

Rhodium(III) Peroxo Complexes Containing Carbene and Phosphine Ligands

Xiao-Yan Yu, Brian O. Patrick, and Brian R. James*

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

Received June 29, 2006

The Rh(I) carbene precursors $[\text{RhCl}(\text{COE})(\text{NHC})]_2$, 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 $\text{RhCl}(\text{NHC})(\text{P-N})$ complexes **4** (NHC = IPr) and **5** (NHC = IMes), where P-N is P,N-chelated *o*-(diphenylphosphino)-*N,N*-dimethylaniline, and the corresponding *cis*- $\text{RhCl}(\text{NHC})(\text{PPh}_3)_2$ 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 $\text{RhCl}(\text{H})_2(\text{IPr})(\text{P-N})$ (**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, $\text{RhCl}(\text{PPh}_3)(\text{P-N})$ (**8**) was synthesized from $\text{RhCl}(\text{PPh}_3)_3$, and this also added O_2 to form a peroxo complex (**13**). All of the complexes were generally characterized by elemental analysis and ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ 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) species² and one cobalt(III) complex³ 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, $\text{IrCl}(\text{O}_2)(\text{NHC})_2$, 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 $\text{RhCl}(\text{NHC})(\text{P-N})$ and the known⁶ *cis*- $\text{RhCl}(\text{NHC})(\text{PPh}_3)_2$ from the $[\text{RhCl}(\text{COE})(\text{NHC})]_2$ precursors and their reactions with O_2 to give, respectively, the Rh(III) η^2 -peroxo species $\text{RhCl}(\text{O}_2)(\text{NHC})(\text{P-N})$ and $\text{RhCl}(\text{O}_2)(\text{NHC})(\text{PPh}_3)_2$, 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

$[\text{RhCl}(\text{COE})(\text{NHC})]_2$ 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, $\text{RhCl}(\text{PPh}_3)(\text{P-N})$ 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 $\text{RhCl}(\text{O}_2)(\text{NHC})_2$, 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

$[\text{RhCl}(\text{COE})(\text{NHC})]_2$ Complexes **1 (NHC = IPr) and **2** (NHC = IMes).** The yellow complex $[\text{RhCl}(\text{COE})(\text{IPr})]_2$ (**1**) was prepared by stirring $[\text{RhCl}(\text{COE})_2]_2$ 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 $\text{Rh}(\text{H})\text{Cl}(\text{IMes}')(\text{IMes})$ (**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**.

* To whom correspondence should be addressed. Tel.: +1 (604) 822-6645. Fax: +1 (604) 822-2847. E-mail: brj@chem.ubc.ca.

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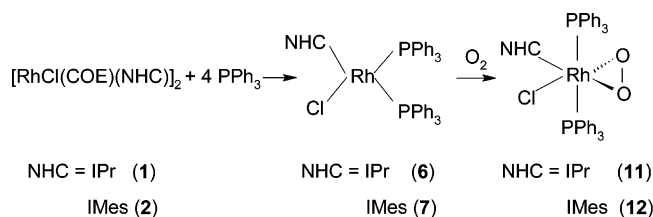
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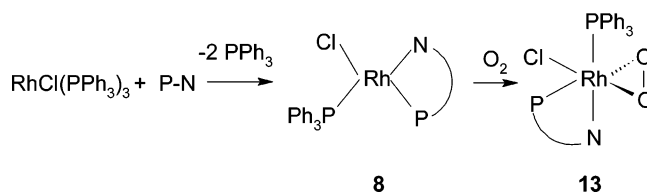
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Scheme 3. Formation of **6**, **7**, **11**, and **12**

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 ^1H 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 $^{31}\text{P}\{^1\text{H}\}$ NMR doublet at δ 48.1 with $J_{\text{RhP}} = 230$ Hz. The ^1H spectrum shows singlets at δ 6.20 (for NCH), 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 $^{13}\text{C}\{^1\text{H}\}$ doublet of doublets for the carbene carbon is seen at δ 183.9 ($J_{\text{RhC}} = 54$, $J_{\text{PC}} = 17$ 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 $\text{RhCl}(\text{COD})(\text{NHC})$ 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*- $\text{RhCl}(\text{NHC})(\text{PPh}_3)_2$ complexes **6** (NHC = IPr) and **7** (NHC = IMes) (Scheme 3). The $^{31}\text{P}\{^1\text{H}\}$ NMR data for **6** and **7** show two doublets of doublets for the inequivalent phosphines. The $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{RhCl}(\text{PPh}_3)_3$ with IMes,⁶ and our ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR data (measured in CDCl_3) agree with reported values;^{6c} the $^{13}\text{C}\{^1\text{H}\}$

Scheme 4. Formation of **8** and **13**

data for **7** have not been given previously, although such data were later reported for some related *cis*- $\text{RhCl}(\text{IMes})(\text{PAr}_3)_2$ 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 $\text{RhCl}(\text{PPh}_3)_3$ with P-N. For the purpose of comparing properties of the $\text{RhCl}(\text{NHC})(\text{P-N})$ complexes **4** and **5** with those of a corresponding complex containing a PPh_3 ligand instead of a carbene ligand, $\text{RhCl}(\text{PPh}_3)(\text{P-N})$ (**8**) was synthesized. The exchange reaction of $\text{RhCl}(\text{PPh}_3)_3$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in C_6D_6 shows two doublets of doublets at δ 57.6 ($J_{\text{RhP}} = 197$, $J_{\text{PP}} = 45$ Hz), likely due to the P-N ligand, and at δ 52.4 (dd, $J_{\text{RhP}} = 175$, $J_{\text{PP}} = 45$ Hz), likely due to the PPh_3 ligand (on the basis of $^{31}\text{P}\{^1\text{H}\}$ 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 ^1H 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 $\text{RhCl}(\text{NHC})(\text{P-N})$ (NHC = IPr (4**), IMes (**5**)), $\text{RhCl}(\text{NHC})(\text{PPh}_3)_2$ (NHC = IPr (**6**), IMes (**7**)), and $\text{RhCl}(\text{PPh}_3)(\text{P-N})$ (**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 $\text{RhCl}(\text{O}_2)(\text{NHC})(\text{P-N})$, 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 $\text{RhCl}(\text{O}_2)(\text{IPr})(\text{P-N})$ (**9**), $\text{RhCl}(\text{O}_2)(\text{IMes})(\text{P-N})$ (**10**), and $\text{RhCl}(\text{O}_2)(\text{PPh}_3)(\text{P-N})$ (**13**)

	9	10	13
formula	$\text{C}_{47}\text{H}_{56}\text{N}_3\text{O}_2\text{PRhCl}\cdot\text{C}_6\text{H}_{14}$	$\text{C}_{41}\text{H}_{44}\text{N}_3\text{O}_2\text{PRhCl}$	$\text{C}_{38}\text{H}_{35}\text{NO}_2\text{P}_2\text{RhCl}\cdot\text{C}_6\text{H}_6$
fw	950.45	780.12	816.08
cryst color, habit	brown, needle	orange, prism	orange, needle
cryst size (mm)	$0.40 \times 0.15 \times 0.10$	$0.20 \times 0.15 \times 0.05$	$0.30 \times 0.10 \times 0.07$
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
<i>a</i> (Å)	14.684(2)	12.0059(4)	10.7428(8)
<i>b</i> (Å)	16.898(2)	31.748(1)	12.605(1)
<i>c</i> (Å)	19.798(2)	10.2883(4)	28.474(2)
β (deg)	90.927(8)	108.068(2)	90
<i>V</i> (Å ³)	4912(1)	3728.1(2)	3855.8(6)
<i>Z</i>	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
<i>R</i> _{int}	0.057	0.043	0.056
no. of variables	555	450	463
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>), all data)	0.091	0.043	0.066
w <i>R</i> 2 (all data)	0.061 ^a	0.072 ^b	0.100 ^c
GOF (all data)	0.82	1.05	0.98

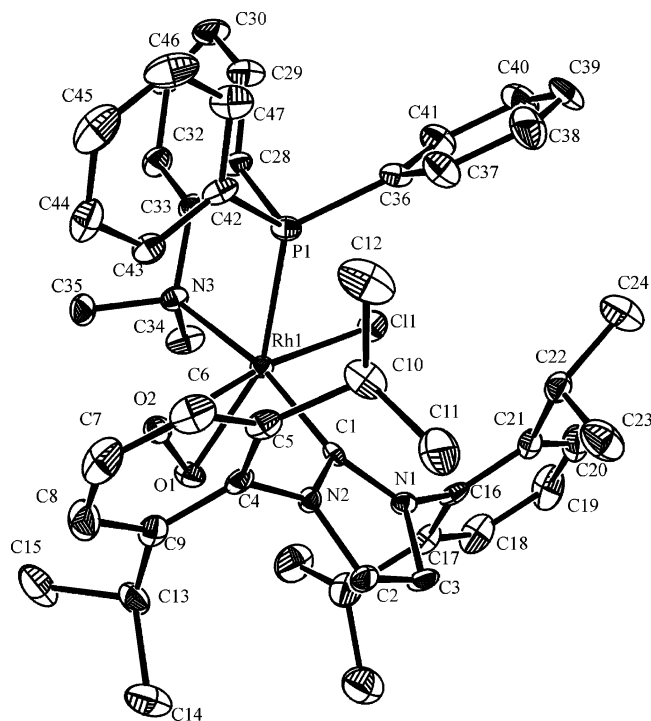
^a $w = 1/[\sigma^2(F_o^2) + (0.0152P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ in all cases. ^b $w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + (0.9607P)]$. ^c $w = 1/[\sigma^2(F_o^2) + (0.0476P)^2]$.

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

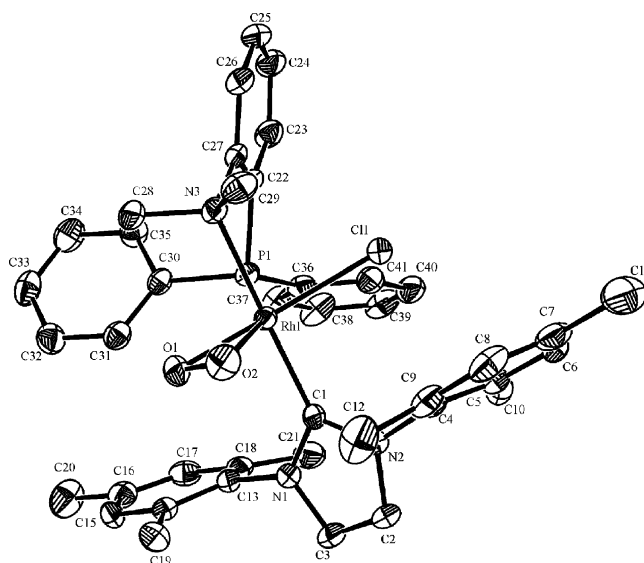
$\text{Rh}(1)-\text{C}(1)$	2.029(3)	$\text{Rh}(1)-\text{P}(1)$	2.2681(9)
$\text{Rh}(1)-\text{O}(1)$	2.0476(19)	$\text{Rh}(1)-\text{Cl}(1)$	2.4192(8)
$\text{Rh}(1)-\text{O}(2)$	1.9625(18)	$\text{O}(1)-\text{O}(2)$	1.450(3)
$\text{Rh}(1)-\text{N}(3)$	2.221(2)		
$\text{O}(2)-\text{Rh}(1)-\text{O}(1)$	42.32(7)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

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

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

**Figure 1.** ORTEP diagram of $\text{RhCl}(\text{O}_2)(\text{IPr})(\text{P-N})$ (**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 ($\text{C}-\text{Rh}-\text{N} = 169-172^\circ$) 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 $\text{RhCl}(\text{O}_2)(\text{IMes})(\text{P-N})$ (**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 $[\text{M} + \text{H}]^+$.

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 $^{31}\text{P}\{^1\text{H}\}$ doublet at δ 35.3 ($J_{\text{RHP}} = 149$ Hz) and a $^{13}\text{C}\{^1\text{H}\}$ doublet of doublets at δ 159.9 ($J_{\text{RHC}} = 51$, $J_{\text{PC}} = 9$ Hz) shifted some 25 ppm upfield from that of the precursor **4**. Similar data are seen for **10**: $\delta_{\text{P}} 34.7$ ($J_{\text{RHP}} = 149$ Hz) and $\delta_{\text{C}} 159.4$ ($J_{\text{RHC}} = 50$, $J_{\text{PC}} = 9$ 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 $\text{RhCl}(\text{NHC})(\text{P-N})$ species, the $\text{RhCl}(\text{NHC})(\text{PPh}_3)_2$ 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 $\text{RhCl}(\text{O}_2)(\text{NHC})(\text{PPh}_3)_2$ (**11** and **12**). We were unable to grow crystals suitable for X-ray analysis, but a simple doublet in the $^{31}\text{P}\{^1\text{H}\}$ 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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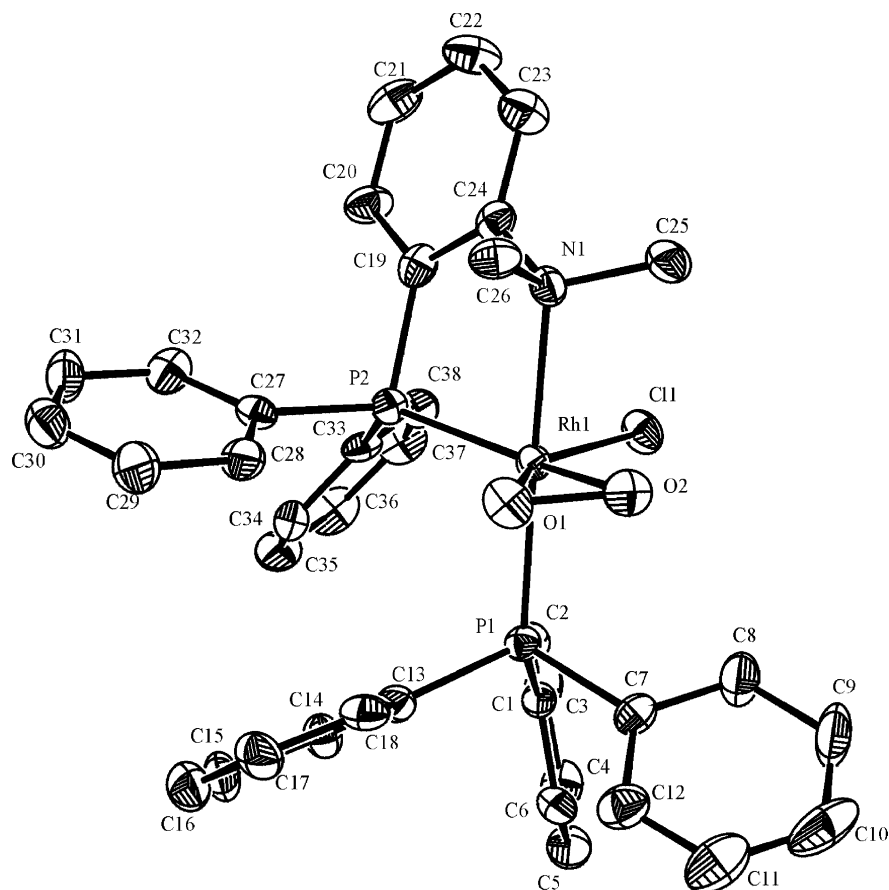


Figure 3. ORTEP diagram of $\text{RhCl}(\text{O}_2)(\text{PPh}_3)(\text{P-N})$ (**13**) with 50% probability thermal ellipsoids.

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*- $\text{RhCl}(\text{IMes})(\text{PPh}_3)_2$, 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 $[\text{RhCl}(\text{COE})(\text{NHC})]_2$, $\text{RhCl}(\text{NHC})(\text{P-N})$, and $\text{RhCl}(\text{NHC})(\text{PPh}_3)_2$ species are all reactive toward oxygen. Indeed, our interest and that of others⁹ 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 complexes²¹ remains to be investigated.

Of note, reaction of O_2 with the NHC-free complex $\text{RhCl}(\text{PPh}_3)(\text{P-N})$ (**8**) in toluene (Scheme 4) follows that with the $\text{RhCl}(\text{NHC})(\text{P-N})$ complexes **4** and **5** (Scheme 2), again rapidly giving $\text{RhCl}(\text{O}_2)(\text{PPh}_3)(\text{P-N})$ (**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 ($\text{P-Rh-N} = 174.18^\circ$), 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(O₂)(PPh₃)(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 PPh₃) are within 0.01–0.02 Å of each other, the shortest one being in **13**, which contains the trans π -acceptor PPh₃. The Rh–P bond lengths of about 2.27 Å lie between those of **9** and **10** and are not exceptional.

The solution ³¹P{¹H} NMR spectrum of **13** is consistent with the solid-state structure and shows two doublets of doublets at δ 45.2 ($J_{\text{RhP}} = 148$, $J_{\text{PP}} = 27$ Hz) and 38.9 ($J_{\text{RhP}} = 130$, $J_{\text{PP}} = 27$ Hz), tentatively assigned (by comparison with data for **9** and **10**) to the P–N and PPh₃ 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 O₂ oxidation of RhCl(PPh₃)₃ and [RhCl(PPh₃)₂]₂ complexes, where formation of OPPh₃ and a bridging oxo species is seen, depending on conditions.²² However, this reactivity results, at least in the case of RhCl(PPh₃)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(PPh₃)(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 PPh₃ ligands that promotes dissociation a PPh₃ 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 nucleophile that replaces the coordinated peroxide; the subsequently generated H₂O₂ 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 O₂ oxidation of phosphines, but we do not intend to pursue this mundane catalysis.

Conclusions

The complexes RhCl(NHC)(P–N) and *cis*-RhCl(NHC)(PPh₃)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(PPh₃)(P–N) complex was also made. All five of the Rh(I) complexes undergo rapid, irreversible oxidative addition of O₂ 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 PPh₃, at least qualitatively, in oxygenation reactivity of the Rh(I) complexes RhCl(L)(P–N), where L = IPr, IMes, PPh₃ and L is trans to the N-donor atom; the π -acceptor PPh₃ 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 N₂ 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(PPh₃)₃,²⁷ and [RhCl(COE)]₂²⁸ 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 ³¹P{¹H}), and 75.0 MHz for ¹³C{¹H} NMR) and Bruker AV 400 (400.0 MHz for ¹H, 162.0 MHz for ³¹P{¹H}), and 100.6 MHz for ¹³C{¹H} NMR) spectrometers. Residual protonated species in the deuterated solvents were used as internal references (δ 7.15 for C₆D₆); 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. ³¹P{¹H} NMR shifts are reported relative to external 85% aqueous H₃PO₄. 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 K α 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 methods²⁹ 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%). ¹H NMR (C₆D₆): δ 7.32 (br, 2H, Ar *p*-H), 7.26 (br, 4H, Ar *m*-H), 6.37 (s, 2H, NCH), 3.29 (br, 4H, CHMe₂), 2.71 (br, 2H, CH=CH olefin), 1.82 (br, 4H, CH₂), 1.62 (br, 12H, CH(CH₃)₂), 1.42 (br, 4H, CH₂), 1.18 (m, 4H, CH₂), 1.00 (br, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (C₆D₆): δ 181.7 (d, *J*_{RhC} = 64, NCN), 146.8 (s, NC), 138.2 (s, ¹Pr-C), 128.7 (s, *p*-CH), 124.9 (s, *m*-CH), 124.4 (s, NCH), 59.6 (d, *J*_{RhC} = 17, =CH olefin), 30.8 (s, CH₂), 30.6 (s, CH₂), 29.3 (s, CHMe₂), 27.6 (s, CH₂), 26.8 (s, CH₃), 24.3 (s, CH₃). Anal. Calcd for C₇₀H₁₀₀N₄Cl₂Rh₂: 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%). ¹H NMR (C₆D₆): δ 6.90 (s, 4H, Ar *m*-H), 6.01 (s, 2H, NCH), 2.76 (br, 2H, CH=CH olefin), 2.31 (s, 18H, CH₃), 1.93 (br, 4H, CH₂), 1.68 (br, 4H, CH₂), 1.45 (br, 4H, CH₂). ¹³C{¹H} NMR (C₆D₆): δ 150.9 (s, NC), 138.3 (s, Ar *p*-C), 137.8 (s, Ar *o*-C), 129.7 (s, Ar *m*-CH), 123.5 (s, NCH), 59.6 (d, *J*_{RhC} = 17, =CH olefin), 31.2 (s, CH₂), 30.3 (s, CH₂), 27.8 (s, CH₂), 23.4 (s, CH₃). Anal. Calcd for C₅₈H₇₆N₄Cl₂Rh₂: 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 H₂. 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 ¹³C{¹H} NMR spectrum measured. ¹H NMR and ³¹P{¹H} 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. ¹H NMR (C₆D₆): δ 7.78–7.72 (m, 2H, Ar *H*), 7.42–6.81 (m, 18H, Ar *H*), 6.69 (s, 2H, NCH), 3.32 (spt, 4H, *J* = 7, CH(CH₃)₂), 2.28 (s, 6H, N(CH₃)₂), 1.45 (d, 12H, *J* = 7, CH(CH₃)₂), 1.12 (d, 12H, *J* = 7, CH(CH₃)₂), -20.99 (dd, 2H, *J*_{PH} = 18, *J*_{RhH} = 29, RhH). ³¹P{¹H} NMR (C₆D₆): 39.2 (d, *J*_{RhP} = 114).

When the reactant mixture of **1** and P-N was stirred under 1 atm of H₂ for 6 h, pure **4** was isolated as a yellow powder, by following the above procedure. Yield: 0.074 g (89%). ¹H NMR (C₆D₆): δ 7.78–7.72 (m, 2H, Ar *H*), 7.41–6.80 (m, 18H, Ar *H*), 6.77 (s, 2H, NCH), 4.20 (spt, 2H, *J* = 7, CH(CH₃)₂), 3.53 (spt, 2H, *J* = 7, CH(CH₃)₂), 3.12 (s, 6H, N(CH₃)₂), 1.98 (d, 6H, *J* = 7, CH(CH₃)₂), 1.21 (d, 6H, *J* = 7, CH(CH₃)₂), 0.86 (d, 6H, *J* = 7, CH(CH₃)₂), 0.84 (d, 6H, *J* = 7, CH(CH₃)₂). ³¹P{¹H} NMR (C₆D₆): 44.5 (d, *J*_{RhP} = 225). ¹³C{¹H} NMR (C₆D₆): δ 186.8 (dd, *J*_{RhC} = 57, *J*_{PC} = 15, NCN), 161.9 (s, NC), 161.7 (s, NC), 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, NCH), 122.2 (s, NCH), 52.6 (s, N(CH₃)₂), 29.9 (s, CH(CH₃)₂), 29.2 (s, CH(CH₃)₂), 27.1 (s, CH(CH₃)₂), 27.0 (s, CH(CH₃)₂), 24.7 (s, CH₃), 23.2 (s, CH₃). ESI-MS (MeOH): *m/z* 794, [M - Cl]⁺ (100%); 389, [IPr + H]⁺ (27%). Anal. Calcd for C₄₇H₅₆N₃PClRh (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%). ¹H NMR (C₆D₆): δ 7.84–7.78 (m, 2H, Ar *H*), 7.04–6.49 (m, 18H, Ar *H*), 6.20 (s, 2H, NCH), 3.07 (s, 6H, N(CH₃)₂), 3.01 (s, 6H, *p*-CH₃), 2.13 (s, 6H, *o*-CH₃), 1.57 (s, 6H, *o*-CH₃). ³¹P{¹H} NMR (C₆D₆): δ 48.1 (d, *J*_{RhP} = 230). ¹³C{¹H} NMR (C₆D₆): δ 183.9 (dd, *J*_{RhC} = 54, *J*_{PC} = 17, NCN), 161.0 (s, NC), 160.7 (s, NC), 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, NCH), 121.6 (s, NCH), 52.2 (s, N(CH₃)₂), 21.9 (s, *p*-CH₃), 21.5 (s, *o*-CH₃), 19.5 (s, *o*-CH₃). ESI-MS (MeOH): *m/z* 710, [M - Cl]⁺ (100%); 305, [IMes + H]⁺ (22%). Anal. Calcd for C₄₁H₄₄N₃PClRh (M = 748.1): C, 65.82; H, 5.93; N, 5.62. Found: C, 65.74; H, 6.19; N, 5.62.

RhCl(IPr)(PPh₃)₂ (6). A solution of **1** (0.064 g, 0.050 mmol) and PPh₃ (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%). ¹H NMR (C₆D₆): δ 7.80–6.59 (m, 38H, Ar *H*), 3.76 (spt, 2H, *J* = 7, CH(CH₃)₂), 3.36 (spt, 2H, *J* = 7, CH(CH₃)₂), 1.49 (d, 6H, *J* = 7, CH(CH₃)₂), 1.08 (d, 6H, *J* = 7, CH(CH₃)₂), 0.88 (d, 6H, *J* = 7, CH(CH₃)₂), 0.56 (d, 6H, *J* = 7, CH(CH₃)₂). ³¹P{¹H} NMR (C₆D₆): 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). ¹³C{¹H} NMR (C₆D₆): δ 187.2 (ddd, *J*_{RhC} = 114, *J*_{PC} = 52, *J*_{PC} = 15, NCN), 146.8 (s, NC), 145.2 (s, NC), 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, NCH), 123.9 (br, NCH), 29.2 (s, CH(CH₃)₂), 28.9 (s, CH(CH₃)₂), 26.5 (s, CH₃), 25.0 (s, CH₃), 23.9 (s, CH₃), 22.8 (s, CH₃). Anal. Calcd for C₆₃H₆₆N₂P₂ClRh (M = 1051.5): C, 71.96; H, 6.33; N, 2.66. Found: C, 72.06; H, 6.41; N, 2.67.

RhCl(IMes)(PPh₃)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 PPh₃. Yield: 0.091 g (94%). ¹H NMR (CDCl₃): 7.35–6.85 (m, 36H, Ar *H*), 3.01 (s, 6H, *p*-CH₃), 2.13 (s, 6H, *o*-CH₃), 1.57 (s, 6H, *o*-CH₃). ³¹P{¹H} NMR (CDCl₃): 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). ¹³C{¹H} NMR (CDCl₃): δ 189.4 (ddd, *J*_{RhC} = 115, *J*_{PC} = 49, *J*_{PC} = 17, NCN), 138.8 (s, NC), 138.0 (s, NC), 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, NCH), 126.5 (d, *J*_{P-C} = 9, NCH), 22.0 (s, *p*-CH₃), 21.5 (s, *o*-CH₃), 19.9 (s, *o*-CH₃). Anal. Calcd for C₅₇H₅₄P₂N₂ClRh (M = 967.4): C, 70.77; H, 5.63; N, 2.90. Found: C, 71.13; H, 5.76; N, 2.76.

RhCl(PPh₃)(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(PPh₃)₃ as the Rh precursor. Yield: 0.057 g (81%). ¹H NMR (C₆D₆): δ 7.78–6.12 (m, 29H, Ar *H*), 3.38 (s, 6H, N(CH₃)₂). ³¹P{¹H} NMR (C₆D₆): 57.6 (dd, *J*_{RhP} = 197, *J*_{PP} = 45), 52.4 (dd, *J*_{RhP} = 175, *J*_{PP} = 45). ¹³C{¹H} NMR (C₆D₆): δ 161.0–122.9 (Ar C), 52.8 (s, N(CH₃)₂). Anal. Calcd for C₃₈H₃₅P₂N₂ClRh (M = 706.0): C, 64.65; H, 5.00; N, 1.98. Found: C, 64.33; H, 5.08; N, 1.70.

RhCl(O₂)(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 O₂ 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. ¹H NMR (C₆D₆): δ 8.15 (m, 2H, Ar *H*), 7.30–6.66 (m, 18H, Ar *H*), 6.47 (s, 2H, NCH), 4.44 (br, 2H, CH(CH₃)₂), 3.37 (s, 3H, N(CH₃)), 2.76 (br, 2H, CH(CH₃)₂), 2.11 (s, 3H, N(CH₃)), 1.87 (br, 6H, CH(CH₃)₂), 1.23 (br, 6H, CH(CH₃)₂),

1.09 (br, 6H, CH(CH₃)₂), 0.88 (br, 6H, CH(CH₃)₂). ³¹P{¹H} NMR (C₆D₆): 35.3 (d, *J*_{RhP} = 149). ¹³C{¹H} NMR (C₆D₆): δ 160.1 (s, NC), 159.9 (dd, *J*_{RhC} = 51, *J*_{PC} = 9, NCN), 159.8 (s, NC), 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, NCH), 121.5 (s, NCH), 52.7 (s, N(CH₃)₂), 50.2 (s, N(CH₃)₂), 29.7 (s, CH(CH₃)₂), 24.4 (s, CH₃), 23.4 (s, CH₃). ESI-MS (MeOH): *m/z* 864, [M + H]⁺ (100%); 847, [M - O]⁺ (18%); 322, [(OP-N) + H]⁺ (37%). Anal. Calcd for C₄₇H₅₆N₃PClO₂Rh (*M* = 864.3): C, 65.31; H, 6.53; N, 4.86. Found: C, 65.35; H, 6.66; N, 5.12.

RhCl(O₂)(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. ¹H NMR (C₆D₆): δ 8.20 (m, 2H, Ar H), 7.88–6.60 (m, 18H, Ar H), 6.05 (s, 2H, NCH), 3.39 (s, 3H, N(CH₃)), 2.26 (s, 6H, CH₃), 2.14 (s, 12H, CH₃), 1.97 (s, 3H, N(CH₃)). ³¹P{¹H} NMR (C₆D₆): 34.7 (d, *J*_{RhP} = 149). ¹³C{¹H} NMR (C₆D₆): δ 160.2 (s, NC), 159.8 (s, NC), 159.4 (dd, *J*_{RhC} = 50, *J*_{PC} = 9, NCN), 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, NCH), 121.5 (s, NCH), 52.8 (s, N(CH₃)₂), 50.1 (s, N(CH₃)₂), 21.5 (s, CH₃), 19.4 (s, CH₃), 19.2 (s, CH₃). ESI-MS (MeOH): *m/z* 780, [M + H]⁺ (82%); 763, [M - O]⁺ (100%); 322, [(OP-N) + H]⁺ (17%). Anal. Calcd for C₄₁H₄₄N₃PClO₂Rh (*M* = 780.1): C, 63.12; H, 5.68; N, 5.39. Found: C, 63.27; H, 5.50; N, 5.29.

RhCl(O₂)(IPr)(PPh₃)₂ (11). A yellow solution of **6** (0.053 g, 0.050 mmol) in benzene (5 mL) was stirred under 1 atm of O₂ 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. ¹H NMR (C₆D₆): δ 7.80–6.99 (m, 36H, Ar H), 6.73 (s, 2H, NCH), 3.26 (spt, 4H, *J* = 7, CH(CH₃)₂), 1.43 (d, 12H, *J* = 7, CH(CH₃)₂), 1.09 (d, 12H, *J* = 7, CH(CH₃)₂).

³¹P{¹H} NMR (C₆D₆): 18.4 (d, *J*_{RhP} = 105). ¹³C{¹H} NMR (C₆D₆): δ 147.6 (s, NC), 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, NCH), 29.1 (s, CH(CH₃)₂), 25.1 (s, CH₃), 23.9 (s, CH₃). Anal. Calcd for C₆₃H₆₆P₂N₂ClO₂Rh (*M* = 1083.5): C, 69.84; H, 6.14; N, 2.59. Found: C, 70.20; H, 6.42; N, 2.61.

RhCl(O₂)(IMes)(PPh₃)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. ¹H NMR (C₆D₆): δ 7.80–6.80 (m, 34H, Ar H), 6.27 (s, 2H, NCH), 2.33 (s, 12H, *o*-CH₃), 2.14 (s, 6H, *p*-CH₃). ³¹P{¹H} NMR (C₆D₆): 16.9 (d, *J*_{RhP} = 104). ¹³C{¹H} NMR (C₆D₆): δ 138.7 (s, NC), 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, NCH), 21.6 (s, *p*-CH₃), 19.0 (s, *o*-CH₃). Anal. Calcd for C₅₇H₅₄P₂N₂ClO₂Rh·1.5C₆H₆ (*M* = 1116.4): C, 71.00; H, 5.69; N, 2.51. Found: C, 71.01; H, 5.88; N, 2.91.

RhCl(O₂)(PPh₃)(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. ¹H NMR (CDCl₃): δ 7.73–7.00 (m, 29H, Ar H), 3.62 (br, 3H, N(CH₃)₂), 2.36 (br, 3H, N(CH₃)₂). ³¹P{¹H} NMR (CDCl₃): 45.6 (dd, *J*_{RhP} = 149, *J*_{PP} = 26), 37.7 (dd, *J*_{RhP} = 127, *J*_{PP} = 26). ¹³C{¹H} NMR (CDCl₃): δ 136.1–127.2 (Ar C), 54.5 (s, N(CH₃)₂), 50.4 (s, N(CH₃)₂). Anal. Calcd for C₃₈H₃₅P₂NClO₂Rh·C₇H₈ (*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.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Crystallographic data for RhCl(O₂)(IPr)(P-N) (**9**), RhCl(O₂)(IMes)(P-N) (**10**), and RhCl(O₂)(PPh₃)(P-N) (**13**) as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM060576I