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Rhodium and Iridium Complexes with α-Diketimine Ligands: Oxidative Addition of H_2 and O_2

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Dedicated to Prof. Dr. Hansgeorg Schnöckel on the occasion of his 70th birthday

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The treatment of $[M(\mu\text{-}Cl)(coe)_2]_2$ (M = Rh, Ir; coe = cyclooctene) with the α-diketimines ArN=C(Me)C(Me)=NAr (Ar = Ph, Xy; Xy = $2,6\text{-}Me_2C_6H_3$) in thf, followed by the addition of CN*t*Bu, gave the α-diketimine complexes [M(Cl){ArN=C(Me)C(Me)=NAr} (CN*t*Bu)] (**1**: M = Rh, Ar = Ph; **2**: M = Rh, Ar = Xy; **3**: M = Ir, Ar = Xy). The reaction of **3** with dihydrogen resulted in the formation of the iridium dihydrido complex $[Ir(Cl)(H)_2$\{XyN=C(Me)C(Me)=NXy\}(CN*t*Bu)] (**4**). The complexes **2** and **3** reacted with O_2 or $^{18}O_2$ to yield the peroxido complexes $[M(Cl)(O_2)$\{XyN=C(Me)C(Me)=NXy\}(CN*t*Bu)] (**5a**: M = Rh; **6a**: M = Ir) and $[M(Cl)(^{18}O_2)$\{XyN=C(Me)C(Me)=NXy\}(CN*t*Bu)] (**5b**: M = Rh; **6b**: M = Ir), respectively. All of the complexes were characterized by NMR and IR spectroscopy. In addition, complexes **3** and **5a** were characterized by X-ray crystallography.

Introduction

Transition metal peroxido complexes are of particular interest when they are formed from molecular oxygen because of the push for "green" oxidations or oxygenations.[1] They can play a key role in these processes.[1–3] Rh^{III} and Ir^{III} peroxido complexes have been reported in the literature, some of which reversibly bind dioxygen.[4,5] We demonstrated that peroxido complexes can be intermediates in the rhodium-mediated formation of peroxides, but they are also useful starting compounds for the formation of rhodium perborates and perboronates.[6] The peroxido complex *trans*-$[Rh(4\text{-}C_5F_4N)(O_2)$(CN*t*Bu)$(PEt_3)_2]$ can be applied in the oxygenation of pinacolborane.[7] Tejel et al. found that 1,5-cyclooctadiene (cod) can be oxygenated to yield 4-cyclooctenone in the coordination sphere of rhodium.[8] The conversion proceeds presumably via an intermediate peroxido species.[8] However, metal-bound phosphanes are prone to oxygenation reactions and, therefore, the corresponding peroxido complexes are often less suitable as oxygenation catalysts.[6,9,10] The synthesis and characterization of the rhodium and iridium peroxido compounds without any phosphane ligands is hence highly desirable. Only a limited number of peroxido compounds that do not include any phosphanes as additional ligands have been reported, which include the complexes with *N*-heterocyclic carbene ligands.[11,12] Cationic rhodium peroxido complexes that contain tetradentate tris(2-pyridylmethyl)amine (tpa) ligands have been described by Gal and co-workers.[13] Exposure of the complexes $[M(tpa)(C_2H_4)][BPh_4]$ (M = Rh, Ir) to air in the solid state led to a peroxygenation to give 3-metalla-1,2-dioxolanes.[13] The cationic peroxido complexes $[Ir(O_2)$(phen)(cod)][X] (X = Cl, I, SCN, phen = phenanthroline) were also described in the literature.[14] The pincer peroxido complex $[Rh(Cl)(O_2)\{2,6\text{-}(C\{Me\}{=}N\textit{i}Pr)_2C_5H_3N\}]$ reacted with $HCl_{(aq.)}$ to give H_2O_2 and $[Rh(Cl)_3\{2,6\text{-}(C\{Me\}{=}N\textit{i}Pr)_2C_5H_3N\}]$.[15] Dioxygen reacted with a Rh^I dimethylbipyridine species to produce the η^2-peroxido complex $[Rh(Cl)(O_2)$(dmbpy)(dmso)] (dmbpy = 4,4′-dimethyl-2,2′-bipyridine, dmso = dimethyl sulfoxide).[16] The complex $[Rh(Cl)(O_2)$(tbbpy)(CN*t*Bu)] (tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) oxygenates PEt_3 to give phosphane oxide and *trans*-[Rh(Cl)(CN*t*Bu)$(PEt_3)_2]$.[17]

α-Diimine ligands are known to stabilize organometallic complexes.[18] However, Rh^I and Ir^I diimine species are fairly rare and most of them have an ionic[19,20] or a dimeric[21] structure.[22–24] Haynes et al. analyzed the oxidative addition of MeI to $[Rh^I$\{ArN=C(Me)C(Me)=NAr\}(CO)] (Ar = $2\text{-}iPrC_6H_4$).[22] Westcott et al. prepared the complex $[Rh(\eta^6\text{-catBcat})$\{ArN=C(Me)C(Me)=NAr\}] (cat = $1,2\text{-}O_2C_6H_4$, Ar = $2,6\text{-}iPr_2C_6H_3$) by addition of B_2cat_3 to [Rh(acac)\{ArN=C(Me)C(Me)=NAr\}] (acac = acetylacetonate).[21a] Rhodium and iridium diimine complexes have been applied as active catalysts for the hydroamination of 2-(2-phenylethynyl)aniline to *N*-(2-methylvinyl)-2-phenylindole.[23a] The synthesis of cationic Rh^I carbonyl diimine complexes has also been reported.[20,25] The synthesis of the cationic iridium diimine complex

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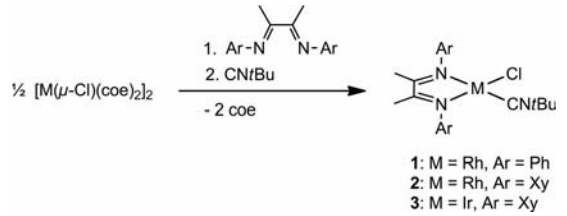
[Ir(Cl)(Cp*){ArN=C(Me)C(Me)=NAr}][Cl] (Cp* = pentamethylcyclopentadienyl, Ar = 4-MeC_6H_4) has been described by Tilset et al.[19] The cyclopentadienyl (Cp) diimine and bipyridine complexes of Rh and Ir have been thoroughly investigated because of their role in proton photoreduction processes,[26] CO_2 reduction,[27] or NADPH/NADP$^+$ redox chemistry.[28]

This report describes the synthesis, structural characterization, and reactivity of a new class of square-planar rhodium(I) and iridium(I) complexes with α-diketimine ligands, and their reactivity towards dihydrogen and dioxygen.

Results and Discussion

The treatment of [M(μ-Cl)(coe)$_2$]$_2$ (M = Rh, Ir; coe = cyclooctene) with 1 equiv. of α-diketimine in thf, followed by the addition of *tert*-butyl isocyanide, afforded the α-diketimine complexes [Rh(Cl){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (**1**: Ar = phenyl), [Rh(Cl){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (**2**: Ar = 2,6-$Me_2C_6H_3$), and [Ir(Cl){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (**3**: Ar = 2,6-$Me_2C_6H_3$) (Scheme 1). The isocyanide was added slowly to the reaction mixture in order to avoid the irreversible formation of the metal(I) salts [M(CN*t*Bu)$_4$][Cl] (M = Rh, Ir).[29] It should be noted that Haynes et al. reported that the synthesis of [Rh(I){PhN=C(Me)C(Me)=NPh}(CO)] from the dimer [Rh(μ-I)(CO)$_2$]$_2$ is not possible.[22] The IR spectrum of the solution indicated the presence of [Rh(I)$_2$(CO)$_2$]$^-$ with [Rh{PhN=C(Me)C(Me)=NPh}$_2$]$^+$ as the counterion.[22] We did not observe any C–H bond activation at one of the methyl groups in the backbone of the diazabutadiene as was found for [Ir(Cl)(Cp*){κ^2-(*C*,*N*)-ArN(H)=C(*C*H$_2$)C(Me)=*N*Ar}][Cl] (Ar = 2,4,6-$Me_3C_6H_2$).[19a]



Scheme 1. The synthesis of the α-diketimine complexes **1**, **2**, and **3**; Xy = 2,6-$Me_2C_6H_3$.

The α-diketimine complexes **1**–**3** are intensely colored species. This is indicative of d(metal)→π*(diimine) charge transfer transitions that are commonly encountered in other diimine metal complexes.[19a,30] Thus, complex **1** is dark brown, complex **2** is dark blue, whereas the Ir chlorido complex **3** is dark green. The complexes **1**–**3** are stable in water, although it has been shown that a coordinated isocyanide at rhodium can react with water by nucleophilic addition.[31] The solid state IR spectra for the rhodium compounds **1** and **2** both show one strong and one medium absorption band for the CN*t*Bu ligand at 2112 cm^{-1} (**1**), 2107 cm^{-1} (**2**) and 2066 cm^{-1} (**1**), 2071 cm^{-1} (**2**), respectively. The solid state IR spectrum for the iridium complex **3** exhibits two strong absorption bands at 2100 and 2067 cm^{-1}. In comparison, the IR spectrum for the [Ir(Cp*){κ^2-(*C*,*N*)-*t*Bu*N*=*C*=N*t*Bu}(CN*t*Bu)] complex shows two absorption bands at 2110 and 2065 cm^{-1} for the terminal isocyanide,[32] whereas the [Rh(Cl)(tbbpy)(CN*t*Bu)] complex exhibits two strong absorption bands at 2089 and 2056 cm^{-1}.[17] The occurrence of two absorption bands in the IR spectra of comparable monoisonitrile complexes has been documented in the literature.[33,34]

The ^{1}H NMR spectrum of **1** in [D$_8$]thf shows two singlets at δ = 1.37 and 0.23 ppm, which were assigned to the methyl groups on the backbone of the α-diketimine ligand. Similar chemical shifts have been found for [Rh(I){ArN=C(Me)C(Me)=NAr}(CO)] (Ar = 2,4,6-$Me_3C_6H_2$) (δ = 1.64 and 1.04 ppm in CD_2Cl_2).[22] A singlet at δ = 1.15 ppm was observed for the *t*Bu group of the coordinated isocyanide. The ^{1}H NMR spectrum for **2** revealed resonances for the methyl groups of the α-diketimine backbone at δ = 0.62 and –0.54 ppm. The corresponding chemical shifts for [Ir(Cl){XyN=C(Me)C(Me)=NXy}(CN*t*Bu)] (**3**) are found at –0.09 and –2.41 ppm, respectively. The ^{13}C NMR spectrum for **1** shows two doublets at δ = 169.78 and 157.41 ppm for the RhN=*C*(CH$_3$) carbon atoms ($^2J_{Rh,C}$ = 3 Hz, $^2J_{Rh,C}$ = 2 Hz) and two doublets at δ = 21.06 and 19.89 ppm for the RhN=C(*C*H$_3$) carbon atoms ($^3J_{Rh,C}$ = 1 Hz). It should be noted that Perutz et al. determined a coupling of $^3J_{Rh,C}$ = 0.9 Hz to rhodium for the quaternary C atom of the *t*Bu group in the complex [Rh(Cp)(CN*t*Bu)$_2$].[34a]

Black crystals of **3** were obtained from a solution of *n*-hexane/thf (19 mL/1 mL) at 243 K. The molecular structure was determined by X-ray diffraction analysis at low temperature (Figure 1). The selected bond lengths and angles are summarized in Table 1. The iridium atom exhibits a square-planar coordination sphere. The Ir1–N1 bond length of 2.053(2) Å for the α-diketimine ligand in the *trans* position to the isocyanide is comparable to that of the corresponding iridium–nitrogen bond length in [Ir(Ar^F)(Br$_{0.6}$,Cl$_{1.4}$)(tbbpy)(CNXy)] [Ar^F = 3,5-$(CF_3)_2C_6H_3$, 2.046(3) Å][35] or in [Ir(Cl)(Cp*){κ^2-(*C*,*N*)-*C*H$_2$C(NXy)C(Me)*N*Xy}] [2.081(2) Å].[19a] The Ir1–N2 bond in **3** [1.966(2) Å] is shorter. This is possibly because of a push-pull interaction that leads to the transfer of electron density from the π-donor chlorido ligand to the α-diketimine ligand, which can act as a π-acceptor.[20d,21a,36] The diimine ligand might also be considered to be a redox non-innocent ligand.[20d,36] It would then be bound as a π-radical monoanion and the C–N distances would be fairly long whereas the C–C bond would be relatively short.[36a,36b] An antiferromagnetic coupling between an Ir^{II} radical and a ligand radical would result in a diamagnetic ground state. The ab initio calculations for [Ir(Cp)(HNCHCHNH)] supported an ene-1,2-diamido-iridium(III) entity description with C–N bond lengths of 1.353 Å and a C–C distance of 1.362 Å.[20d,36d] However, the C=N bond lengths in the α-diimine ligand in **3** are 1.311(4) and 1.325(3) Å and the separation for the C1–C2 bond length is 1.447(4) Å. The iridium–carbon bond length of 1.897(3) Å for the isocyanide group in **3** is shorter than that of the corresponding Ir–C bond length in $[\mathrm{Ir(Ar^F)(Br_{0.6},Cl_{1.4})(tbbpy)(CNXy)}]$ [2.001(5) Å][35] or in $[\mathrm{Ir}\{\kappa^2\text{-}(C,C)\text{-}C\mathrm{H_2C(Me)_2}\text{-}o\text{-}C_6\mathrm{H_4}\}\{\mathrm{C(CO_2Et){=}CH(CO_2Et)}\}\mathrm{(tbbpy)(CNXy)}]$ [1.962(4) Å].[37] The C21–N3 bond length [1.157(4) Å] was comparable to the bond lengths found for other complexes with isocyanide ligands, such as $[\mathrm{Ir(Cp^*)(\mu\text{-}H)(\mu\text{-}dmpm)(CN}t\mathrm{Bu)Ir(Cp^*)(H)][OTf]_2}$ [dmpm = bis(dimethylphosphanyl)methane; 1.16(2) Å].[38] Compound **3** displays a bent $\mathrm{C{-}N{-}CMe_3}$ linkage with a C21–N3–C22 bond angle of 166.1(3)°, which is comparable with that observed for the latter complex [175(1)°].

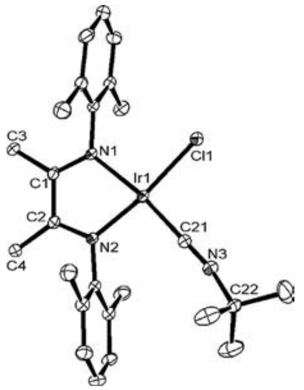
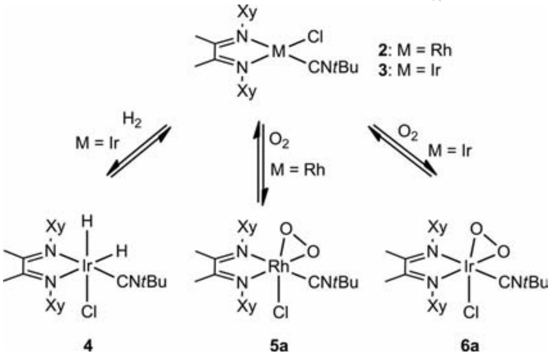


Figure 1. An ORTEP diagram of **3**. The ellipsoids are drawn at the 50% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for [Ir(Cl){XyN=C(Me)C(Me)=NXy}(CN*t*Bu)] (**3**).

Ir1–N1	2.053(2)	N1–C1	1.311(4)
Ir1–N2	1.966(2)	N2–C2	1.325(3)
Ir1–Cl1	2.3142(7)	C1–C2	1.447(4)
Ir1–C21	1.897(3)	N3–C22	1.453(4)
C21–N3	1.157(4)		
Cl1–Ir1–N1	94.19(7)	C21–Ir1–N1	169.98(12)
Cl1–Ir1–N2	170.17(7)	C21–Ir1–N2	95.91(11)
N1–Ir1–N2	77.18(10)	C21–N3–C22	166.1(3)
Cl1–Ir1–C21	93.23(9)		

In order to elucidate the reactivity of **1**, **2**, and **3** towards oxidative addition reactions,[16] we investigated the complexes reactivity towards dihydrogen. The rhodium compounds **1** and **2** did not react with dihydrogen under ambient conditions in contrast to the rhodium bipyridine complex [Rh(Cl)(tbbpy)(CN*t*Bu)].[17] However, on treatment of a solution of [Ir(Cl){XyN=C(Me)C(Me)=NXy}(CN*t*Bu)] (**3**) with H_2, the dihydrido complex $[\mathrm{Ir(Cl)(H)_2}\{\mathrm{XyN{=}C(Me)C(Me){=}NXy}\}(\mathrm{CN}t\mathrm{Bu})]$ (**4**) was formed (Scheme 2). In solution **4** was not very stable and was readily reconverted to **3** and H_2 on bubbling argon through the solution. After 23 h the ^1H NMR spectrum of a solution of **4** in $[D_8]$thf indicated that complex **3** was present in 44%.



Scheme 2. The reactivity of the Rh and Ir diketimine compounds **2** and **3** towards H_2 and O_2.

The IR spectrum for **4** exhibited a strong and broad absorption band at 2140 cm^{-1}, which was assigned to the isocyanide vibration. Absorption bands that could be assigned to the $Ir(H)_2$ moiety were not found. Possibly these bands were overlapped by the iridium isocyanide stretching vibrations. The strong background fluorescence made the acquisition of the Raman data (Nd:YAG 1064 nm) impossible. The ^1H NMR spectrum for **4** shows six signals between 2.85 and 1.38 ppm for the four nonequivalent methyl groups in the aryl moiety and the two methyl groups on the α-diketimine backbone. The singlet at δ = 0.75 ppm was attributed to the *t*Bu group of the metal-bound isocyanide. The presence of two hydrides at the iridium center was revealed by the signals at –17.20 and –19.73 ppm. The coupling constant of J = 6.9 Hz between the two hydrides is consistent with a mutually *cis* orientation for these two ligands.[39] In comparison, the *cis* dihydrido complex $[\mathrm{Ir(bpin)(H)_2(tbbpy)(coe)}]$ (bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl) has a coupling constant of J = 5.3 Hz between the two hydrido ligands.[40]

The $^1H,^{13}C$-HMBC spectrum shows two cross peaks, which have a similar intensity, for the coupling of the hydride resonances with the resonances of the metal-bound carbon of the isocyanide ligand at –17.20/121 and –19.73/121 ppm (Figure 2). This could indicate a *cis*-orientation for both of the metal-bound hydrogens to the isocyanide group.

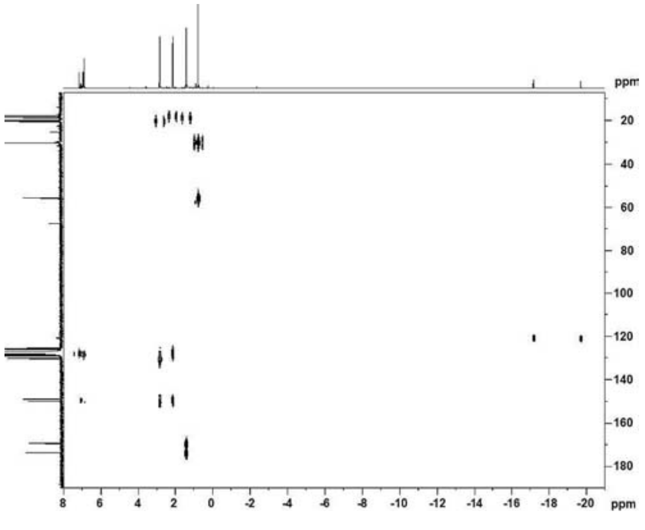


Figure 2. The $^1H,^{13}C$-HMBC spectrum of **4** in C_6D_6.

In the ^{13}C NMR domain the signal for the quaternary carbon atom attached to the iridium (δ = 121 ppm) indicated a rather electron-poor metal center.[41] It should be noted that the cationic complex [{Ir(H)(μ-pz) $(CN\textit{t}Bu)_2\}_2$-(μ-Cl)][OTf] (pz = pyrazolate) shows one broad signal in the ^{13}C NMR spectrum at δ = 108.3 ppm, which was assigned to the isocyanide entity at the Ir^{III} center, the latter was also electron poor.[42] The iridaphosphirane complex [Ir(Cp*){κ^2-(*C*,*P*)-*P*(Mes*)*C*=NXy}(CNXy)] (Mes* = 2,4,6-$(tBu)_3C_6H_2$) shows a signal in the ^{13}C NMR spectrum at δ = 141.5 ppm for the isocyanide carbon.[43] In addition, the molecular structure of **4** in the solid state was determined by X-ray crystallography. Complex **4** crystallizes in the orthorhombic crystal system in the chiral space group $P2_12_12_1$. Although the data were of poor quality, the analysis confirmed the configuration at the iridium. The dihydrido complex **4** adopts a structure with the chlorido ligand in the *cis* position to the isocyanide.

The exposure of a benzene solution of the dark blue compound **2** to molecular oxygen led to the precipitation of the brown peroxido complex $[Rh(Cl)(O_2)\{XyN{=}C(Me)C(Me){=}NXy\}(CN\textit{t}Bu)]$ (**5a**) within 3 h (Scheme 2). The treatment of **2** with $^{18}O_2$ gave the isotopologue, $[Rh(Cl)(^{18}O_2)\{XyN{=}C(Me)C(Me){=}NXy\}(CN\textit{t}Bu)]$ (**5b**). Compounds **5a** and **5b** are only soluble in polar solvents such as thf or 1,2-difluorobenzene. The dioxygen is not bound very strongly to the rhodium and it dissociates after prolonged treatment under vacuum or when argon is bubbled through a solution of **5a** in thf to give **2**. The ^{1}H NMR spectrum of a freshly prepared solution of **5a** in 1,2-difluorobenzene indicated that **2** was present in 56%; after 20 h only complex **2** was detected. In the solid state complex **5a** extrudes O_2 overnight. It has been shown that in solution the complexes *trans*-$[Rh(X)(CNXy)(PPh_3)_2]$ (X = Cl, Br, SC_6F_5, C_2Ph)[5a] bind molecular oxygen reversibly, whereas the complex $[Rh(Cl)(tbbpy)(CN\textit{t}Bu)]$[17] binds O_2 irreversibly. The formation of $[Ir(Cl)(O_2)\{XyN{=}C(Me)C(Me){=}NXy\}(CN\textit{t}Bu)]$ (**6a**) and $[Ir(Cl)(^{18}O_2)\{XyN{=}C(Me)C(Me){=}NXy\}(CN\textit{t}Bu)]$ (**6b**) from **3** proceeded in the solid state under an atmosphere of O_2 and $^{18}O_2$, respectively. The treatment of a solution of **3** in thf with O_2 also gave a certain amount of **6a** according to the IR spectra. However, the conversion was less selective and the other products produced in the reaction could not be characterized. The iridium peroxido complex **6a** is stable in the solid state for one week, whereas the ^{1}H NMR spectrum of a solution of **6a** in thf showed that **3** was present in 10% after 4 h. For **5a** and **6a** we assumed the configurations that are depicted in Scheme 2. The former configuration was confirmed by X-ray crystallography (see below).

The complexes **5a**, **5b**, **6a**, and **6b** were characterized by their spectroscopic data. The IR spectrum of the rhodium peroxido complex **5a** exhibits an absorption band at 2208 cm^{-1} and the iridium peroxido complex **6a** has one absorption band at 2178 cm^{-1}, which can be assigned to the isocyanide stretching vibration at the Rh^{III} or Ir^{III} metal center. In comparison, an absorption band at 2195 cm^{-1} was found for the rhodium peroxido complex $[Rh(Cl)(O_2)(tbbpy)(CN\textit{t}Bu)]$[17] and one at 2161 cm^{-1} was found for the tetrafluoropyridyl complex *trans*-$[Rh(4\text{-}C_5F_4N)(O_2)(CN\textit{t}Bu)(PEt_3)]$.[6a] The absorption band at 2096 cm^{-1} was assigned to the isocyanide stretching vibration for $[Ir(CH_2SiMe_3)(Me)(SiMe_3)(tbbpy)(CN\textit{t}Bu)]$ (the isocyanide is located in the *trans* position to the SiMe$_3$ ligand).[37] It should be noted that the phosphane-pincer Rh^I compound, $[Rh\{2,6\text{-}C_6HMe_2(CH_2P\textit{t}Bu_2)_2\}(\eta^1\text{-}N_2)]$, and the (*N*-heterocyclic carbene)rhodium(I) species, *cis*-$[Rh(Cl)(IMes)(PPh_3)_2]$ [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene], reacted with dioxygen to give the oxygenated rhodium derivatives, but with no concomitant change in the oxidation state of the transition metal.[11] The conversion of **2** and **3** into the dioxygen complexes **5a** and **6a**, respectively, was also accompanied by the appearance of a strong band in the IR spectra at 884 and 843 cm^{-1}, respectively. The band shifted to 833 and 796 cm^{-1} for the ^{18}O labeled isotopologues **5b** and **6b**, respectively, and were assigned unequivocally to the O–O stretching vibration of the η^2-peroxido ligands (Figures 3 and 4).[9,44]

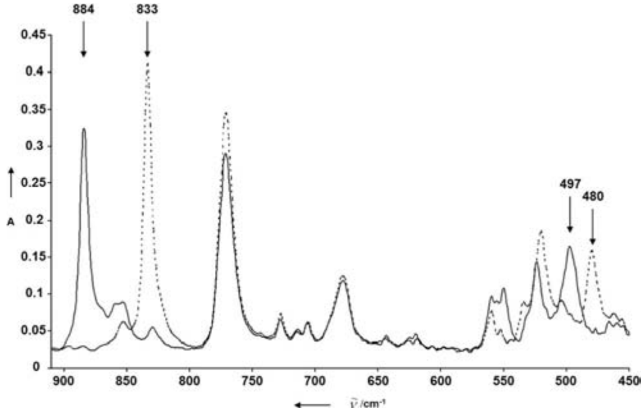


Figure 3. Part of the IR spectra for **5a** (——) and **5b** (-----) (ATR, diamond).

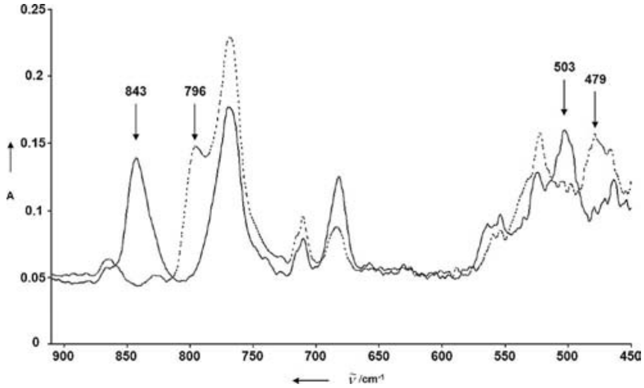


Figure 4. Part of the IR spectra for **6a** (——) and **6b** (-----) (ATR, diamond).

The absorption band at 497 cm^{-1} for **5a** shifted to 480 cm^{-1} for **5b** and was tentatively assigned to the RhO moiety. Analogously, the absorption band at 503 cm^{-1} for **6a** and 479 cm^{-1} for **6b** was assigned to the IrO moiety.

The ^{1}H NMR spectrum for **5a** in [D$_6$]benzene shows four signals between 2.86 and 2.16 ppm for the four nonequivalent methyl groups and two signals at 1.42 and 1.36 ppm for the two methyl groups on the α-diketimine backbone. The singlet at δ = 0.56 ppm for **5a** was attributed to the *t*Bu group of the metal-bound isocyanide. The ^{1}H NMR spectrum for **6a** in 1,2-difluorobenzene revealed six signals for the methyl groups of the diimine ligand. The signal at δ = 0.76 ppm was attributed to the *t*Bu group of the metal-bound isocyanide for **6a**.

In order to obtain more information about the geometry and bond lengths in complex **5a**, its structure was determined by X-ray diffraction analysis at 180 K (Figure 5). Suitable crystals for **5a** were obtained from a thf solution of the complex at 243 K. Selected bond lengths and angles are summarized in Table 2. If the oxygen is treated as a bidentate ligand then the η^2-peroxido complex **5a** adopts the distorted octahedral structure with the peroxido ligand in the *trans* position to the chlorido and α-diketimine ligand. Alternatively, if the dioxygen is treated as though it occupies a single coordination site, then the structure is approximately trigonal-bipyramidal. The rhodium–nitrogen bond lengths of the α-diketimine ligand to the metal in **5a** [2.056(13) and 1.970(14) Å] are comparable to those of the rhodium–nitrogen bond lengths in [Rh(Cl)(O$_2$)(tbbpy)(CN*t*Bu)] [2.072(8) and 2.051(9) Å][17] and in the cation [Rh{κ^2-(*N*,*P*)-*N*(*i*Pr)=CH-*o*-C$_6$H$_4$*P*Ph$_2$}$_2$(O$_2$)][BPh$_4$], where the Rh–N bond is located in the *trans* position to one of the oxygen atoms [2.111(7) Å].[5b] The rhodium–carbon bond of the isocyanide group in **5a** [1.877(17) Å] is nearly identical to those found in the complexes [Rh(Cl)(O$_2$)(tbbpy)(CN*t*Bu)] [1.931(12) Å][17] and *trans*-[Rh(SC$_6$F$_5$)(O$_2$)(CNXy)(PPh$_3$)$_2$] [1.939(4) Å].[5a] The oxygen–oxygen bond length in **5a** [1.448(14) Å] is comparable to those found for the complexes [Rh(Cl)(O$_2$)(tbbpy)(CN*t*Bu)] [1.406(9) Å],[17] *trans*-[Rh(SC$_6$F$_5$)(O$_2$)(CNXy)(PPh$_3$)$_2$] [1.436(3) Å],[5a] *trans*-[Rh(4-C$_5$F$_4$N)(O$_2$)(CN*t*Bu)(PEt$_3$)] [1.452(3) Å],[6a] and other rhodium η^2-peroxido complexes.[4e,45]

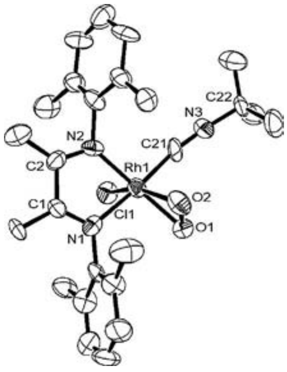


Figure 5. An ORTEP diagram of **5a**. The ellipsoids are drawn at the 50 % probability level.

Table 2. Selected bond lengths [Å] and angles [°] for [Rh(Cl)(O$_2$){XyN=C(Me)C(Me)=NXy}(CN*t*Bu)] (**5a**).

Rh1–O1	1.981(11)	Rh1–N1	2.056(13)
Rh1–O2	1.959(18)	Rh1–N2	1.970(14)
O1–O2	1.448(14)	C21–N3	1.23(2)
Rh1–Cl1	2.417(4)	N3–C22	1.45(2)
Rh1–C21	1.877(17)		
O2–Rh1–N2	117.6(5)	N2–Rh1–C21	97.9(7)
O2–Rh1–N1	91.0(5)	N1–Rh1–N2	76.91(5)
O2–Rh1–C21	86.8(6)	Cl1–Rh1–N2	88.8(4)
Cl1–Rh1–N1	94.1(3)	C21–N3–C22	168.6(16)
Cl1–Rh1–C21	91.0(5)	O2–Rh1–O1	43.1(4)

Conclusions

In conclusion, we have described the synthesis of new α-diketimine Rh$^{\mathrm{I}}$ and Ir$^{\mathrm{I}}$ compounds. The reactivity studies led to the isolation of an iridium dihydrido complex **4**, as well as the formation of Rh$^{\mathrm{III}}$ and Ir$^{\mathrm{III}}$ peroxido compounds **5a** and **6a**. The reactions with molecular oxygen are reversible, which might hamper their use in oxidation or oxygenation reactions. In comparison, the complex [Rh(Cl)(tbbpy)(CN*t*Bu)][17] binds dioxygen irreversibly, but its peroxido complex is insoluble. However, preliminary studies revealed that PEt$_3$ was oxygenated by **6a** to give the phosphane oxide. Trace amounts of 9-fluorenone and hydrogen peroxide were detected after the treatment of **6a** with 9-fluorenol.

Experimental Section

General Methods and Instrumentation: The synthetic work was carried out with a Schlenk line or an argon-filled glove box where the oxygen levels were below 10 ppm. All of the solvents were purified and dried by conventional methods and were distilled under an argon atmosphere before use. ^{16}O$_2$ and CN*t*Bu were obtained from Aldrich. *tert*-Butyl isocyanide was distilled before use. ^{18}O$_2$ was purchased from CAMPRO Scientific. The diphenyl- and di-*ortho*-xylyl-α-diketimines,[22,46] as well as the complexes [Rh(μ-Cl)(coe)$_2$]$_2$ and [Ir(μ-Cl)(coe)$_2$]$_2$,[47] were prepared according to the literature. The NMR spectra were recorded with a Bruker AV 400 NMR or with a Bruker DPX 300 spectrometer at 25 °C. The ^{1}H/^{13}C NMR chemical shifts were referenced to residual C$_6$D$_5$H at 7.15/128.00 ppm or to [D$_8$]thf at 1.73/25.72 ppm. The ^{13}C NMR experiments were recorded with a delay time of 10s. The microanalyses were obtained with a Euro EA HEKAtech elemental analyzer. The infrared spectra were recorded with a Bruker Vector 22 spectrometer that was equipped with an ATR unit (diamond).

[Rh(Cl){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (Ar = Phenyl) (1): A solution of the diphenyl-α-diketimine (128 mg, 0.541 mmol) in thf (8 mL) was added dropwise to a solution of [Rh(μ-Cl)(coe)$_2$]$_2$ (194 mg, 0.270 mmol) in thf (13 mL). A color change from orange to dark red was observed. The reaction mixture was stirred for 3.5 h at room temperature and then *tert*-butyl isocyanide (61 μL, 0.541 mmol) was added. The reaction mixture was then stirred for 12 h at room temperature and the volatiles were removed in vacuo. The residue was washed twice with a mixture of *n*-hexane (10 mL) and thf (1 mL) and then twice with *n*-hexane (10 mL). The dark brown product was dried under vacuum; yield 200 mg (81 %). C$_{21}$H$_{25}$ClN$_3$Rh (457.80): calcd. C 55.10, H 5.50, N 9.18; found C 54.98, H 5.38, N 8.99. IR (ATR): $\tilde{\nu}$ = 3055 (w), 2986 (w), 2934 (w), 2112 (s, C≡N), 2066 (m, C≡N), 1592 (m), 1564 (m), 1485 (s), 1449 (m), 1388 (m), 1368 (m), 1337 (s), 1251 (m), 1205 (m), 1070 (m), 989 (s), 865 (m), 825 (m), 747 (s), 739 (m), 695 (s), 621 (s), 523 (m), 463 (m) cm^{-1}. ^{1}H NMR (400 MHz, [D$_8$]thf): δ = 7.47–7.18 (m, 10 H, Ph-H), 1.37 (s, 3 H, CH$_3$), 1.16 (s, 9 H, *t*Bu), 0.23 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, [D$_8$]thf): δ = 169.78 (d, $^{2}J_{\mathrm{Rh,C}}$ = 3 Hz, C=N), 157.41 (d, $^{2}J_{\mathrm{Rh,C}}$ = 2 Hz, C=N), 160.88, 151.98, 129.86, 128.56, 126.77, 126.34, 123.78, 123.75 (C-Ar), 57.23 [*C*(CH$_3$)$_3$], 31.09 [C(*C*H$_3$)$_3$], 21.06 (d, $^{3}J_{\mathrm{Rh,C}}$ = 1 Hz, CH$_3$), 19.89 (d, $^{3}J_{\mathrm{Rh,C}}$ = 1 Hz, CH$_3$) ppm, the signal for the isocyanide carbon was not observed.

[Rh(Cl){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (Ar = 2,6-Me$_2$C$_6$H$_3$) (2): A solution of the di-*ortho*-xylyl-α-diketimine (371 mg, 1.260 mmol) in thf (10 mL) was added dropwise to a solution of [Rh(μ-Cl)(coe)$_2$]$_2$ (455 mg, 0.634 mmol) in thf (10 mL). A color change from orange to raspberry red was observed. The reaction mixture was stirred for 1 h at room temperature and then *tert*-butyl isocyanide (144 μL, 1.260 mmol) was added. A color change to dark blue was observed. The reaction mixture was stirred for 12 h at room temperature and the volatiles were removed in vacuo. The remaining crude product was washed four times with *n*-hexane (7 mL) and dried under vacuum. A dark blue substance remained; yield 562 mg (86%). C$_{25}$H$_{33}$ClN$_3$Rh (513.91): calcd. C 58.43, H 6.47, N 8.18; found C 58.30, H 6.44, N 8.34. IR (ATR): ṽ = 3015 (w), 2977 (w), 2929 (w), 2107 (s, C≡N), 2071 (m, C≡N), 1566 (w), 1466 (m), 1439 (m), 1368 (m), 1337 (m), 1261 (w), 1236 (m), 1207 (m), 1090 (w), 1037 (w), 994 (m), 921 (w), 869 (m), 832 (w), 765 (s), 760 (s), 708 (m), 561 (w), 524 (w), 502 (w), 458 (m), 431 (w) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.17–6.94 (m, 6 H, Ar-H), 2.43 (s, 6 H, Ar-CH$_3$), 2.24 (s, 6 H, Ar-CH$_3$), 0.75 (s, 9 H, *t*Bu), 0.62 (s, 3 H, CH$_3$), –0.54 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 168.25 (d, $^{2}J_{\mathrm{Rh,C}}$ = 3 Hz, C=N), 153.71 (d, $^{2}J_{\mathrm{Rh,C}}$ = 1 Hz, C=N), 157.81, 149.46, 129.32, 129.03, 125.84, 125.45 (C-Ar, two signals are covered by the C$_6$D$_5$H signal), 56.00 [*C*(CH$_3$)$_3$], 30.05 [C(*C*H$_3$)$_3$], 19.09 (CH$_3$-Ar), 18.69 (d, $^{3}J_{\mathrm{Rh,C}}$ = 2 Hz, CH$_3$), 17.95 (CH$_3$-Ar), 17.64 (d, $^{3}J_{\mathrm{Rh,C}}$ = 1 Hz, CH$_3$) ppm, the signal for the isocyanide carbon was not detected.

[Ir(Cl){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (Ar = 2,6-Me$_2$C$_6$H$_3$) (3): A solution of the di-*ortho*-xylyl-α-diketimine (346 mg, 1.183 mmol) in thf (10 mL) was added dropwise to a solution of [Ir(μ-Cl)(coe)$_2$]$_2$ (530 mg, 0.591 mmol) in thf (30 mL). A color change from orange to green was observed. The reaction mixture was stirred for 2 h at room temperature. Then a solution of *tert*-butyl isocyanide (134 μL, 1.183 mmol) in thf (7 mL) was added dropwise. The dark green reaction mixture was stirred for 12 h at room temperature and the volatiles were removed in vacuo. The remaining crude product was washed three times with a mixture of *n*-hexane (9.5 mL) and thf (0.5 mL) and dried under vacuum. A dark green substance remained; yield 691 mg (97%). C$_{25}$H$_{33}$ClIrN$_3$ (603.22): calcd. C 49.78, H 5.51, N 6.97; found C 50.43, H 5.62, N 6.61. IR (ATR): ṽ = 3016 (w), 2978 (w), 2924 (w), 2100 (s, C≡N), 2067 (s, C≡N), 1591 (w), 1528 (w), 1465 (m), 1439 (m), 1391 (m), 1366 (s), 1349 (s), 1263 (m), 1240 (m), 1209 (s), 1089 (m), 1035 (w), 994 (m), 903 (w), 886 (m), 835 (w), 764 (s), 760 (s), 721 (m), 712 (m), 562 (m), 529 (m), 471 (s) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.22–7.17, 7.08–6.88 (both m, 6 H, Ar-H), 2.47 (s, 6 H, Ar-CH$_3$), 2.14 (s, 6 H Ar-CH$_3$), 0.87 (s, 9 H, *t*Bu), –0.09 (s, 3 H, CH$_3$), –2.41 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 178.42, 159.73 (C=N), 156.58, 152.52, 127.20, 126.20, 125.85 (C-Ar, three signals are covered by the C$_6$D$_5$H signal), 55.94 [*C*(CH$_3$)$_3$], 30.24 [C(*C*H$_3$)$_3$], 22.83 (CH$_3$), 19.09 (CH$_3$-Ar), 18.96 (CH$_3$), 17.54 (CH$_3$-Ar) ppm, the signal for the isocyanide carbon was not detected.

[Ir(Cl)(H)$_2${ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (Ar = 2,6-Me$_2$C$_6$H$_3$) (4): A dark green solution of **3** (72 mg, 0.119 mmol) in benzene (10 mL) was treated with H$_2$ for 5 min. After stirring for 12 h at room temperature under a H$_2$ atmosphere, the brown reaction mixture was dried in vacuo for a short period of time; yield 72 mg (99%). C$_{25}$H$_{35}$ClIrN$_3$ (605.24): calcd. C 49.61, H 5.83, N 6.94; found C 49.40, H 5.79, N 7.24. IR (ATR): ṽ = 2971 (w), 2923 (m), 2854 (w), 2140 (s, br, C≡N), 2052 (w), 2023 (w), 1590 (w), 1466 (m), 1442 (m), 1381 (m), 1368 (m), 1260 (m), 1225 (s), 1210 (s), 1095 (m), 1035 (m), 991 (m), 863 (m), 822 (m), 803 (m), 766 (s), 706 (w), 680 (m), 558 (w), 516 (m), 475 (m) cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.08–6.88 (m, 6 H, Ar-H), 2.85, 2.84, 2.16, 2.14 (all s, 12 H, Ar-CH$_3$), 1.40, 1.38 (s, 6 H, CH$_3$), 0.75 (s, 9 H, *t*Bu), –17.20 (d, $^{2}J_{\mathrm{H,H}}$ = 6.9 Hz, 1 H, IrH), –19.73 (d, $^{2}J_{\mathrm{H,H}}$ = 6.9 Hz, 1 H, IrH) ppm. ^{1}H NMR (300 MHz, [D$_8$]thf): δ = 7.17–6.96 (m, 6 H, Ar-H), 2.58, 2.53, 2.18, 2.13, 2.10, 2.09 (s, 12 H, Ar-CH$_3$, and 6 H, CH$_3$), 1.06 (s, 9 H, *t*Bu), –18.31 (d, $^{2}J_{\mathrm{H,H}}$ = 6.9 Hz, 1 H, IrH), –20.29 (d, $^{2}J_{\mathrm{H,H}}$ = 6.9 Hz, 1 H, IrH) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 173.99, 169.70 (C=N), 150.17, 149.26, 130.67, 130.63, 129.48, 128.96, 128.57, 126.58, 126.00 (C-Ar, three signals are covered by the C$_6$D$_5$H signal), 121.24 (Ir-C), 56.07 [*C*(CH$_3$)$_3$], 30.38 [C(*C*H$_3$)$_3$], 20.71, 20.50 (CH$_3$), 19.10, 18.98, 18.33, 18.31 (CH$_3$-Ar) ppm.

[Rh(Cl)(O$_2$){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (Ar = 2,6-Me$_2$C$_6$H$_3$) (5a): A dark blue solution of [Rh(Cl){ArN=C(Me)-C(Me)=NAr}(CN*t*Bu)] (**2**) (124 mg, 0.241 mmol) in benzene (7 mL) was treated with oxygen for 2 min. The sample turned red brown and a brown precipitate was observed. After 3 h at room temperature under an O$_2$ atmosphere, the reaction mixture was filtered and the residue was treated twice with *n*-hexane (3 mL). The brown residue was dried in vacuo for a short period of time; yield 124 mg (94%). IR (ATR): ṽ = 2980 (w), 2909 (w), 2208 (s, C≡N), 2115 (w), 1467 (m), 1437 (w), 1382 (m), 1372 (m), 1227 (m), 1190 (m), 1095 (w), 1036 (w), 999 (m), 884 (s, ^{16}O–^{16}O), 853 (w), 771 (s), 678 (m), 620 (w), 550 (m), 523 (m), 497 (m, Rh^{16}O) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.02–6.87 (m, 6 H, Ar-H), 2.86, 2.58, 2.37, 2.16 (s, 12 H, Ar-CH$_3$), 1.42, 1.36 (s, 6 H, CH$_3$), 0.56 (s, 9 H, *t*Bu) ppm. ^{1}H NMR (300 MHz, C$_6$D$_6$ capillary, C$_6$H$_4$F$_2$): δ = 2.77, 2.61, 2.50, 2.30 (s, 12 H, Ar-CH$_3$), 2.21 (s, 6 H, CH$_3$), 0.86 (s, 9 H, *t*Bu) ppm, the ArH signals are covered by the C$_6$H$_4$F$_2$ signal. Although the compound was spectroscopically pure, satisfactory microanalytical data could not be obtained despite several attempts. It appears that the reversibility of the reaction with O$_2$ hampered our efforts.

[Rh(Cl)(^{18}O$_2$){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (Ar = 2,6-Me$_2$C$_6$H$_3$) (5b): A dark blue solution of **2** (45 mg, 0.088 mmol) in benzene (2 mL) was cooled in vacuo to 77 K for 10 min. ^{18}O$_2$ was then added and the solution was slowly warmed to room temperature. The color of the solution changed from dark blue to dark red and a brown precipitate was formed. After 2 h the reaction mixture was filtered and the residue was dried for a very brief period in vacuo; yield 26 mg (55%). IR (ATR): ṽ = 2980 (m), 2910 (w), 2208 (s, C≡N), 2118 (w), 1467 (m), 1437 (w), 1382 (m), 1372 (m), 1227 (m), 1190 (m), 1095 (w), 1036 (w), 999 (m), 853 (w), 833 (s, ^{18}O–^{18}O), 771 (s), 678 (w), 560 (w), 520 (m), 480 (m, Rh^{18}O) cm^{-1}.

[Ir(Cl)(O$_2$){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (Ar = 2,6-Me$_2$C$_6$H$_3$) (6a): A dark green solid of [Ir(Cl){ArN=C(Me)-C(Me)=NAr}(CN*t*Bu)] (**3**) (344 mg, 0.570 mmol) was treated with oxygen for 3 min. After 3.5 h the sample turned dark brown. After 21 h at room temperature and under an O$_2$ atmosphere, the solid was washed three times with a mixture of *n*-hexane (10 mL) and benzene (3 mL) and then twice with *n*-hexane (5 mL). The brown residue was dried for a very brief period in vacuo; yield 326 mg (90%). IR (ATR): ṽ = 2980 (w), 2918 (w), 2178 (s, C≡N), 2052 (w), 1628 (w), 1588 (w), 1466 (m), 1384 (m), 1369 (m), 1334 (m), 1260 (w), 1230 (s), 1200 (s), 1095 (w), 1036 (w), 991 (m), 922 (w), 843 (s, $^{16}O–^{16}O$), 769 (s), 682 (s), 564 (m), 554 (m), 524 (m), 503 (s, $Ir^{16}O$), 464 (m) cm^{-1}. ^1H NMR (300 MHz, C_6D_6 capillary, $C_6H_4F_2$): δ = 2.57, 2.45, 2.17, 2.14, 2.00, 1.95 (s, 12 H, Ar-CH_3, and 6 H, CH_3), 0.76 (s, 9 H, *t*Bu) ppm, the ArH signals are covered by the $C_6H_4F_2$ signal. Although the compound was spectroscopically pure, satisfactory microanalytical data could not be obtained despite several attempts. It appears that the reversibility of the reaction with O_2 hampered our efforts.

[Ir(Cl)($^{18}O_2$){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (Ar = 2,6-$Me_2C_6H_3$) (6b): [Ir(Cl){ArN=C(Me)C(Me)=NAr}(CN*t*Bu)] (**3**) (44 mg, 0.073 mmol), a dark green solid, was cooled to 77 K for 10 min in vacuo. Then $^{18}O_2$ was added and the mixture was slowly warmed to room temperature. After 24 h the color of the solid turned from dark green to brown. IR (ATR): ṽ = 2982 (w), 2918 (w), 2870 (w), 2180 (s, C≡N), 2052 (w), 1585 (w), 1466 (m), 1384 (m), 1370 (m), 1334 (m), 1259 (w), 1230 (s), 1201 (s), 1096 (w), 1035 (w), 991 (m), 922 (w), 796 (s, $^{18}O–^{18}O$), 769 (s), 684 (s), 560 (m), 554 (m), 522 (m), 479 (s, $Ir^{18}O$), 466 (m) cm^{-1}.

Structure Determination: The black crystals for **3** were obtained at room temperature from a solution of complex **3** in *n*-hexane/thf (9.5 mL/0.5 mL). The diffraction data were collected with a Stoe IPDS 2θ diffractometer for a fragment with the dimensions of $0.32 \times 0.16 \times 0.14$ mm^3. $C_{25}H_{33}ClIrN_3$, *M* = 603.19, monoclinic, space group $P2_1/c$, a = 14.9260(6) Å, b = 13.0619(5) Å, c = 14.0412(6) Å, V = 2429.45(17) Å^3, $\rho_{calcd.}$ = 1.649 $g\,cm^{-3}$, T = 100(2) K, Z = 4, μ(Mo-K_α) = 5.622 mm^{-1}, 42966 reflections measured, 6550 unique (R_{int} = 0.0968). Final R_1, wR_2 values on all data: 0.0378, 0.0810. R_1, wR_2 values for 5978 reflections with $I_0 > 2\sigma(I_0)$ = 0.0341, 0.0790; residual electron density +3.258/–4.189 e Å^{-3}. The dark red crystals for **5a** were obtained under an O_2 atmosphere at 243 K from a solution of the complex in thf. The diffraction data were collected with a Stoe IPDS diffractometer for a fragment with the dimensions of $0.08 \times 0.08 \times 0.08$ mm^3. $C_{25}H_{33}ClN_3O_2Rh$, *M* = 545.90, orthorhombic, space group $P2_12_12_1$, a = 10.810(2) Å, b = 14.110(2) Å, c = 17.025(5) Å, V = 2596.9(10) Å^3, $\rho_{calcd.}$ = 1.396 $g\,cm^{-3}$, T = 180(2) K, Z = 4, μ(Mo-K_α) = 0.786 mm^{-1}, 21515 reflections measured, 2535 unique (R_{int} = 0.2286), Mo-K_α radiation (λ = 0.71073 Å). Final R_1, wR_2 values on all data: 0.1097, 0.1426. R_1, wR_2 values for 1303 reflections with $I_0 > 2\sigma(I_0)$ = 0.0614, 0.01226; residual electron density +0.659/–1.034 e Å^{-3}. Both of the structures were solved by direct methods (SHELXS-97) and were refined with the full-matrix least-squares method on F^2 (SHELX-97).[48] The hydrogen atoms were placed at the calculated positions and were refined by using a riding model.

CCDC-811453 (for **5a**) and -811454 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] See for example: a) R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**; b) C. Limberg, *Angew. Chem.* **2003**, *115*, 6112–6136; *Angew. Chem. Int. Ed.* **2003**, *42*, 5932–5954; c) C. Limberg, F. Meyer (Eds.), *Topics in Organometallic Chemistry*, Springer, **2007**, vol. 22; d) J.-M. Brégeault, *Dalton Trans.* **2003**, 3289–3302; e) J.-E. Bäckvall (Ed.), *Modern Oxidation Methods*, Wiley-VCH, Weinheim, **2004**; f) J.-J. Girerd, F. Banse, A. J. Simaan, *Metal Oxo and Metal-Peroxo Species*, in: *Catalytic Oxidations* (Ed.: B. Meunier), Springer, Berlin, **2000**, vol. 97, p. 145–177.

[2] a) T. Nishimura, N. Kakiuchi, T. Onoue, K. Ohe, S. Uemura, *J. Chem. Soc. Perkin Trans. 1* **2000**, 1915–1918; b) F. Igersheim, H. Mimoun, *Nouv. J. Chim.* **1980**, *4*, 711–713; c) M. Krom, R. G. E. Coumans, J. M. M. Smits, A. W. Gal, *Angew. Chem.* **2002**, *114*, 596–599; *Angew. Chem. Int. Ed.* **2002**, *41*, 575–579; d) M. Krom, R. G. E. Coumans, J. M. M. Smits, A. W. Gal, *Angew. Chem.* **2001**, *113*, 2164–2166; *Angew. Chem. Int. Ed.* **2001**, *40*, 2106–2108; e) B. De Bruin, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2004**, *116*, 4236–4251; *Angew. Chem. Int. Ed.* **2004**, *43*, 4142–4157; f) C. Bianchini, C. Mealli, A. Meli, D. M. Proserpio, M. Peruzzini, F. Vizza, P. Frediani, *J. Organomet. Chem.* **1989**, *369*, C6–C10; g) C. Tejel, M. A. Ciriano, M. P. Del Río, F. J. Van Den Bruele, D. G. H. Hetterscheid, N. Tsichlis i Spithas, B. De Bruin, *J. Am. Chem. Soc.* **2008**, *130*, 5844–5855; h) A. W. Gal, F. H. A. Bolder, *J. Organomet. Chem.* **1977**, *142*, 375–385; i) D. H. M. W. Thewissen, H. L. M. Van Gaal, *J. Organomet. Chem.* **1979**, *172*, 69–79.

[3] a) N. R. Conley, L. A. Labios, D. M. Pearson, C. C. L. McCrory, R. M. Waymouth, *Organometallics* **2007**, *26*, 5447–5453; b) S. S. Stahl, *Angew. Chem.* **2004**, *116*, 3480–3501; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400–3420; c) B. A. Steinhoff, I. A. Guzei, S. S. Stahl, *J. Am. Chem. Soc.* **2004**, *126*, 11268–11278; d) D. R. Jensen, M. J. Schultz, J. A. Mueller, M. S. Sigman, *Angew. Chem.* **2003**, *115*, 3940–3843; *Angew. Chem. Int. Ed.* **2003**, *42*, 3810–3813; e) M. M. Konnick, B. A. Gandhi, I. A. Guzei, S. S. Stahl, *Angew. Chem.* **2006**, *118*, 2970–2973; *Angew. Chem. Int. Ed.* **2006**, *45*, 2904–2907; f) B. A. Steinhoff, S. R. Fix, S. S. Stahl, *J. Am. Chem. Soc.* **2002**, *124*, 766–767; g) G.-J. Ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Adv. Synth. Catal.* **2002**, *344*, 355–369; h) J. A. Mueller, C. P. Goller, M. S. Sigman, *J. Am. Chem. Soc.* **2004**, *126*, 9724–9734; i) J. M. Keith, R. J. Nielsen, J. Oxgaard, W. A. Goddard III, *J. Am. Chem. Soc.* **2005**, *127*, 13172–13179; j) C. N. Cornell, M. S. Sigman, *Inorg. Chem.* **2007**, *46*, 1903–1909; k) K. M. Gligorich, M. S. Sigman, *Angew. Chem.* **2006**, *118*, 6764–6767; *Angew. Chem. Int. Ed.* **2006**, *45*, 6612–6615; l) J. Piera, J.-E. Bäckvall, *Angew. Chem.* **2008**, *120*, 3558–3576; *Angew. Chem. Int. Ed.* **2008**, *47*, 3506–3523; m) M. M. Konnick, S. S. Stahl, *J. Am. Chem. Soc.* **2008**, *130*, 5753–5762.

[4] a) C. Tejel, M. A. Ciriano, S. Jiménez, V. Passarelli, J. A. López, *Angew. Chem.* **2008**, *120*, 2123-2126; *Angew. Chem. Int. Ed.* **2008**, *47*, 2093–2096; b) A. Y. Verat, H. Fan, M. Pink, Y.-S. Chen, K. G. Caulton, *Chem. Eur. J.* **2008**, *14*, 7680–7686; c) X.-Y. Yu, B. O. Patrick, B. R. James, *Organometallics* **2006**, *25*, 4870–4877; d) H. Werner, N. Mahr, M. E. Schneider, M. Bosch, J. Wolf, *Polyhedron* **2004**, *23*, 2645–2657; e) J. Vicente, J. Gil-Rubio, J. Guerrero-Leal, D. Bautista, *Organometallics* **2004**, *23*, 4871–4881; f) M. Paneque, S. Sirol, M. Trujillo, E. Carmona, E. Gutiérrez-Puebla, M. A. Monge, C. Ruiz, F. Malbosc, C. S.-L. Berre, P. Kalck, M. Etienne, J. C. Daran, *Chem. Eur. J.* **2001**, *7*, 3868–3879; g) C. Pettinari, F. Marchetti, A. Cingolani, G. Bianchini, A. Drozdov, V. Vertlib, S. Troyanov, *J. Organomet. Chem.* **2002**, *651*, 5–14; h) D. G. Ho, R. Ismail, N. Franco, R. Gao, E. P. Leverich, I. Tsyba, N. N. Ho, R. Bau, M. Selke, *Chem. Commun.* **2002**, 570–571; i) G. Argouarch, O. Samuel, O. Riant, J.-C. Daran, H. B. Kagan, *Eur. J. Org. Chem.* **2000**, *16*, 2893–2899; j) P. R. Sharp, D. W. Hoard, C. L. Barnes, *J. Am. Chem. Soc.* **1990**, *112*, 2024–2026; k) J. R. Bleeke, M. Shokeen, E. S. Wise, N. P. Rath, *Organometallics* **2006**, *25*, 2486–2500; l) A. Vigalok, L. J. W. Shimon, D. Milstein, *Chem. Commun.* **1996**, 1673–1674; m) M. C. Nicasio, M. Paneque, P. J.

Pérez, A. Pizzano, M. L. Poveda, L. Rey, S. Sirol, S. Taboada, M. Trujillo, A. Monge, C. Ruiz, E. Carmona, *Inorg. Chem.* **2000**, *39*, 180–188; n) J. Vicente, J. Gil-Rubio, J. Guerrero-Leal, D. Bautista, *Dalton Trans.* **2009**, 3854–3866.

[5] a) L. Carlton, L. V. Mokoena, M. A. Fernandes, *Inorg. Chem.* **2008**, *47*, 8696–8703; b) C. A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, G. Scapacci, *J. Chem. Soc., Dalton Trans.* **1992**, 3371–3376; c) L. Vaska, L. S. Chen, *J. Chem. Soc., Chem. Commun.* **1971**, 1080–1081; d) M. Selke, L. Rosenberg, J. M. Salvo, C. S. Foote, *Inorg. Chem.* **1996**, *35*, 4519–4522; e) S. D. Perera, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1995**, 633–639; f) D. B. Williams, W. Kaminsky, J. M. Mayer, K. I. Goldberg, *Chem. Commun.* **2008**, 4195–4197; g) S. E. Watkins, D. C. Craig, S. B. Colbran, *J. Chem. Soc., Dalton Trans.* **2002**, 2423–2436.

[6] a) M. Ahijado, T. Braun, D. Noveski, N. Kocher, B. Neumann, D. Stalke, H.-G. Stammler, *Angew. Chem.* **2005**, *117*, 7107–7111; *Angew. Chem. Int. Ed.* **2005**, *44*, 6947–6951; b) M. Ahijado, T. Braun, *Angew. Chem.* **2008**, *120*, 2996–3000; *Angew. Chem. Int. Ed.* **2008**, *47*, 2954–2958; c) G. Meier, T. Braun, *Angew. Chem.* **2011**, *123*, 3338–3342; *Angew. Chem. Int. Ed.* **2011**, *50*, 3380–3384.

[7] M. Ahijado, T. Braun, A. Penner, *Angew. Chem.* **2008**, *120*, 8999–9003; *Angew. Chem. Int. Ed.* **2008**, *47*, 8867–8871.

[8] a) M. P. del Río, M. A. Ciriano, C. Tejel, *Angew. Chem.* **2008**, *120*, 2536–2539; *Angew. Chem. Int. Ed.* **2008**, *47*, 2502–2505; b) C. Tejel, M. A. Ciriano, E. Sola, M. P. del Río, G. Ríos-Moreno, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **2005**, *117*, 3331–3335; *Angew. Chem. Int. Ed.* **2005**, *44*, 3267–3271; c) C. Tejel, M. P. del Río, J. A. López, M. A. Ciriano, *Chem. Eur. J.* **2010**, *16*, 11261–11265.

[9] Y. Takahashi, M. Hashimoto, S. Hikichi, M. Akita, Y. Moro-oka, *Angew. Chem.* **1999**, *111*, 3259–3262; *Angew. Chem. Int. Ed.* **1999**, *38*, 3074–3077.

[10] a) M. J. Y. Chen, J. K. Kochi, *J. Chem. Soc., Chem. Commun.* **1977**, 204–205; b) C. W. Dudley, G. Read, P. J. C. Walker, *J. Chem. Soc., Dalton Trans.* **1974**, 1926–1931; c) G. Read, M. Urgelles, *J. Chem. Soc., Dalton Trans.* **1985**, 1591–1596; d) Y. Takahashi, M. Hashimoto, S. Hikichi, Y. Moro-oka, M. Akita, *Inorg. Chim. Acta* **2004**, *357*, 1711–1724; e) P. Paul, B. Tyagi, *J. Coord. Chem.* **1996**, *40*, 213–225; f) H. L. M. Van Gaal, F. L. A. Van Den Bekerom, *J. Organomet. Chem.* **1977**, *134*, 237–248; g) L. Carlton, R. Weber, *Inorg. Chem.* **1996**, *35*, 5843–5850; h) L. Carlton, *Magn. Reson. Chem.* **2004**, *42*, 760–768; i) A. Morvillo, M. Bressan, *J. Organomet. Chem.* **1987**, *332*, 337–343; j) D. M. Rounhill, G. H. Allen, R. A. Bechtold, W. B. Beaulieu, *Inorg. Chim. Acta* **1981**, *54*, L99–L100; k) J.-C. Wang, L. Y. Chou, W.-Y. Hsien, L.-K. Liu, *Acta Crystallogr., Sect. C* **1994**, *50*, 879–882; l) P. Barbaro, C. Bianchini, F. Laschi, S. Midollini, S. Moneti, G. Scapacci, P. Zanello, *Inorg. Chem.* **1994**, *33*, 1622–1630.

[11] a) J. M. Praetorius, D. P. Allen, R. Wang, J. D. Webb, F. Grein, P. Kennepohl, C. M. Crudden, *J. Am. Chem. Soc.* **2008**, *130*, 3724–3725; b) C. M. Frech, L. J. W. Shimon, D. Milstein, *Helv. Chim. Acta* **2006**, *89*, 1730–1739.

[12] a) J. M. Praetorius, R. Wang, C. M. Crudden, *Eur. J. Inorg. Chem.* **2009**, 1746–1751; b) C. Y. Tang, W. Smith, D. Vidovic, A. L. Thompson, A. B. Chaplin, S. Aldridge, *Organometallics* **2009**, *28*, 3059–3066.

[13] a) M. Krom, T. P. J. Peters, R. G. E. Coumans, T. J. J. Sciarone, J. Hoogboom, S. I. Ter Beek, P. J. P. Schlebos, J. M. M. Smits, R. De Gelder, A. W. Gal, *Eur. J. Inorg. Chem.* **2003**, 1072–1087; b) B. De Bruin, T. P. J. Peters, J. B. M. Wilting, S. Thewissen, J. M. M. Smits, A. W. Gal, *Eur. J. Inorg. Chem.* **2002**, 2671–2680; c) D. G. H. Hetterscheid, M. Bens, B. De Bruin, *Dalton Trans.* **2005**, 979–984.

[14] D. J. A. De Waal, T. I. A. Gerber, W. J. Louw, R. Van Eldik, *Inorg. Chem.* **1982**, *21*, 2002–2006.

[15] H. F. Haarman, F. R. Bregman, P. W. N. M. Van Leeuwen, K. Vrieze, *Organometallics* **1997**, *16*, 979–985.

[16] R. Dorta, L. J. W. Shimon, H. Rozenberg, D. Milstein, *Eur. J. Inorg. Chem.* **2002**, 1827–1834.

[17] A. Penner, T. Schröder, T. Braun, B. Ziemer, *Eur. J. Inorg. Chem.* **2009**, 4464–4470.

[18] See for example: a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203; b) C. M. Killian, L. K. Johnson, M. Brookhart, *Organometallics* **1997**, *16*, 2005–2007; c) V. Rosenberger, G. Fendesak, H. tom Dieck, *J. Organomet. Chem.* **1991**, *411*, 445–456; d) V. Rosenberger, H. tom Dieck, *Chem. Ber.* **1990**, *123*, 83–85; e) G. Gerdes, P. Chen, *Organometallics* **2003**, *22*, 2217–2225.

[19] a) B. J. Wik, C. Rømming, M. Tilset, *J. Mol. Catal. A* **2002**, *189*, 23–32; b) M. A. Garralda, R. Hernández, L. Ibarlucea, M. I. Arriortua, M. K. Urtiaga, *Inorg. Chim. Acta* **1995**, *232*, 9–17; c) L. Fidalgo, M. A. Garralda, R. Hernández, L. Ibarlucea, *Inorg. Chim. Acta* **1993**, *207*, 121–125.

[20] a) E. Delgado-Laita, E. Sanchez-Muñoyerro, *Polyhedron* **1984**, *3*, 799–804; b) M. Bikrani, L. Fidalgo, M. A. Garralda, *Polyhedron* **1996**, *15*, 83–89; c) M. Bikrani, M. A. Garralda, L. Ibarlucea, E. Pinilla, M. R. Torres, *Inorg. Chim. Acta* **1998**, *282*, 230–236; d) S. Berger, F. Baumann, T. Scheiring, W. Kaim, *Z. Anorg. Allg. Chem.* **2001**, *627*, 620–630.

[21] a) S. J. Geier, E. E. Chapman, D. I. McIsaac, C. M. Vogels, A. Decken, S. A. Westcott, *Inorg. Chem. Commun.* **2006**, *9*, 788–791; b) H. tom Dieck, J. Klaus, J. Kopf, *J. Chem. Soc., Chem. Commun.* **1982**, 574–575.

[22] L. Gonsalvi, J. A. Gaunt, H. Adams, A. Castro, G. J. Sunley, A. Haynes, *Organometallics* **2003**, *22*, 1047–1054.

[23] a) D. F. Kennedy, B. A. Messerle, S. L. Rumble, *New J. Chem.* **2009**, *33*, 818–824; b) D. W. Shaffer, S. A. Ryken, R. A. Zarkesh, A. F. Heyduk, *Inorg. Chem.* **2011**, *50*, 13–21; c) S. Greulich, A. Klein, A. Knödler, W. Kaim, *Organometallics* **2002**, *21*, 765–769; d) F. Breher, C. Böhler, G. Frison, J. Harmer, L. Liesum, A. Schweiger, H. Grützmacher, *Chem. Eur. J.* **2003**, *9*, 3859–3866; e) J. F. Van Baar, J. M. Klerks, P. Overbosch, D. J. Stufkens, K. Vrieze, *J. Organomet. Chem.* **1976**, *112*, 95–103.

[24] V. Garcia, M. A. Garralda, L. Ibarlucea, *Transition Met. Chem.* **1985**, *10*, 288–291.

[25] H. Van Der Poel, G. Van Koten, K. Vrieze, *Inorg. Chim. Acta* **1981**, *51*, 253–262.

[26] a) W. Kaim, R. Reinhardt, J. Waldhor, J. Fiedler, *J. Organomet. Chem.* **1996**, *524*, 195–202; b) R. Reinhardt, W. Kaim, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1998–2005; c) W. Kaim, R. Reinhardt, M. Sieger, *Inorg. Chem.* **1994**, *33*, 4453–4459; d) M. Ladwig, W. Kaim, *J. Organomet. Chem.* **1992**, *439*, 79–90; e) M. Ladwig, W. Kaim, *J. Organomet. Chem.* **1991**, *419*, 233–243; f) U. Kölle, B.-S. Kang, P. Infelta, P. Comte, M. Grätzel, *Chem. Ber.* **1989**, *122*, 1869–1880; g) U. Kölle, M. Grätzel, *Angew. Chem.* **1987**, *99*, 572–574; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 567–570.

[27] C. Caix, S. Chardon-Noblat, A. Deronzier, *J. Electroanal. Chem.* **1997**, *434*, 163–170.

[28] a) H. C. Lo, O. Buriez, J. B. Kerr, R. H. Fish, *Angew. Chem.* **1999**, *111*, 1524–1527; *Angew. Chem. Int. Ed.* **1999**, *38*, 1429–1432; b) F. Hollmann, A. Schmid, E. Steckhan, *Angew. Chem.* **2001**, *113*, 190–193; *Angew. Chem. Int. Ed.* **2001**, *40*, 169–171; c) D. Westerhausen, S. Herrmann, W. Hummel, E. Steckhan, *Angew. Chem.* **1992**, *104*, 1496–1498; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1529–1531; d) E. Steckhan, S. Herrmann, R. Rupert, E. Dietz, M. Frede, E. Spika, *Organometallics* **1991**, *10*, 1568–1577; e) R. Ruppert, S. Herrmann, E. Steckhan, *J. Chem. Soc., Chem. Commun.* **1988**, 1150–1151; f) R. Ruppert, S. Herrmann, E. Steckhan, *Tetrahedron Lett.* **1987**, *28*, 6583–6586.

[29] a) J. W. Dart, M. K. Lloyd, J. A. McCleverty, R. Mason, *J. Chem. Soc., Chem. Commun.* **1971**, 1197–1198; b) P. R. Branson, M. Green, *J. Chem. Soc., Dalton Trans.* **1972**, 1303–1310; c) C. Tejel, Y.-M. Shi, M. A. Ciriano, A. J. Edwards, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **1996**, *108*, 707–709; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 633–634.

[30] W. Kaim, A. Klein, S. Hasenzahl, H. Stoll, S. Záliš, J. Fiedler, *Organometallics* **1998**, *17*, 237–247.

[31] T. Boschi, S. Licoccia, R. Paolesse, P. Tagliatesta, G. Pelizzi, F. Vitali, *Organometallics* **1989**, *8*, 330–336.

[32] D. S. Glueck, J. Wu, F. J. Hollander, R. G. Bergman, *J. Am. Chem. Soc.* **1991**, *113*, 2041–2054.

[33] W. D. Jones, E. T. Hessell, *Organometallics* **1990**, *9*, 718–727.

[34] a) S. T. Belt, S. B. Duckett, D. M. Haddleton, R. N. Perutz, *Organometallics* **1989**, *8*, 748–759; b) J. C. A. Boeyens, N. J. Coville, K. S. Soldenhoff, *Afr. J. Chem.* **1984**, *37*, 153–160; c) G. W. Harris, J. C. A. Boeyens, N. J. Coville, *J. Organomet. Chem.* **1983**, *255*, 87–94.

[35] Y.-K. Sau, K.-W. Chan, Q.-F. Zhang, I. D. Williams, W.-H. Leung, *Organometallics* **2007**, *26*, 6338–6345.

[36] a) N. Muresan, K. Chlopek, T. Weyhermüller, F. Neese, K. Wieghardt, *Inorg. Chem.* **2007**, *46*, 5327–5337; b) N. Muresan, C. C. Lu, M. Ghosh, J. C. Peters, M. Abe, L. M. Henling, T. Weyhermüller, E. Bill, K. Wieghardt, *Inorg. Chem.* **2008**, *47*, 4579–4590; c) W. Kaim, M. Sieger, S. Greulich, B. Sarkar, J. Fiedler, S. Záliš, *J. Organomet. Chem.* **2010**, *695*, 1052–1058; d) S. Greulich, W. Kaim, A. F. Stange, H. Stoll, J. Fiedler, S. Záliš, *Inorg. Chem.* **1996**, *35*, 3998–4002; e) S. Hasenzahl, H.-D. Hausen, W. Kaim, *Chem. Eur. J.* **1995**, *1*, 95–99.

[37] Y.-K. Sau, H.-K. Lee, I. D. Williams, W.-H. Leung, *Chem. Eur. J.* **2006**, *12*, 9323–9335.

[38] K. Fujita, H. Nakaguma, F. Hanasaka, R. Yamaguchi, *Organometallics* **2002**, *21*, 3749–3757.

[39] a) M. Ahijado Salomon, T. Braun, I. Krossing, *Dalton Trans.* **2008**, 5197–5206; b) M. Ahijado Salomon, A.-K. Jungton, T. Braun, *Dalton Trans.* **2009**, 7669–7677.

[40] T. M. Boller, J. M. Murphy, M. Hapke, T. Ishiyama, N. Miyaura, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 14263–14278.

[41] a) D. L. Cronin, J. R. Wilkinson, L. J. Todd, *J. Magn. Reson.* **1975**, *17*, 353–361; b) R. W. Stephany, M. J. A. de Bie, W. Drenth, *Org. Magn. Reson.* **1974**, *6*, 45–47; c) M. Novotny, D. F. Lewis, S. J. Lippard, *J. Am. Chem. Soc.* **1972**, *94*, 6961–6968; d) E. L. Muetterties, *Inorg. Chem.* **1974**, *13*, 495–496; e) L. J. Todd, J. R. Wilkinson, *J. Organomet. Chem.* **1974**, *77*, 1–25.

[42] C. Tejel, M. A. Ciriano, M. Millaruelo, J. A. López, F. J. Lahoz, L. A. Oro, *Inorg. Chem.* **2003**, *42*, 4750–4758.

[43] H. Aktas, J. Mulder, F. J. J. De Kanter, J. C. Slootweg, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2009**, *131*, 13531–13537.

[44] a) A. Nakamura, Y. Tatsuno, S. Otsuka, *Inorg. Chem.* **1972**, *11*, 2058–2064; b) A. Nakamura, Y. Tatsuno, M. Yamamoto, S. Otsuka, *J. Am. Chem. Soc.* **1971**, *93*, 6052–6057; c) M. P. Lanci, D. W. Brinkley, K. L. Stone, V. V. Smirnov, J. P. Roth, *Angew. Chem.* **2005**, *117*, 7439–7442; *Angew. Chem. Int. Ed.* **2005**, *44*, 7273–7276.

[45] a) K. Osakada, K. Hataya, T. Yamamoto, *Inorg. Chem.* **1993**, *32*, 2360–2365; b) M. J. Bennett, P. B. Donaldson, *Inorg. Chem.* **1977**, *16*, 1581–1589; c) V. Cîrcu, M. A. Fernandes, L. Carlton, *Polyhedron* **2002**, *21*, 1775–1778.

[46] a) E. Lemp, A. L. Zanocco, G. Günther, N. Pizarro, *Tetrahedron* **2006**, *62*, 10734–10746; b) L. N. Ferguson, T. C. Goodwin, *J. Am. Chem. Soc.* **1949**, *71*, 633–637.

[47] a) A. Van Der Ent, A. L. Onderlinden, *Inorg. Synth.* **1990**, *28*, 90–91; b) J. L. Herde, J. C. Lambert, C. V. Senoff, *Inorg. Synth.* **1974**, *15*, 18–20.

[48] a) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**; b) G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Germany, **1997**.

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