Disproportionation of Rh^{II}(cod) to Rh^{I}(cod) and Rh^{III}(cyclooct-2,5-dien-1-yl): Hydrogen Atom Transfer vs Electron and Proton Transfer

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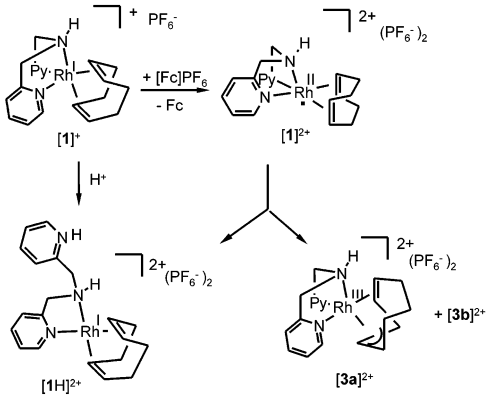
Summary: One-electron oxidation of [(dpa)Rh^{I}(cod)]$^{+}$ yields [(dpa)Rh^{II}(cod)]$^{2+}$, which reversibly binds dioxygen. In solution [(dpa)Rh^{II}(cod)]$^{2+}$ disproportionates to [(Hdpa)Rh^{I}(cod)]$^{2+}$ and two isomers of [(dpa)Rh^{III}(cyclooctadienyl)]$^{2+}$. This reaction proceeds most likely via abstraction of an allylic hydrogen atom by the Rh^{II} metallo radical.

Rhodium centers at conventional P-ligand sites find wide application in homogeneous catalysis (hydrogenation, hydroformylation) because of their ability to switch between the oxidation states rhodium(I) and rhodium(III) via oxidative-addition and reductive-elimination steps. The organometallic chemistry of "open shell" d^7 rhodium(II) centers has been nearly unexplored. With few exceptions, rhodium(II) complexes have been stabilized by preventing close contacts (of reagents or other rhodium(II) centers) to the rhodium(II) center through coordinative saturation or application of ligands with sufficient steric bulk. This prevents disproportionation to rhodium(I) and rhodium(III) or formation of dinuclear $Rh^{II}-Rh^{II}$ species.[1] Nevertheless, rhodium(II) and iridium(II) species such as [(Por)M^{II}] (M = Rh, Ir, por^{2-} = bulky *meso*-tetraarylporphyrinate) show a remarkable reactivity toward a variety of otherwise rather inert substrates.[2] [(por)M^{II}] complexes have been reported to activate H_2, Si−H and Sn−H bonds, benzylic and allylic C−H bonds, and even methane under mild conditions. Apparently the [(por)M^{II}] fragment behaves as a metallo radical. This is clearly demonstrated by the reactions of [(por)M^{II}] with CO and ethene resulting in complexes [(por)M^{III}−C(O)C(O)−M^{III}(por)], [(por)M^{III}−CH_2CH_2−M^{III}(por)], and by the reactions of [(por)M^{II}] with hydrogen, benzene and methane to give [(por)M^{III}(H)] and [(por)M^{III}(R)] (R = H, C_6H_5, CH_3). Clearly, the reactivity of N-ligand-supported rhodium(II) is rather different from that of conventional P-ligand-supported rhodium(I) and rhodium(III). The inability of [(por)M^{II}] to promote cis-reaction patterns of coordinated substrates prevents applications of its reactivity in desirable transformations of, for example, methane. Alkyl−Rh^{III} species, obtained by homolytic C−H bond activation by Rh^{II}, might insert into C=C and C=X (X = C, O, S, etc.) double bonds if these can coordinate cis to the alkyl group thus obtained. Such reactions are potentially useful for functionalization of an alkyl moiety.

Scheme 1. Protonation and Oxidation of 1^{+} to $1H^{2+}$ and 1^{2+}: Disproportionation of 1^{2+} to 3^{2+} and $1H^{2+}$



Recently we isolated Ir^{II}−ethene fragments supported by the N_4 ligands Me_ntpa (n = 2, 3).[3] In contrast to por^{2-} ligands, these do allow cis-reactivity patterns. We have now further investigated the chemistry of non-porphyrinate N ligand M^{II}−olefin complexes. In this paper we report the synthesis and characterization of the N_3 ligand complex [(dpa)Rh^{II}(cod)]$^{2+}$ (dpa = dipicolylamine; cod = (*Z*,*Z*)-1,5-cyclooctadiene) and its ability to activate an allylic C−H bond in the olefinic substrate.

Electrochemical oxidation of $\mathbf{1}^{+}$ (Scheme 1) has been investigated by cyclic voltammetry in acetone and dichloromethane. In both solvents oxidation of $\mathbf{1}^{+}$ to $\mathbf{1}^{2+}$ proved to be reversible on the electrochemical time scale (acetone, $E_{1/2}$ = 0.065 V; CH_2Cl_2, $E_{1/2}$ = 0.119 V; both vs Fc/Fc^{+}).[4] Oxidation of $\mathbf{1}^{2+}$ to $\mathbf{1}^{3+}$ in acetone proved irreversible. A very broad oxidation wave was observed; anodic currents start to flow at $E \approx 1.0$ V vs Fc/Fc^{+}. Oxidation of $\mathbf{1}^{2+}$ to $\mathbf{1}^{3+}$ thus requires a potential >0.9 V vs Fc/Fc^{+}. Chemical oxidation of $\mathbf{1}^{+}$ by treatment with $Fc^{+}PF_6^{-}$ in dichloromethane resulted in the formation of $\mathbf{1}^{2+}$ as a dark green precipitate (Scheme 1).[5]

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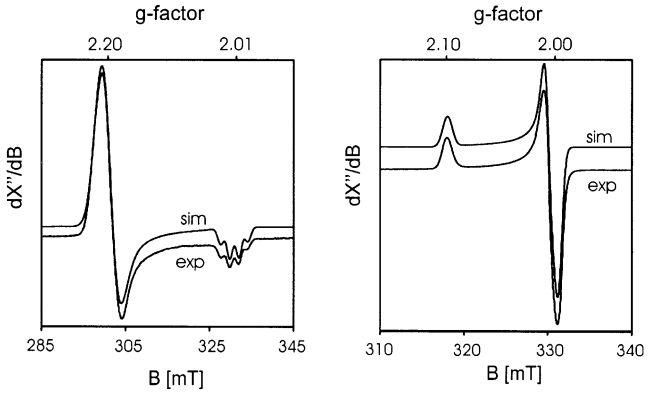


Figure 1. X-Band EPR spectrum of $\mathbf{1}^{2+}$ (left) and superoxide complex $\mathbf{2}^{2+}$ (right) in frozen acetone at 20 K. Conditions: frequency 9.3024 GHz for $\mathbf{1}^{2+}$, 9.2999 GHz for $\mathbf{2}^{2+}$, modulation amplitude = 4 G, attenuation 30 dB. The simulation of $\mathbf{1}^{2+}$ was obtained with the parameters: $g_{\|} = 2.0105$, $g_{\perp} = 2.2150$, $A_{\|}^{Rh} = 61$ MHz, $A_{\perp}^{Rh}$ (not resolved) = 45 MHz. The simulation of $\mathbf{2}^{2+}$ was obtained with the parameters $g_{\|} = 2.0891$, $g_{\perp} = 2.0090$, $A_{\perp}^{Rh} \leq 22$ MHz (not resolved) (free superoxide[7d,13] $g_{11} = 2.01$, $g_{22} = 2.01$, $g_{33} = 2.10$; $[(por)Rh^{III}-O_2^-]$[7] $g_{11} = 1.996$, $g_{22} = 2.005$, $g_{33} = 2.08$).

The EPR spectrum of $\mathbf{1}^{2+}$ in frozen acetone at 20 K is shown in Figure 1. Simulation yields $g_{\|} = 2.0105$ and $g_{\perp} = 2.2150$.[6] The signal at $g_{\perp}$ is broadened, most probably by a hyperfine coupling with the rhodium nucleus ($A_{\perp}^{Rh} \approx 45$ Hz). The hyperfine coupling pattern for $g_{\|}$ was simulated by assuming a hyperfine coupling with rhodium, $A_{\|}^{Rh} = 61$ MHz, and a superhyperfine coupling with one of the nitrogens, $A_{\|}^{N} = 61$ MHz. The axial symmetry of the EPR spectrum and the observed hyperfine patterns suggest that $\mathbf{1}^{2+}$ is square pyramidal, with the two cod double bonds and the two pyridine nitrogens coordinated in the basal plane (x,y) and the amine nitrogen at the apical position (z). This is in contrast to the trigonal-bipyramidal geometry of crystalline $\mathbf{1}^{+}$ observed by X-ray diffraction.[4] Most likely, the SOMO of $\mathbf{1}^{2+}$ consists predominantly of the rhodium d_{z^2} orbital with a small antibonding contribution from an orbital on N_{amine}.

Upon treatment of $\mathbf{1}^{2+}$ in acetone with dioxygen, a new EPR spectrum resulted with g values comparable to those of previously reported rhodium−superoxide complexes[7] (Figure 1). In contrast to free superoxide in acetone, which decomposes instantaneously after addition of dichloromethane at room temperature,[8] EPR signals of $\mathbf{2}^{2+}$ in acetone proved relatively stable in the presence of dichloromethane.

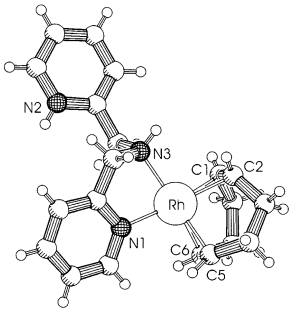
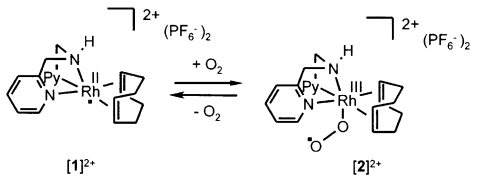


Figure 2. X-ray structure of $\mathbf{1}H^{2+}$. Selected bond lengths (Å) and angles (deg): Rh−N(1) = 2.105(5), Rh−N(3) = 2.135(5), Rh−C(1) = 2.125(7), Rh−C(2) = 2.143(8), Rh−C(5) = 2.135(7), Rh−C(6) = 2.125(7); N(1)−Rh−N(3) = 79.6(2), N(1)−Rh−C(6) = 99.6(3), C(6)−Rh−C(1) = 82.3(3), C(6)−Rh−C(5) = 38.5(3).

Scheme 2. Reversible Binding of Dioxygen to $\mathbf{1}^{2+}$



In acetone at −78 °C, both $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ convert within 3 days to $\mathbf{1}H^{2+}$ (50%) and a 2:1 mixture of the two isomeric cycloocta-2,5-dien-1-yl complexes $\mathbf{3a}^{2+}$ (33%) and $\mathbf{3b}^{2+}$ (17%) (Scheme 1). Complex $\mathbf{1}^{2+}$ apparently disproportionates to $[(dpaH)Rh^{I}(cod)]^{2+}$ and two isomers of $[(dpa)Rh^{III}(cycloocta\text{-}2,5\text{-}dien\text{-}1\text{-}yl)]^{2+}$, $\mathbf{3a}^{2+}/\mathbf{3b}^{2+}$. As the same products result from the superoxo complex $\mathbf{2}^{2+}$, oxygenation of $\mathbf{1}^{2+}$ to $\mathbf{2}^{2+}$ is probably reversible (Scheme 2), in marked contrast to the previously observed irreversible C−O bond formation upon reaction of $[(Me_3\text{-}tpa)Ir^{II}(ethene)]^{2+}$ with dioxygen.[3] We were able to identify the major cyclooctadienyl compound $\mathbf{3a}^{2+}$, but we were not able to obtain pure samples of the minor compound $\mathbf{3b}^{2+}$ free from $\mathbf{3a}^{2+}$. NMR signals of $\mathbf{3b}^{2+}$ are very similar to those of $\mathbf{3a}^{2+}$, and due to strong overlap of signals we were not able to determine the exact coordination geometry of $\mathbf{3b}^{2+}$.

Crystals of $\mathbf{1}H^{2+}$ suitable for X-ray diffraction slowly precipitated from a suspension of $Fc^+PF_6^-$ in a solution of $\mathbf{1}^{+}$ in dichloromethane at room temperature over a period of 4 days.[9]

Complex $\mathbf{1}H^{2+}$ has a square-planar coordination geometry (Figure 2), in which the protonated pyridine ring of the dpa ligand no longer coordinates to the rhodium center. Complex $\mathbf{1}H^{2+}$ has previously been observed by ^{1}H NMR upon protonation of $\mathbf{1}^{+}$.[4]

Crystals of $\mathbf{3a}^{2+}$ suitable for X-ray diffraction were obtained from acetone/dioxane.[10]

The κ^3-dpa ligand is facially coordinated in a pseudo-octahedral coordination geometry (Figure 3). The three remaining coordination sites are occupied by the olefinic

(5) To 500 mg of $[\mathbf{1}^{+}]PF_6$ in 50 mL of dichloromethane was added 225 mg of $[Fc^{+}]PF_6$ (0.8 equiv) under a nitrogen atmosphere. The solution was stirred for 24 h, resulting in a dark green precipitate, which was collected by filtration and subsequently washed with dichloromethane. $[\mathbf{1}](PF_6)_2 \cdot CH_2Cl_2$ was obtained in 82% yield (580 mg). $\mu_{eff} = 1.96\ \mu_B$. ESI$^+$-MS (acetone): m/z 204.5 $[\mathbf{3}^{2+} - (PF_6)_2]$, 233.5 $[\mathbf{3}^{2+} - (PF_6)_2 + \text{acetone}]$, 410 $[\mathbf{1}^{+} - PF_6]$, 554 $[\mathbf{3}^{2+} - (PF_6)]$. Anal. Calcd for $C_{20}H_{25}N_3RhP_2F_{12} \cdot CH_2Cl_2$: C, 32.12; H, 3.46; N, 5.35; Found C, 32.31; H, 3.41; N, 5.51.

(6) Experimental X-band EPR spectra were recorded on a Bruker ER220 spectrometer. The spectra were simulated by iteration of the anisotropic g values, (super)hyperfine coupling constants, and line widths. We thank Dr. F. Neese (MPI Strahlenchemie, Mülheim a/d Ruhr, Germany) for a copy of his EPR simulation program.

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(9) *Crystal data for* $\mathbf{1}H^{2+}$: $C_{20}H_{26}N_3RhP_3F_{12} \cdot {}^1/_2CH_2Cl_2$, $M_r = 741.74$, monoclinic, $a = 32.085(9)$ Å, $b = 10.0677(11)$ Å, $c = 18.052(4)$ Å, $V = 5537(2)$ Å^3, $T = 293(2)$ K, space group $C2/c$, $Z = 8$, λ(Cu Kα) = 1.541 84 Å, 5358 reflections measured on an Enraf-Nonius CAD4 diffractometer, of which 5248 were unique ($R_{int} = 0.1008$). Final R indices: R1 = 0.0625 (for 3457 reflections considered observed ($I > 2\sigma(I)$), wR2 = 0.1810 (all data).

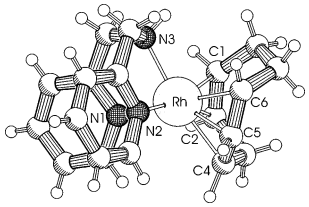
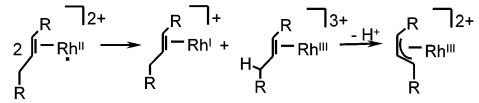
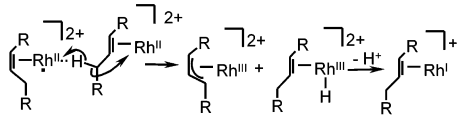


Figure 3. X-ray structure of $\mathbf{3a}^{2+}$. Selected bond lengths (Å) and angles (deg): Rh−N(1) = 2.104(7), Rh−N(2) = 2.062(6), Rh−N(3) = 2.136(6), Rh−C(1) = 2.236(9), Rh−C(2) = 2.233(9), Rh−C(4) = 2.245(8), Rh−C(5) = 2.148(9), Rh−C(6) = 2.173(9); N(2)−Rh−N(1) = 84.6(3), N(2)−Rh−N(3) = 80.0(3), N(1)−Rh−N(3) = 79.0(3), C(2)−Rh−C(1) = 34.7(4), C(6)−Rh−C(4) = 67.5(4), C(5)−Rh−C(1) = 99.8-(4).

Scheme 3. Possible Mechanisms for the Disproportionation of $\mathbf{1}^{2+}$ to $\mathbf{3a}^{2+}$/$\mathbf{3b}^{2+}$ and $\mathbf{1}H^{2+}$





double bond and the allyl moiety of the η^2:η^3-cycloocta-2,5-dien-1-yl fragment.

Clearly, one-electron oxidation of $\mathbf{1}^{+}$ to $\mathbf{1}^{2+}$ triggers activation of an allylic C−H bond of coordinated cod. Two mechanisms are conceivable for this process. In mechanism a, $\mathbf{1}^{2+}$ disproportionates to $\mathbf{1}^{+}$ and $\mathbf{1}^{3+}$ via outer-sphere one-electron transfer (Scheme 3a). Subsequently $\mathbf{1}^{3+}$ deprotonates at one of the allylic positions, yielding $\mathbf{3a}^{2+}$ and $\mathbf{3b}^{2+}$, and protonates $\mathbf{1}^{+}$ at one of the pyridine positions, to give $\mathbf{1}H^{2+}$. In mechanism b, the metallo radical complex $\mathbf{1}^{2+}$ abstracts an allylic hydrogen atom from a second $\mathbf{1}^{2+}$, thus yielding the hydride complex $[(dpa)Rh^{III}(H)(cod)]^{2+}$ and $\mathbf{3a}^{2+}$ and $\mathbf{3b}^{2+}$ (Scheme 3b). Transfer of the hydride as H^{+} to a pyridine nitrogen would generate $\mathbf{1}H^{2+}$. Since the reduction potential of the couple $\mathbf{1}^{3+}/\mathbf{1}^{2+}$ lies at least 0.8 V above the couple $\mathbf{1}^{2+}/\mathbf{1}^{+}$ (see above), one-electron transfer of $\mathbf{1}^{2+}$ to another $\mathbf{1}^{2+}$ must be endothermic by at least 18 kcal mol^{-1}. The kinetic barrier (ΔG^{act}) of the electron-transfer disproportionation mechanism a must thus be at least this value ($\Delta G^{act} \geq 18$ kcal mol^{-1}), which is barely accessible at room temperature. The disproportionation to $\mathbf{1}H^{2+}$ and $\mathbf{3a}^{2+}$ and $\mathbf{3b}^{2+}$ occurs even at −78 °C, which makes this mechanism (a in Scheme 3) unlikely. Our preliminary observation that disproportionation of the iridium analogue of $\mathbf{1}^{2+}$ yields an N ligand Ir^{III}−cycloocta-2,5-dien-1-yl complex and an N ligand Ir^{III}−cod−hydride species supports the hydrogen abstraction mechanism. Looking at CPK models, one would expect H atom abstraction to be hindered by the ligand bulk. However, the reaction might be preceded by dissociation of an N donor or one of the cod double bonds, thus providing access to the Rh^{II} center.[11]

Formation of Rh^{III}(cycloocta-2,5-dienyl) upon oxidation of (derivatives of) cyclopentadienyl complexes of Rh^{I}(cod) has been observed before,[12] but there was no mechanistic explanation for the mysterious hydrogen atom loss. Most probably this reaction proceeds via a similar route: i.e., hydrogen atom transfer from Rh^{II}-(cod) to Rh^{II} resulting in Rh^{III}(cycloocta-2,5-dienyl) and Rh^{I}(cod)/H^{+}. In the presence of an excess of the oxidant, Rh^{I}(cod) would quantitatively convert to Rh^{III}(cycloocta-2,5-dienyl) and H^{+}. We have investigated the reactivity of $\mathbf{1}^{2+}$ in acetone toward H_2 and formaldehyde at −78 °C, but in both cases only formation of $\mathbf{1}H^{2+}$ and $\mathbf{3a}^{2+}$/$\mathbf{3b}^{2+}$ was observed. Clearly the disproportionation reaction is faster than the potential activation of substrate bonds by the Rh^{II} center of $\mathbf{1}^{2+}$.

Apparently Rh^{II} centers at nonporphorinate nitrogen donor sites have metallo radical character. In future studies we will attempt to prepare analogues of $\mathbf{1}^{2+}$ that lack reactive allylic C−H bonds. Initial experiments with a norbornadiene−Rh^{II} complex analogous to $\mathbf{1}^{2+}$ suggest that if formation of an allyl moiety is prevented, disproportionation is inhibited and the Rh^{II} species are more stable. This should allow us to study the reactivity of cis-vacant rhodium(II) olefin fragments toward dioxygen and other substrates.

Supporting Information Available: Figures giving ORTEP representations, text and tables giving crystallographic data for $\mathbf{1}H^{2+}$ and $\mathbf{3}^{2+}$, as well as data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) [**1**]$(PF_6)_2$·CH_2Cl_2 (100 mg, 0.14 mmol) was dissolved in acetone at −78 °C for 3 days until $\mathbf{1}^{2+}$ was completely converted to $\mathbf{1}H^{2+}$ and $\mathbf{3a}^{2+}$/$\mathbf{3b}^{2+}$. Crystals of $\mathbf{3a}^{2+}$(10 mg, 10%) suitable for X-ray diffraction were obtained from this solution top-layered with dioxane. Assignment of the NMR signals follows the numbering scheme in Figure 4. ^{1}H NMR (500 MHz, [D_6]acetone, 298 K): δ 9.63 (d, $^3J_{H,H}$ = 5.5 Hz, 1H, Py *H*6), 8.55 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, Py′ *H*6), 7.54 (m, 2H, Py *H*5, Py′ *H*5), 7.96 (m, 2H, Py *H*4, Py′ *H*4), 7.68 (m, 2H, Py *H*3, Py′ *H*3), 5.71 (dd[A,B], $^3J_{NH,H}$ = 5.9 Hz, $^2J_{H,H}$ = 17.0 Hz, 2H, CH_2NH), 5.44 (m, 2H, C1*H*, C2*H*), 5.17 (m, 1H, C6*H*), 5.06 (m, 1H, C4*H*), 5.03 (d, $^2J_{H,H}$ = 16.9 Hz, CH_2-NH), 4.41 (m, 1H, C5*H*), 3.91 (m, 1H, C8*H*), 3.27 (m, 1H, C3*H*), 3.10 (m, 1H, C8*H*), 2.53 (m, 1H, C7*H*), 2.40 (m, 1H, C3*H*), 2.10 (m, 1H, C7*H*). ^{13}C NMR (125 MHz, [D_6]acetone, 298 K): δ 152.7 (Py *C*2), 152.3 (Py′ *C*2), 145.8 (Py *C*6), 142.4 (Py′ *C*6), 132.7 (Py *C*4), 132.2 (Py′ *C*4), 120.3 (Py *C*5), 118.8 (Py *C*2), 118.3 (Py′ *C*2), 116.4 (Py′ *C*5), 98.9 (*C*6), 98.4 (*C*4), 94.4 (*C*H_2NH), 89.9 (*C*5), 66.5 (*C*1), 65.3 (*C*2), 23.8 (C7), 22.4 (C3), 11.8 (*C*8). Anal. Calcd for $C_{20}H_{24}N_3RhP_3F_{12}$·$C_4H_8O_2$: C, 34.25; H, 3.74; N, 5.99. Found: C, 34.15; H, 3.62; N, 5.80. *Crystal data for* $\mathbf{3a}^{2+}$: $C_{20}H_{24}N_3RhP_2F_{12}$·$C_4H_8O_2$, M_r = 787.38, monoclinic, a = 10.9720-(12) Å, b = 15.514(3) Å, c = 18.2190(18) Å, V = 3048.7(7) Å^3, T = 293-(2) K, space group $P2_1/c$, Z = 4, λ(Mo Kα) = 0.710 73 Å, 7347 reflections measured on an Enraf-Nonius CAD4 diffractometer, of which 6992 were unique (R_{int} = 0.0255). Final R indices: R1 = 0.0791 (for 3739 reflections considered observed ($I > 2\sigma(I)$), wR2 = 0.2381 (all data).

(11) Four-coordinate Rh^{II} complexes have been observed before; see for example: (a) Willems, S. T. H.; Russcher, J. C.; Budzelaar, P. H. M.; de Bruin, B.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Chem. Commun.* **2002**, 148. (b) Gerisch, M.; Krumper, J. R.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 5818. (c) García, M. P.; Jiménez, M. V.; Oro, L. A.; Lahoz, F. J.; Casas, J. M.; Alonso, P. J. *Organometallics* **1993**, *12*, 3257.

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