2$ with IMes in hexane, even in the presence of 4 equiv of the carbene, we isolated the yellow species $[RhCl(COE)(IMes)]_2$ (**2**), which was stable in hexane. However, reaction of **2** with 2 equiv of IMes in benzene/C_6D_6 or THF generates **2a** over several hours, as monitored by ^1H NMR; the methyl δ 2.31 singlet of **2** is replaced by a singlet at δ 1.70 for the metalated CH_2, and a broad, high-field hydride resonance is found at δ −27.3. Clearly **2** is the precursor to **2a**. Similar solvent-dependent reactivity has been found by Nolan's group in reactions of $[RhCl(COE)_2]_2$ with I^{t}Bu (1,3-bis(*tert*-butyl)imidazol-2-ylidene) and was attributed to differences in solvent polarities and solubilities of the carbene complexes.[7]

Complexes **1** and **2** in benzene are O_2-sensitive and decompose to give free COE and possibly paramagnetic Rh(II) carbene species, as judged by the loss of all of the carbene ligand ^1H NMR signals. However, in the presence of added phosphines or the P-N ligand, oxidation products of the type $RhCl(O_2)(NHC)L_2$ may be synthesized, where L_2 = P-N, $(PPh_3)_2$ (see below).

Reactions of [RhCl(COE)(NHC)]$_2$ with P-N and with PPh$_3$. The synthesis of RhCl(IPr)(P-N), the precursor for the peroxide, is unusual in that there is no direct reaction between complex **1** and 2 equiv of the P-N ligand in benzene under Ar, but surprisingly, under 1 atm of H_2, formation of RhCl(IPr)(P-N) (**4**) does occur over a few hours via the intermediate dihydride species $Rh(H)_2Cl(IPr)(P\text{-}N)$ (**3**) (Scheme 2). This two-step synthesis of **4**, unlike the direct synthesis under Ar of the IMes analogue **5** from **2** (see Scheme 2 and below), requires removal of the COE by hydrogenation; the synthetic process for **4** was readily monitored in C_6D_6 by in situ ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. During the first 1 h, the ^1H NMR spectrum shows a singlet at δ 1.50 for the cyclooctane CH_2 protons and a doublet of doublets for two equivalent hydrides of **3** at δ −20.99 (J_{RhH} = 29, J_{PH} = 18 Hz); the $^{31}P\{^1H\}$ NMR spectrum displays two doublets at δ 39.2 (J_{RhP} = 114 Hz) and 44.5 (J_{RhP} = 225 Hz), attributed to species **3** and **4**, respectively (free P-N has a singlet $^{31}P\{^1H\}$ resonance at δ −11.2). A yellow mixture of **3** and **4** could be isolated after 30 min, and after this was redissolved in C_6D_6 in the absence of H_2, the ratio of **4** to **3** gradually increased and the signal for dissolved H_2 then became evident at δ 4.50. NMR resonances for **3** were assigned from the mixed sample of **3** and **4**, on the basis of the NMR data of isolated pure **4**. Other ^1H signals for **3** were a singlet at δ 6.69 for NC*H*, a septet at δ 3.32 for the equivalent methines of the IPr ligand, a singlet at δ 2.28 for the methyl protons of the P-N ligand, and two doublets for the methyl groups of the IPr ligand at δ 1.45 and 1.12, implying free rotation around the Rh−C bond.[12] Because of the decomposition of **3** to **4**, satisfactory $^{13}C\{^1H\}$ NMR spectra for this species could not be obtained.

Scheme 2. Formation of 3, 4, 5, 9, and 10



After a further 6 h of reaction, **3** had been quantitatively converted to **4**, which does not react with H_2 to regenerate **3**. Complex **4** is isolated as a yellow powder in 89% yield; **3** has not been isolated pure, but IR data of the **3**/**4** mixture reveal ν_{RhH} at 2111 cm^{-1}. The J_{RhP} value of 114 Hz for **3** indicates that the P atom is trans to the carbene and cis to the Cl, while the J_{RhP} value of 225 Hz for **4** supports a geometry with the P atom cis to carbene and trans to Cl.[6] Of note, the two hydrides in **3** are equivalent and thus mutually trans, although a *cis*-dihydrido species formed via oxidative addition of H_2 is a likely, but not essential,[13] precursor to **3**. The principle of microscopic reversibility implies that reductive elimination of H_2 from a *trans*-dihydride is not impossible. Trans hydrido ligands are unusual but are not unknown for octahedral dihydrido complexes of platinum metals, including Rh.[14,15]

Complex **4** was characterized by elemental analysis, mass spectra, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, as well as by the $^{31}P\{^1H\}$ data given above. The ^1H spectrum shows a singlet at δ 6.77 for NC*H*, two septets at δ 4.20 and 3.53 for the IPr methine protons, a singlet at δ 3.12 for the equivalent methyl protons of the P-N ligand, and four sets of doublets for inequivalent IPr methyl groups, now indicating restricted rotation around the Rh−C bond or less likely the N_{imid}−C_{arene} bond.[12] The $^{13}C\{^1H\}$ NMR signal for the carbene carbon appears as a doublet of doublets centered at δ 186.8 (J_{RhC} = 57, J_{PC} = 15 Hz), 34 ppm upfield from the corresponding resonance for free IPr, but not beyond the range for other Rh(I) carbene complexes.[16]

The mechanistic details of the fascinating **1** → **3** → **4** conversions remain to be elucidated; they are clearly governed by the steric bulk of IPr (vs that of IMes), because the corresponding RhCl(IMes)(P-N) complex (**5**) is prepared via a more conventional route, not involving H_2 (Scheme 2).

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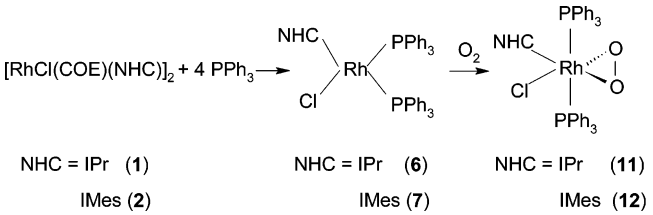
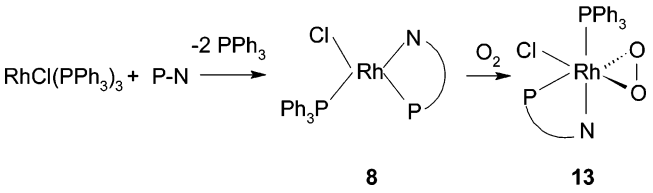
Scheme 3. Formation of 6, 7, 11, and 12



Scheme 4. Formation of 8 and 13



Complex **5** is synthesized in high yield as a yellow powder by direct reaction of **2** with 2 equiv of P-N ligand under Ar, the reaction generating cyclooctene (detected by ^{1}H NMR spectroscopy) rather than the cyclooctane generated during formation of **4**. The geometry of **5** corresponds to that of **4** (with the phosphine cis to carbene and trans to Cl), as judged by the ^{31}P{^{1}H} NMR doublet at δ 48.1 with J_{RhP} = 230 Hz. The ^{1}H spectrum shows singlets at δ 6.20 (for NC*H*), δ 3.07 (for the P-N methyl protons), δ 3.01 (for the *p*-methyl protons of IMes), and δ 2.13 and 1.57 (for inequivalent *o*-methyl protons of IMes, presumably again because of restricted rotation around the Rh−C bond). The ^{13}C{^{1}H} doublet of doublets for the carbene carbon is seen at δ 183.9 (J_{RhC} = 54, J_{PC} = 17 Hz). If the synthesis of **5** is carried out under H_2, no intermediate hydride is seen, although cyclooctane is now observed. It seems that the bulkier IPr hinders direct replacement of coordinated COE by the P-N ligand, while IMes does not. The dramatically different steric effects of IMes and IPr were noted also in the reactivities of **1** or **2** in benzene with further NHC ligand. Worth noting is that the known monomeric RhCl(COD)(NHC) complexes[16a] do not react with the P-N ligand at room temperature even under an atmosphere of H_2.

Reactions of the rhodium precursor **1** or **2** with 4 equiv of PPh_3 under Ar at room temperature rapidly generate the readily isolated, yellow *cis*-RhCl(NHC)$(PPh_3)_2$ complexes **6** (NHC = IPr) and **7** (NHC = IMes) (Scheme 3). The ^{31}P{^{1}H} NMR data for **6** and **7** show two doublets of doublets for the inequivalent phosphines. The ^{13}C{^{1}H} signal of the carbene carbon of **6** is a doublet of doublets of doublets at δ 187.2 because of coupling to the Rh and the two inequivalent P atoms; a similar signal is seen for **7**. Complex **7** has been prepared previously by reacting $RhCl(PPh_3)_3$ with IMes,[6] and our ^{1}H and ^{31}P{^{1}H} NMR data (measured in $CDCl_3$) agree with reported values;[6c] the ^{13}C{^{1}H} data for **7** have not been given previously, although such data were later reported for some related *cis*-RhCl(IMes)$(PAr_3)_2$ complexes, and these similarly show a ddd pattern for the carbene C resonance.[6a] The new synthetic method described here for **6** and **7** provides a convenient, obvious route into rhodium(I) mono(carbene) complexes containing other tertiary phosphine ligands.

Reaction of $RhCl(PPh_3)_3$ with P-N. For the purpose of comparing properties of the RhCl(NHC)(P-N) complexes **4** and **5** with those of a corresponding complex containing a PPh_3 ligand instead of a carbene ligand, RhCl(PPh_3)(P-N) (**8**) was synthesized. The exchange reaction of $RhCl(PPh_3)_3$ with 1 equiv of P-N in toluene generates this species, which is readily isolated by precipitation with hexane (Scheme 4). The yellow complex is soluble in benzene, CH_2Cl_2, and THF, and the ^{31}P{^{1}H} NMR spectrum in C_6D_6 shows two doublets of doublets at δ 57.6 (J_{RhP} = 197, J_{PP} = 45 Hz), likely due to the P-N ligand, and at δ 52.4 (dd, J_{RhP} = 175, J_{PP} = 45 Hz), likely due to the PPh_3 ligand (on the basis of ^{31}P{^{1}H} data for complexes **4**−**7**), the P atoms being mutually cis as judged by the J_{RhP} values;[17] an in situ spectrum during the synthesis of **8** shows generation of the PPh_3 singlet at δ −4.0 and disappearance of the P-N singlet at δ −11.2. The ^{1}H spectrum shows a singlet at δ 3.38 for the P-N methyl protons. The geometry of **8** has the Cl trans to the P atom of the P-N ligand and the PPh_3 trans to the N atom, and is analogous to that of **4** and **5** with the NHC replaced by PPh_3.

Reactions of O_2 with RhCl(NHC)(P-N) (NHC = IPr (4), IMes (5)), RhCl(NHC)$(PPh_3)_2$ (NHC = IPr (6), IMes (7)), and RhCl(PPh_3)(P-N) (8). Exposure of a toluene solution of **4** or **5** at room temperature to 1 atm of O_2 results in rapid and complete conversion to the peroxo complexes Rh$Cl(O_2)$(NHC)(P-N), where NHC = IPr (**9**), IMes (**10**) (Scheme 2). Brown crystals of **9** and orange crystals of **10** suitable for X-ray analysis were grown by addition of hexane to benzene solutions of the

Table 1. Crystallographic Data for the Complexes Rh$Cl(O_2)$(IPr)(P-N) (9), Rh$Cl(O_2)$(IMes)(P-N) (10), and Rh$Cl(O_2)(PPh_3)$(P-N) (13)

	9	**10**	**13**
formula	$C_{47}H_{56}N_3O_2PRhCl\cdot C_6H_{14}$	$C_{41}H_{44}N_3O_2PRhCl$	$C_{38}H_{35}NO_2P_2RhCl\cdot C_6H_6$
fw	950.45	780.12	816.08
cryst color, habit	brown, needle	orange, prism	orange, needle
cryst size (mm)	0.40 × 0.15 × 0.10	0.20 × 0.15 × 0.05	0.30 × 0.10 × 0.07
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a (Å)	14.684(2)	12.0059(4)	10.7428(8)
b (Å)	16.898(2)	31.748(1)	12.605(1)
c (Å)	19.798(2)	10.2883(4)	28.474(2)
β (deg)	90.927(8)	108.068(2)	90
V (Å^3)	4912(1)	3728.1(2)	3855.8(6)
Z	4	4	4
μ (mm^{-1})	0.477	0.612	0.633
total no. of rflns	52 494	29 996	17 126
no. of unique rflns	9721	6514	6501
R_{int}	0.057	0.043	0.056
no. of variables	555	450	463
R1 ($I > 2\sigma(I)$, all data)	0.091	0.043	0.066
wR2 (all data)	0.061[a]	0.072[b]	0.100[c]
GOF (all data)	0.82	1.05	0.98

[a] $w = 1/[\sigma^2(F_o^2) + (0.0152P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ in all cases. [b] $w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + (0.9607P)]$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0476P)^2]$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for RhCl(O$_2$)(IPr)(P-N) (9) with Estimated Standard Deviations in Parentheses

Rh(1)−C(1)	2.029(3)	Rh(1)−P(1)	2.2681(9)
Rh(1)−O(1)	2.0476(19)	Rh(1)−Cl(1)	2.4192(8)
Rh(1)−O(2)	1.9625(18)	O(1)−O(2)	1.450(3)
Rh(1)−N(3)	2.221(2)		
O(2)−Rh(1)−O(1)	42.32(7)	N(3)−Rh(1)−Cl(1)	85.55(6)
C(1)−Rh(1)−N(3)	169.14(10)	O(1)−Rh(1)−Cl(1)	117.73(6)
N(3)−Rh(1)−P(1)	83.78(6)	Rh(1)−O(2)−O(1)	71.98(11)
O(2)−Rh(1)−Cl(1)	159.62(6)	Rh(1)−O(1)−O(2)	65.70 (10)
C(1)−Rh(1)−Cl(1)	98.38(8)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for RhCl(O$_2$)(IMes)(P-N) (10) with Estimated Standard Deviations in Parentheses

Rh(1)−C(1)	2.038(2)	Rh(1)−P(1)	2.2901(7)
Rh(1)−O(1)	1.9710(16)	Rh(1)−Cl(1)	2.4339(6)
Rh(1)−O(2)	2.0645(17)	O(1)−O(2)	1.450(2)
Rh(1)−N(3)	2.235(2)		
O(2)−Rh(1)−O(1)	42.03(7)	N(3)−Rh(1)−Cl(1)	84.53(5)
C(1)−Rh(1)−N(3)	171.52(8)	O(1)−Rh(1)−Cl(1)	159.97(6)
N(3)−Rh(1)−P(1)	80.35(5)	Rh(1)−O(2)−O(1)	65.53(9)
O(2)−Rh(1)−Cl(1)	118.28(6)	Rh(1)−O(1)−O(2)	72.44(10)
C(1)−Rh(1)−Cl(1)	94.39(7)		

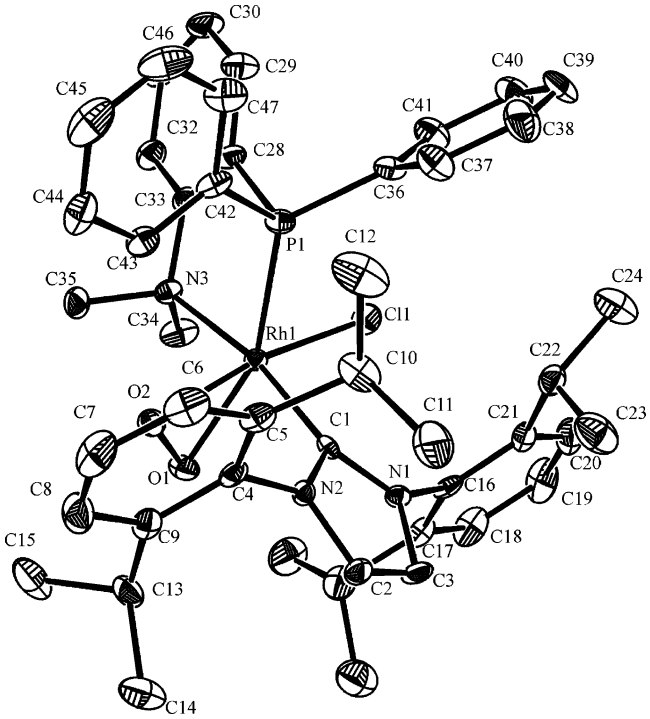


Figure 1. ORTEP diagram of RhCl(O$_2$)(IPr)(P-N) (**9**) with 50% probability thermal ellipsoids.

complexes. Some crystal data are given in Table 1, and selected bond lengths and angles are given in Tables 2 and 3. Complex **9** crystallizes with one disordered hexane molecule in the asymmetric unit, which was modeled in two orientations. The structures (Figures 1 and 2) show distorted-octahedral geometry at the Rh, with the carbene carbon and the N-donor atom being mutually trans (C−Rh−N = 169−172°) and the side-on η^2-peroxide and the Cl and P atoms constituting a highly distorted square-planar arrangement; within each structure, the Rh−O bond lengths differ by 0.08−0.09 Å, while the O−Rh−O angle is about 42°. The diisopropylphenyl and mesityl substituents

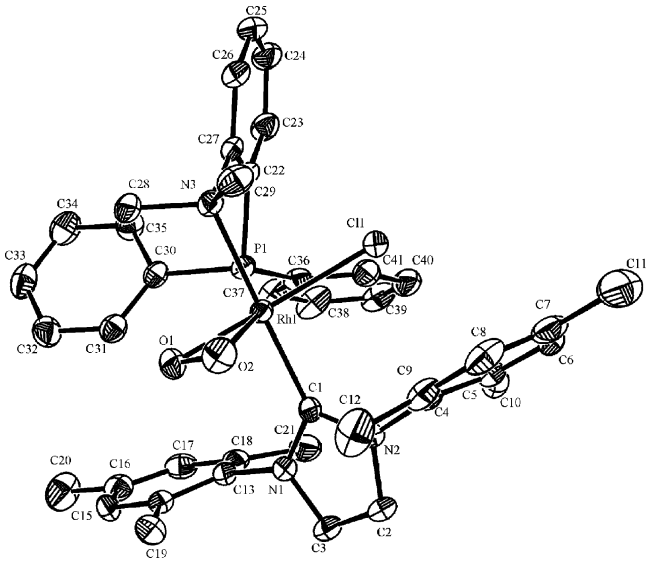


Figure 2. ORTEP diagram of RhCl(O$_2$)(IMes)(P-N) (**10**) with 50% probability thermal ellipsoids.

of **9** and **10**, respectively, are twisted significantly with respect to the central imidazole ring, for example, in **9** by an average of 85.95°, but this is not unusual.[16a] The Rh−C bond lengths of 2.029 and 2.038 Å are close to those reported for other Rh carbene complexes (whether they are formally Rh(I) or Rh(III)),[6,7,16] and the O−O bond length of 1.450(3) Å is typical for coordinated peroxide.[1,18,19] The peroxide IR band for **9** and **10** is seen in the expected region[1,18,19] at 871 and 870 cm^{-1}, respectively, and positive ion ESI-MS analyses in MeOH show a major *m*/*z* peak corresponding to $[M + H]^+$.

The solid-state structures of **9** and **10** are maintained in solution, as evidenced by NMR data in C_6D_6, which for **9** show a $^{31}P\{^1H\}$ doublet at δ 35.3 (J_{RhP} = 149 Hz) and a $^{13}C\{^1H\}$ doublet of doublets at δ 159.9 (J_{RhC} = 51, J_{PC} = 9 Hz) shifted some 25 ppm upfield from that of the precursor **4**. Similar data are seen for **10**: δ_P 34.7 (J_{RhP} = 149 Hz) and δ_C 159.4 (J_{RhC} = 50, J_{PC} = 9 Hz). The ^1H NMR spectrum of **9** shows inequivalent Me groups for the P-N ligand (singlets at δ 3.37 and 2.11), while broad signals at δ 4.44 and 2.76 are due to the IPr methine protons, and four broad peaks in the δ 1.87−0.88 region result from the inequivalent IPr methyl protons. For **10**, the ^1H NMR spectrum similarly shows two singlets for the P-N methyls and IMes-methyl signals at δ 2.26 and 2.14 for the *p*- and *o*-methyl groups, respectively.

Like the RhCl(NHC)(P-N) species, the RhCl(NHC)(PPh$_3$)$_2$ complexes **6** (NHC = IPr) and **7** (NHC = IMes) also readily undergo oxidative addition of O_2 to generate the corresponding orange Rh(III) peroxo complexes RhCl(O$_2$)(NHC)(PPh$_3$)$_2$ (**11** and **12**). We were unable to grow crystals suitable for X-ray analysis, but a simple doublet in the $^{31}P\{^1H\}$ spectrum at δ 18.4 for **11** and at δ 16.9 for **12** reveals equivalent P atoms that are almost certainly trans, as judged by the J_{RhP} values of 105 and 104 Hz, respectively;[6,17] the peroxide oxygens are then trans to the Cl and carbene C atoms (Scheme 3), as opposed to being trans to the Cl and P atoms in **9** and **10** (Scheme 2). The trans phosphines, in comparison with the P atom (of P-N) trans to

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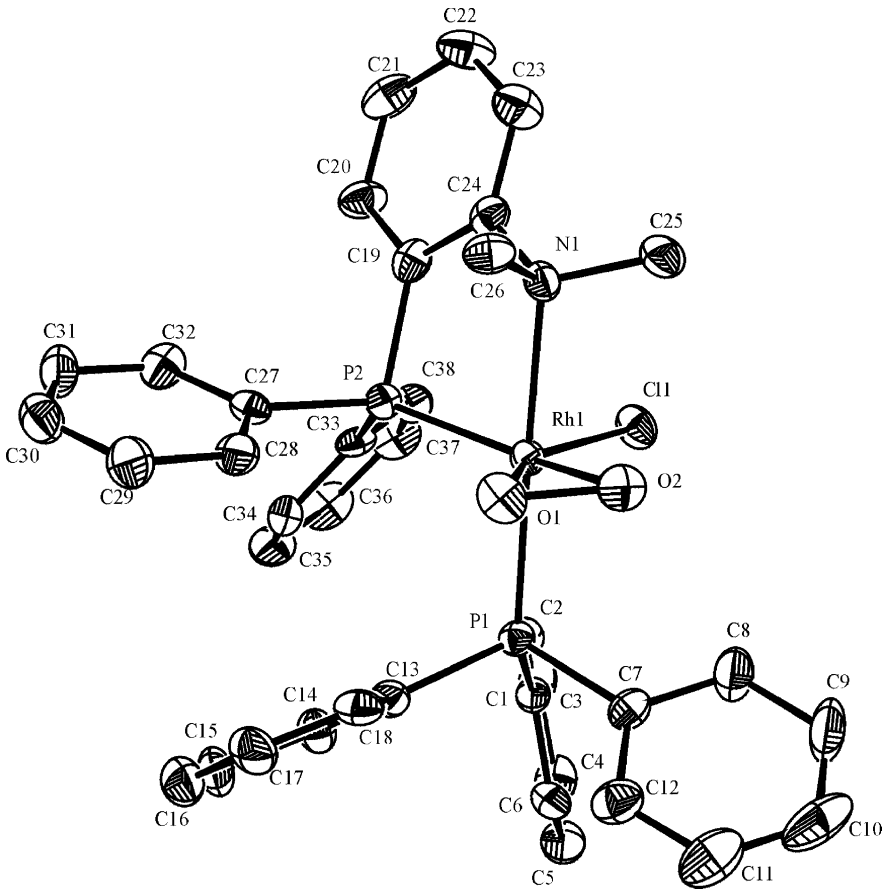

Figure 3. ORTEP diagram of $RhCl(O_2)(PPh_3)$(P-N) (**13**) with 50% probability thermal ellipsoids.

an O atom in **9** and **10**, give rise to higher field ^{31}P signals and lower J_{RhP} values by ~45 Hz. The ^1H NMR spectrum of **11** reveals two sets of equivalent IPr methyl protons (doublets at δ 1.43 and 1.09) and that for **12** shows singlets at δ 2.33 and 2.14 for the *o*- and *p*-methyl substituents, respectively. The carbene ^{13}C resonances could not be delineated, presumably because they are shifted into the phenyl C atom region of the spectrum. The IR peroxide band is seen at 852 and 851 cm^{-1} for **11** and **12**, respectively.

The O_2 is strongly bonded in all of the above four NHC phosphine complexes **9**−**12** and, for example, is not removed from the complexes under vacuum at room temperature or by introduction of 1 atm of N_2 (or H_2) to benzene solutions of the complexes. Such irreversible O_2 binding within Rh complexes is relatively rare.[18] Further, solutions of complexes **9**−**12** are completely stable when stored for 1 day under an atmosphere of air or oxygen. Our paper, together with the recent conference abstracts,[8,9] report the first examples of Rh peroxo complexes bearing ancillary NHC ligands. These complexes are of significance in that there is a report noting that *cis*-$RhCl(IMes)(PPh_3)_2$, which was being used as a catalyst in hydroformylation of styrene,[6c] decomposes in solution under O_2 to generate a green solution containing uncomplexed PPh_3 and triphenylphosphine oxide.[6c] Presumably, any such dissociation involves the peroxo product that we report on here. There is a growing amount of literature reporting on the replacement in Rh complexes of phosphines by NHC ligands in attempts to devise more effective catalysts, particularly within hydrogenation and hydroformylation systems,[6,20] and the replacement of phosphine ligands by NHC ligands has been noted to generate complexes that are "stable towards air and moisture".[20] Clearly, our work shows that such statements cannot be taken literally in a general sense, because solutions of $[RhCl(COE)(NHC)]_2$, RhCl(NHC)(P-N), and $RhCl(NHC)(PPh_3)_2$ species are all reactive toward oxygen. Indeed, our interest and that of others[9] are in the use of such Rh complexes for catalytic oxidations; whether Rh−NHC catalysts can lead to O atom transfer oxidations more selective than the more common free-radical processes initiated by NHC-free Rh(III) peroxo complexes[21] remains to be investigated.

Of note, reaction of O_2 with the NHC-free complex $RhCl(PPh_3)$(P-N) (**8**) in toluene (Scheme 4) follows that with the RhCl(NHC)(P-N) complexes **4** and **5** (Scheme 2), again rapidly giving $RhCl(O_2)(PPh_3)$(P-N) (**13**) quantitatively and irreversibly in solution in high isolated yield. Although **13** was isolated and was characterized as a toluene solvate by spectroscopy and elemental analysis, an orange crystal suitable for X-ray analysis was obtained by recrystallization of the complex from benzene; the structure is shown in Figure 3, with selected bond distances and angles listed in Table 4. The complex crystallizes with one molecule of benzene in the asymmetric unit. The structure corresponds to that of **9** and **10**, but with the PPh_3 in place of the NHC: the distorted-octahedral geometry now has the PPh_3 and the N-donor atom essentially trans (P−Rh−N = 174.18°), with the η^2-peroxide, the Cl atom, and the P atom of the P-N ligand again forming a quite distorted square-planar arrangement. The structure is remarkably analogous to those of **9** and **10** (Tables 2−4). The Rh peroxo moieties have very similar

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Table 4. Selected Bond Distances (Å) and Angles (deg) for RhCl(O_2)(PPh_3)(P-N) (13) with Estimated Standard Deviations in Parentheses

Rh(1)−N(1)	2.213(5)	Rh(1)−P(1)	2.2747(15)
Rh(1)−O(1)	1.998(4)	Rh(1)−Cl(1)	2.3931(14)
Rh(1)−O(2)	2.054(3)	O(1)−O(2)	1.445(5)
Rh(1)−P(2)	2.2725(14)		
O(2)−Rh(1)−O(1)	41.76(15)	P(2)−Rh(1)−P(1)	101.42(6)
N(1)−Rh(1)−P(2)	82.72(12)	O(1)−Rh(1)−Cl(1)	152.81(12)
N(1)−Rh(1)−P(1)	174.18(13)	Rh(1)−O(2)−O(1)	67.0(2)
O(2)−Rh(1)−Cl(1)	111.17(12)	Rh(1)−O(1)−O(2)	71.2(2)
N(1)−Rh(1)−Cl(1)	88.59(13)		

geometries, and even the Rh−N bond lengths (trans to carbene or PPh_3) are within 0.01−0.02 Å of each other, the shortest one being in **13**, which contains the trans π-acceptor PPh_3. The Rh−P bond lengths of about 2.27 Å lie between those of **9** and **10** and are not exceptional.

The solution $^{31}P\{^1H\}$ NMR spectrum of **13** is consistent with the solid-state structure and shows two doublets of doublets at δ 45.2 (J_{RhP} = 148, J_{PP} = 27 Hz) and 38.9 (J_{RhP} = 130, J_{PP} = 27 Hz), tentatively assigned (by comparison with data for **9** and **10**) to the P-N and PPh_3 ligands, respectively, the J_{RhP} values being consistent with the two P atoms being mutually cis.[6,17] The ^1H spectrum shows singlets at δ 3.69 and 2.31 for inequivalent methyl protons of the P-N ligand. The peroxide stretch in the IR is seen at 873 cm^{-1}.

Of note, the clean oxygenation chemistry of complexes **4**−**8** contrasts markedly with the complicated O_2 oxidation of RhCl(PPh_3)$_3$ and [RhCl(PPh_3)$_2$]$_2$ complexes, where formation of $OPPh_3$ and a bridging oxo species is seen, depending on conditions.[22] However, this reactivity results, at least in the case of RhCl(PPh_3)$_3$, from dissociation of a phosphine ligand. The clean formation of a peroxo species via oxidative addition clearly does not result simply from the presence of a less oxidizable NHC ligand, since the RhCl(PPh_3)(P-N) complex shows the same oxygenation chemistry as the RhCl(NHC)(P-N) analogues. The more complex reactivity possibly results from the presence of trans PPh_3 ligands that promotes dissociation a PPh_3 ligand; none of the complexes **4**−**8** contains trans phosphine moieties, although the peroxides **11** and **12** have trans phosphines. The established mechanism for formation of phosphine oxides from phosphine complexes of low-valent platinum metals involves the presence of some free phosphine, which initially acts as a nucelophile that replaces the coordinated peroxide; the subsequently generated H_2O_2 and the oxidized metal turn out to be the actual oxidizing agents of the phosphine.[21d] In line with this mechanism, preliminary tests suggest that the peroxides **9**−**13** do catalyze the O_2 oxidation of phosphines, but we do not intend to pursue this mundane catalysis.

Conclusions

The complexes RhCl(NHC)(P-N) and *cis*-RhCl(NHC)(PPh_3)$_2$, where NHC = IPr, IMes and P-N = P,N-chelated *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline, were synthesized from [RhCl(COE)(NHC)]$_2$ precursors; production of RhCl(IPr)(P-N) requires use of a hydrogen atmosphere and the intermediate formation of the dihydrido intermediate RhCl(H_2)(IPr)(P-N). The RhCl(PPh_3)(P-N) complex was also made. All five of the Rh(I) complexes undergo rapid, irreversible oxidative addition of O_2 under ambient conditions to generate the corresponding stable Rh(III) peroxo complexes, three of which have been characterized crystallographically. The studies show, perhaps surprisingly, that NHC ligands behave much like PPh_3, *at least qualitatively*, in oxygenation reactivity of the Rh(I) complexes RhCl(L)(P-N), where L = IPr, IMes, PPh_3 and L is trans to the N-donor atom; the π-acceptor PPh_3 might have been expected to decrease the propensity for oxidative addition,[23] and more quantitative kinetic data may still reveal this.

Experimental Section

All manipulations were performed under Ar unless stated otherwise, using standard Schlenk techniques. Reagent grade solvents (Fisher Scientific) were dried using standard procedures and prior to use were purged with a stream of Ar. Deuterated solvents (Cambridge Isotope Laboratories) were similarly dried and then distilled under N_2 prior to use. Common chemicals were obtained from Fisher Scientific; these and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl; Strem) were used as received. IPr,[24] IMes,[25] the P-N ligand,[26] RhCl(PPh_3)$_3$,[27] and [RhCl(COE)$_2$]$_2$[28] were synthesized according to the reported procedures.

NMR spectra were recorded at room temperature (~20 °C) on Bruker AV 300 (300.0 MHz for ^1H, 121.4 MHz for $^{31}P\{^1H\}$, and 75.0 MHz for $^{13}C\{^1H\}$ NMR) and Bruker AV 400 (400.0 MHz for ^1H, 162.0 MHz for $^{31}P\{^1H\}$, and 100.6 MHz for $^{13}C\{^1H\}$ NMR) spectrometers. Residual protonated species in the deuterated solvents were used as internal references (δ 7.15 for C_6D_6); all ^1H shifts are reported in ppm (s = singlet, d = doublet, m = multiplet, spt = septet, and br = broad), relative to external TMS, with *J* values in Hz. $^{31}P\{^1H\}$ NMR shifts are reported relative to external 85% aqueous H_3PO_4. Mass spectral data (reported as *m*/*z* values) were acquired on a Bruker Esquire ES spectrometer in this department (Dr. Y. Ling). IR spectra (KBr) were recorded on ATI Mattson Genesis and Bomem-Michelson MB-100 FT-IR spectrometers; the peroxide bands in the 850−875 cm^{-1} range were readily identified by comparing the IR spectra of the peroxide complexes with those of their precursor complexes. Elemental analyses were performed by Mr. M. Lakha of this department on a Carlo Erba EA 1108 analyzer.

Crystal Structure Determinations. Measurements were performed at 173 ± 0.1 K on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo Kα radiation (0.710 69 Å). Some crystallographic data and selected bond lengths and angles for complexes **9**, **10**, and **13** are shown in Tables 1−4. All the structures were solved using direct methods[29] and expanded using Fourier techniques.[30] For **9**, carbons in a disordered solvate hexane molecule were refined isotropically; all other non-hydrogen atoms were refined anisotropically. Complex **13** crystallizes as a racemic twin with a molecule of benzene in the asymmetric unit; final refinements were carried out using the TWIN/BASF functions of SHELXL, with a final value indicating a roughly 2:1 ratio of the two enantiomers. All refinements were performed using the SHELXTL program.[31] All hydrogen atoms were included in calculated positions but were not refined.

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[RhCl(COE)(IPr)]$_2$ (1). A suspension of [RhCl(COE)$_2$]$_2$ (0.036 g, 0.050 mmol) and IPr (0.039 g, 0.100 mmol) in hexane (10 mL) was stirred for 4 h at room temperature. Initial dissolution after a few minutes was followed by precipitation. The resulting suspension was concentrated to half its original volume, and the yellow solid was collected and dried in vacuo. Yield: 0.050 g (79%). ^{1}H NMR (C_6D_6): δ 7.32 (br, 2H, Ar *p*-*H*), 7.26 (br, 4H, Ar *m*-*H*), 6.37 (s, 2H, NC*H*), 3.29 (br, 4H, C*H*Me$_2$), 2.71 (br, 2H, C*H*═C*H* olefin), 1.82 (br, 4H, CH_2), 1.62 (br, 12H, CH(CH_3)$_2$), 1.42 (br, 4H, CH_2), 1.18 (m, 4H, CH_2), 1.00 (br, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 181.7 (d, J_{RhC} = 64, N*C*N), 146.8 (s, N*C*), 138.2 (s, ^{i}Pr-*C*), 128.7 (s, *p*-*C*H), 124.9 (s, *m*-*C*H), 124.4 (s, N*C*H), 59.6 (d, J_{RhC} = 17, ═*C*H olefin), 30.8 (s, *C*H$_2$), 30.6 (s, *C*H$_2$), 29.3 (s, *C*HMe$_2$), 27.6 (s, *C*H$_2$), 26.8 (s, *C*H$_3$), 24.3 (s, *C*H$_3$). Anal. Calcd for $C_{70}H_{100}N_4Cl_2Rh_2$: C, 65.98; H, 7.91; N, 4.40. Found: C, 65.82; H, 8.00; N, 4.45.

[RhCl(COE)(IMes)]$_2$ (2). This yellow complex was prepared in a manner analogous to that described for **1**, but using IMes (0.030 g, 0.100 mmol). Yield: 0.047 g (85%). ^{1}H NMR (C_6D_6): δ 6.90 (s, 4H, Ar *m*-*H*), 6.01 (s, 2H, NC*H*), 2.76 (br, 2H, C*H*═C*H* olefin), 2.31 (s, 18H, CH_3), 1.93 (br, 4H, CH_2), 1.68 (br, 4H, CH_2), 1.45 (br, 4H, CH_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 150.9 (s, N*C*), 138.3 (s, Ar *p*-*C*), 137.8 (s, Ar *o*-*C*), 129.7 (s, Ar *m*-*C*H), 123.5 (s, N*C*H), 59.6 (d, J_{RhC} = 17, ═*C*H olefin), 31.2 (s, *C*H$_2$), 30.3 (s, *C*H$_2$), 27.8 (s, *C*H$_2$), 23.4 (s, *C*H$_3$). Anal. Calcd for $C_{58}H_{76}N_4Cl_2Rh_2$: C, 62.99; H, 6.93; N, 5.07. Found: C, 63.30; H, 7.20; N, 5.00.

RhCl(H)$_2$(IPr)(P-N) (3) and RhCl(IPr)(P-N) (4). A solution of [RhCl(COE)(IPr)]$_2$ (**1**; 0.064 g, 0.050 mmol) and P-N (0.031 g, 0.100 mmol) in toluene (5 mL) was stirred for 30 min at room temperature under 1 atm of H_2. The resulting yellowish solution was then concentrated, when addition of hexane (10 mL) precipitated a mixture of **3** and **4** as a yellow powder that was collected and dried under vacuum. In toluene solution, complex **3** decomposed to **4** over several hours, and pure **3** could not be isolated or its ^{13}C{^{1}H} NMR spectrum measured. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra of **3** were obtained from the in situ reaction and from a solution of the **3**/**4** mixture, since pure **4** could be isolated (see below). IR (KBr): 2111 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.78−7.72 (m, 2H, Ar *H*), 7.42−6.81 (m, 18H, Ar *H*), 6.69 (s, 2H, NC*H*), 3.32 (spt, 4H, J = 7, C*H*(CH$_3$)$_2$), 2.28 (s, 6H, N(CH_3)$_2$), 1.45 (d, 12H, J = 7, CH(CH_3)$_2$), 1.12 (d, 12H, J = 7, CH(CH_3)$_2$), −20.99 (dd, 2H, J_{PH} = 18, J_{RhH} = 29, Rh*H*). ^{31}P{^{1}H} NMR (C_6D_6): 39.2 (d, J_{RhP} = 114).

When the reactant mixture of **1** and P-N was stirred under 1 atm of H_2 for 6 h, pure **4** was isolated as a yellow powder, by following the above procedure. Yield: 0.074 g (89%). ^{1}H NMR (C_6D_6): δ 7.78−7.72 (m, 2H, Ar *H*), 7.41−6.80 (m, 18H, Ar *H*), 6.77 (s, 2H, NC*H*), 4.20 (spt, 2H, J = 7, C*H*(CH$_3$)$_2$), 3.53 (spt, 2H, J = 7, C*H*(CH$_3$)$_2$), 3.12 (s, 6H, N(CH_3)$_2$), 1.98 (d, 6H, J = 7, CH(CH_3)$_2$), 1.21 (d, 6H, J = 7, CH(CH_3)$_2$), 0.86 (d, 6H, J = 7, CH(CH_3)$_2$), 0.84 (d, 6H, J = 7, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): 44.5 (d, J_{RhP} = 225). ^{13}C{^{1}H} NMR (C_6D_6): δ 186.8 (dd, J_{RhC} = 57, J_{PC} = 15, N*C*N), 161.9 (s, N*C*), 161.7 (s, N*C*), 149.4 (s, Ar *C*), 144.6 (s, Ar *C*), 139.1 (s, Ar *C*), 138.6 (s, Ar *C*), 137.6 (s, Ar *C*), 137.1(s, Ar *C*), 134.1 (s, Ar *C*), 132.6 (s, Ar *C*), 132.3 (s, Ar *C*), 132.2 (s, Ar *C*), 131.1 (s, Ar *C*), 130.5 (s, Ar *C*), 128.7 (s, Ar *C*), 128.2 (s, Ar *C*), 128.1 (s, Ar *C*), 128.0 (s, Ar *C*), 126.8 (s, Ar *C*), 126.7 (s, Ar *C*), 122.4 (s, N*C*H), 122.2 (s, N*C*H), 52.6 (s, N(*C*H$_3$)$_2$), 29.9 (s, *C*H(CH$_3$)$_2$), 29.2 (s, *C*H(CH$_3$)$_2$), 27.1 (s, *C*H-(CH$_3$)$_2$), 27.0 (s, *C*H(CH$_3$)$_2$), 24.7 (s, *C*H$_3$), 23.2 (s, *C*H$_3$). ESI-MS (MeOH): *m*/*z* 794, [M − Cl]$^+$ (100%); 389, [IPr + H]$^+$ (27%). Anal. Calcd for $C_{47}H_{56}N_3PClRh$ (M = 832.3): C, 67.82; H, 6.78; N, 5.05. Found: C, 67.42; H, 7.10; N, 5.13.

RhCl(IMes)(P-N) (5). A solution of [RhCl(COE)(IMes)]$_2$ (**2**; 0.055 g, 0.050 mmol) and P-N (0.031 g, 0.100 mmol) in toluene (5 mL) was stirred for 4 h at room temperature, and the resulting yellowish solution was concentrated to ∼2 mL. Addition of hexane (10 mL) precipitated a yellow powder that was collected and dried in vacuo. Yield: 0.069 g (92%). ^{1}H NMR (C_6D_6): δ 7.84−7.78 (m, 2H, Ar *H*), 7.04−6.49 (m, 18H, Ar *H*), 6.20 (s, 2H, NC*H*), 3.07 (s, 6H, N(CH_3)$_2$), 3.01 (s, 6H, *p*-CH_3), 2.13 (s, 6H, *o*-CH_3), 1.57 (s, 6H, *o*-CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 48.1 (d, J_{RhP} = 230). ^{13}C{^{1}H} NMR (C_6D_6): δ 183.9 (dd, J_{RhC} = 54, J_{PC} = 17, N*C*N), 161.0 (s, N*C*), 160.7 (s, N*C*), 142.4 (s, Ar *C*), 141.9 (s, Ar *C*), 138.8 (s, Ar *C*), 138.5 (s, Ar *C*), 138.3 (s, Ar *C*), 135.5(s, Ar *C*), 134.6 (s, Ar *C*), 134.4 (s, Ar *C*), 133.6 (s, Ar *C*), 132.3 (s, Ar *C*), 132.1 (s, Ar *C*), 130.2 (s, Ar *C*), 129.1 (s, Ar *C*), 128.6 (s, Ar *C*), 128.1 (s, Ar *C*), 127.3 (s, Ar *C*), 127.2 (s, Ar *C*), 123.3 (s, Ar *C*), 121.7 (s, N*C*H), 121.6 (s, N*C*H), 52.2 (s, N(*C*H$_3$)$_2$), 21.9 (s, *p*-*C*H$_3$), 21.5 (s, *o*-*C*H$_3$), 19.5 (s, *o*-*C*H$_3$). ESI-MS (MeOH): *m*/*z* 710, [M − Cl]$^+$ (100%); 305, [IMes + H]$^+$ (22%). Anal. Calcd for $C_{41}H_{44}N_3PClRh$ (M = 748.1): C, 65.82; H, 5.93; N, 5.62. Found: C, 65.74; H, 6.19; N, 5.62.

RhCl(IPr)(PPh$_3$)$_2$ (6). A solution of **1** (0.064 g, 0.050 mmol) and PPh$_3$ (0.052 g, 0.200 mmol) in benzene (5 mL) was stirred for 4 h at room temperature; subsequent workup, as described for complex **5**, gave the yellow complex **6**. Yield: 0.097 g (92%). ^{1}H NMR (C_6D_6): δ 7.80−6.59 (m, 38H, Ar *H*), 3.76 (spt, 2H, J = 7, C*H*(CH$_3$)$_2$), 3.36 (spt, 2H, J = 7, C*H*(CH$_3$)$_2$), 1.49 (d, 6H, J = 7, CH(CH_3)$_2$), 1.08 (d, 6H, J = 7, CH(CH_3)$_2$), 0.88 (d, 6H, J = 7, CH(CH_3)$_2$), 0.56 (d, 6H, J = 7, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): 47.3 (dd, J_{RhP} = 210, J_{PP} = 40, P trans to Cl), 36.4 (dd, J_{RhP} = 120, J_{P-P} = 40, P cis to Cl). ^{13}C{^{1}H} NMR (C_6D_6): δ 187.2 (ddd, J_{RhC} = 114, J_{PC} = 52, J_{PC} = 15, N*C*N), 146.8 (s, N*C*), 145.2 (s, N*C*), 136.4 (s, Ar *C*), 134.9(s, Ar *C*), 134.8 (s, Ar *C*), 132.3 (s, Ar *C*), 132.2 (s, Ar *C*), 132.1 (s, Ar *C*), 132.0 (s, Ar *C*), 128.7 (s, Ar *C*), 128.6 (s, Ar *C*), 127.7 (s, Ar *C*), 127.6 (s, Ar *C*), 124.8 (br, N*C*H), 123.9 (br, N*C*H), 29.2 (s, *C*H(CH$_3$)$_2$), 28.9 (s, *C*H(CH$_3$)$_2$), 26.5 (s, *C*H$_3$), 25.0 (s, *C*H$_3$), 23.9 (s, *C*H$_3$), 22.8 (s, *C*H$_3$). Anal. Calcd for $C_{63}H_{66}N_2P_2ClRh$ (M = 1051.5): C, 71.96; H, 6.33; N, 2.66. Found: C, 72.06; H, 6.41; N, 2.67.

RhCl(IMes)(PPh$_3$)$_2$ (7). This yellow complex was prepared in a manner analogous to that described for **6**, but using 0.055 g (0.050 mmol) of **2** and 0.052 g (0.200 mmol) of PPh$_3$. Yield: 0.091 g (94%). ^{1}H NMR ($CDCl_3$): 7.35−6.85 (m, 36H, Ar *H*), 3.01 (s, 6H, *p*-CH_3), 2.13 (s, 6H, *o*-CH_3), 1.57 (s, 6H, *o*-CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): 50.3 (dd, J_{RhP} = 210, J_{PP} = 40, P trans to Cl), 37.0 (dd, J_{RhP} = 119, J_{PP} = 40, P cis to Cl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 189.4 (ddd, J_{RhC} = 115, J_{PC} = 49, J_{PC} = 17, N*C*N), 138.8 (s, N*C*), 138.0 (s, N*C*), 137.7 (s, Ar *C*), 137.4 (s, Ar *C*), 137.1 (s, Ar *C*), 135.8(s, Ar *C*), 135.6 (s, Ar *C*), 134.9 (s, Ar *C*), 134.8 (s, Ar *C*), 129.7 (s, Ar *C*), 128.6 (s, Ar *C*), 128.2 (s, Ar *C*), 127.6 (s, Ar *C*), 126.8 (d, J_{P-C} = 9, N*C*H), 126.5 (d, J_{P-C} = 9, N*C*H), 22.0 (s, *p*-*C*H$_3$), 21.5 (s, *o*-*C*H$_3$), 19.9 (s, *o*-*C*H$_3$). Anal. Calcd for $C_{57}H_{54}P_2N_2ClRh$ (M = 967.4): C, 70.77; H, 5.63; N, 2.90. Found: C, 71.13; H, 5.76; N, 2.76.

RhCl(PPh$_3$)(P-N) (8). This yellow complex was prepared in a manner analogous to that described for **5** but using 0.093 g (0.100 mmol) of RhCl(PPh$_3$)$_3$ as the Rh precursor. Yield: 0.057 g (81%). ^{1}H NMR (C_6D_6): δ 7.78−6.12 (m, 29H, Ar *H*), 3.38 (s, 6H, N(CH_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): 57.6 (dd, J_{RhP} = 197, J_{PP} = 45), 52.4 (dd, J_{RhP} = 175, J_{PP} = 45). ^{13}C{^{1}H} NMR (C_6D_6): δ 161.0−122.9 (Ar *C*), 52.8 (s, N(*C*H$_3$)$_2$). Anal. Calcd for $C_{38}H_{35}P_2NClRh$ (M = 706.0): C, 64.65; H, 5.00; N, 1.98. Found: C, 64.33; H, 5.08; N, 1.70.

RhCl(O$_2$)(IPr)(P−N) (9). A yellow solution of **4** (0.042 g, 0.050 mmol) in toluene (5 mL) was stirred under 1 atm of O_2 for 10 min at room temperature. The resulting brown solution was concentrated to ∼2 mL, when hexane (10 mL) was added to precipitate the product that was collected and dried in vacuo. Yield: 0.041 g (95%). IR (KBr): 871 cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.15 (m, 2H, Ar *H*), 7.30−6.66 (m, 18H, Ar *H*), 6.47 (s, 2H, NC*H*), 4.44 (br, 2H, C*H*(CH$_3$)$_2$), 3.37 (s, 3H, N(CH_3)), 2.76 (br, 2H, C*H*(CH$_3$)$_2$), 2.11 (s, 3H, N(CH_3)), 1.87 (br, 6H, CH(CH_3)$_2$), 1.23 (br, 6H, CH(CH_3)$_2$),

1.09 (br, 6H, CH(CH_3)$_2$), 0.88 (br, 6H, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): 35.3 (d, J_{RhP} = 149). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.1 (s, N*C*), 159.9 (dd, J_{RhC} = 51, J_{PC} = 9, N*C*N), 159.8(s, N*C*), 139.9 (s, Ar *C*), 139.3 (s, Ar *C*), 136.4 (s, Ar *C*), 136.2 (s, Ar *C*), 136.2 (s, Ar *C*), 134.6 (s, Ar *C*), 134.1 (s, Ar *C*), 133.8 (s, Ar *C*), 133.3 (s, Ar *C*), 132.7 (s, Ar *C*), 131.1 (s, Ar *C*), 130.5 (s, Ar *C*), 130.2 (s, Ar *C*), 129.7 (s, Ar *C*), 129.1 (s, Ar *C*), 129.0 (s, Ar *C*), 127.0 (s, Ar *C*), 126.4 (s, Ar *C*), 126.0 (s, Ar *C*), 121.7 (s, N*C*H), 121.5 (s, N*C*H), 52.7 (s, N(*C*H$_3$)$_2$), 50.2 (s, N(*C*H$_3$)$_2$), 29.7 (s, *C*H(CH$_3$)$_2$), 24.4 (s, *C*H$_3$), 23.4 (s, *C*H$_3$). ESI-MS (MeOH): *m*/*z* 864, [M + H]$^+$ (100%); 847, [M − O]$^+$ (18%); 322, [(OP-N) + H]$^+$ (37%). Anal. Calcd for $C_{47}H_{56}N_3PClO_2Rh$ (*M* = 864.3): C, 65.31; H, 6.53; N, 4.86. Found: C, 65.35; H, 6.66; N, 5.12.

RhCl(O$_2$)(IMes)(P-N) (10). This orange complex was prepared in a manner analogous to that described for **9** but using 0.037 g (0.050 mmol) of **5**. Yield: 0.037 g (95%). IR (KBr): 870 cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.20 (m, 2H, Ar *H*), 7.88−6.60 (m, 18H, Ar *H*), 6.05 (s, 2H, NC*H*), 3.39 (s, 3H, N(CH_3)), 2.26 (s, 6H, CH_3), 2.14 (s, 12H, CH_3), 1.97 (s, 3H, N(CH_3)). ^{31}P{^{1}H} NMR (C_6D_6): 34.7 (d, J_{RhP} = 149). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.2 (s, N*C*), 159.8-(s, N*C*), 159.4 (dd, J_{RhC} = 50, J_{PC} = 9, N*C*N), 141.0 (s, Ar *C*), 140.5 (s, Ar *C*), 139.6 (s, Ar *C*), 138.6 (s, Ar *C*), 138.1 (s, Ar *C*), 136.7 (s, Ar *C*), 136.5 (s, Ar *C*), 136.4 (s, Ar *C*), 136.3 (s, Ar *C*), 136.2 (s, Ar *C*), 135.6 (s, Ar *C*), 135.4 (s, Ar *C*), 135.0 (s, Ar *C*), 132.3 (s, Ar *C*), 132.2 (s, Ar *C*), 129.2 (s, Ar *C*), 126.3 (s, Ar *C*), 126.2 (s, Ar *C*), 125.0 (s, Ar *C*), 121.6 (s, N*C*H), 121.5 (s, N*C*H), 52.8 (s, N(*C*H$_3$)$_2$), 50.1 (s, N(*C*H$_3$)$_2$), 21.5 (s, *C*H$_3$), 19.4 (s, *C*H$_3$), 19.2 (s, *C*H$_3$). ESI-MS (MeOH): *m*/*z* 780, [M + H]$^+$ (82%); 763, [M − O]$^+$ (100%); 322, [(OP-N) + H]$^+$ (17%). Anal. Calcd for $C_{41}H_{44}N_3PClO_2Rh$ (*M* = 780.1): C, 63.12; H, 5.68; N, 5.39. Found: C, 63.27; H, 5.50; N, 5.29.

RhCl(O$_2$)(IPr)(PPh$_3$)$_2$ (11). A yellow solution of **6** (0.053 g, 0.050 mmol) in benzene (5 mL) was stirred under 1 atm of O_2 for 2 h at room temperature. The resulting suspension was concentrated to ∼2 mL; addition of hexane (10 mL) precipitated further orange product that was collected and dried in vacuo. Yield: 0.051 g (94%). IR (KBr): 852 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.80−6.99 (m, 36H, Ar *H*), 6.73 (s, 2H, NC*H*), 3.26 (spt, 4H, *J* = 7, C*H*(CH$_3$)$_2$), 1.43 (d, 12H, *J* = 7, CH(CH_3)$_2$), 1.09 (d, 12H, *J* = 7, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): 18.4 (d, J_{RhP} = 105). ^{13}C{^{1}H} NMR (C_6D_6): δ 147.6 (s, N*C*), 146.6 (s, Ar *C*), 145.6 (s, Ar *C*), 133.0 (s, Ar *C*), 132.5 (s, Ar *C*), 131.6 (s, Ar *C*), 130.3 (s, Ar *C*), 130.0 (s, Ar *C*), 128.9 (s, Ar *C*), 128.8 (s, Ar *C*), 127.4 (s, Ar *C*), 127.3 (s, Ar *C*), 124.0 (br, N*C*H), 29.1 (s, *C*H(CH$_3$)$_2$), 25.1 (s, *C*H$_3$), 23.9 (s, *C*H$_3$). Anal. Calcd for $C_{63}H_{66}P_2N_2ClO_2Rh$ (*M* = 1083.5): C, 69.84; H, 6.14; N, 2.59. Found: C, 70.20; H, 6.42; N, 2.61.

RhCl(O$_2$)(IMes)(PPh$_3$)$_2$ (12). This orange complex was prepared in a manner analogous to that described for **11** but using 0.048 g (0.050 mmol) of **7**. Yield: 0.047 g (84%). IR (KBr): 851 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.80−6.80 (m, 34H, Ar *H*), 6.27 (s, 2H, NC*H*), 2.33 (s, 12H, *o*-CH_3), 2.14 (s, 6H, *p*-CH_3). ^{31}P{^{1}H} NMR (C_6D_6): 16.9 (d, J_{RhP} = 104). ^{13}C{^{1}H} NMR (C_6D_6): δ 138.7 (s, N*C*), 135.8 (s, Ar *C*), 135.6 (s, Ar *C*), 132.9 (s, Ar *C*), 132.8 (s, Ar *C*), 132.7 (s, Ar *C*), 131.9 (s, Ar *C*), 129.7 (s, Ar *C*), 129.5 (s, Ar *C*), 129.1 (s, Ar *C*), 128.9 (s, Ar *C*), 128.6 (s, Ar *C*), 123.6 (br, N*C*H), 21.6 (s, *p*-*C*H$_3$), 19.0 (s, *o*-*C*H$_3$). Anal. Calcd for $C_{57}H_{54}P_2N_2ClO_2Rh\cdot 1.5C_6H_6$ (*M* = 1116.4): C, 71.00; H, 5.69; N, 2.51. Found: C, 71.01; H, 5.88; N, 2.91.

RhCl(O$_2$)(PPh$_3$)(P-N) (13). This complex was prepared in a manner analogous to that described for **9** but using 0.035 g (0.050 mmol) of **8**. Yield: 0.037 g (89%). IR (KBr): 873 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.73−7.00 (m, 29H, Ar *H*), 3.62 (br, 3H, N(CH_3)$_2$), 2.36 (br, 3H, N(CH_3)$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): 45.6 (dd, J_{RhP} = 149, J_{PP} = 26), 37.7 (dd, J_{RhP} = 127, J_{PP} = 26). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 136.1−127.2 (Ar *C*), 54.5 (s, N(*C*H$_3$)$_2$). 50.4 (s, N(*C*H$_3$)$_2$). Anal. Calcd for $C_{38}H_{35}P_2NClO_2Rh\cdot C_7H_8$ (*M* = 830.0): C, 65.06; H, 5.18; N, 1.69. Found: C, 65.29; H, 5.08; N, 1.78. An orange crystal suitable for X-ray analysis was grown by recrystallization of the solid from benzene.

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Supporting Information Available: Crystallographic data for RhCl(O$_2$)(IPr)(P-N) (**9**), RhCl(O$_2$)(IMes)(P-N) (**10**), and RhCl(O$_2$)-(PPh$_3$)(P-N) (**13**) as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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