Enhanced Reactivity of 2-Rhodaoxetanes through a Labile Acetonitrile Ligand

Bas de Bruin,[a] Johanna A. W. Verhagen,[a] Caroline H. J. Schouten,[a] Anton W. Gal,*[a] Derek Feichtinger,[b] and Dietmar A. Plattner[b]

Abstract: New cationic, square-planar, ethene complexes $[(Rbpa)Rh^{I}(C_2H_4)]^+$ $[\mathbf{2a}]^+$–$[\mathbf{2c}]^+$ (Rbpa = *N*-alkyl-*N,N*-di(2-pyridylmethyl)amine; $[\mathbf{2a}]^+$: alkyl = R = Me; $[\mathbf{2b}]^+$: R = Bu; $[\mathbf{2c}]^+$: R = Bz) have been selectively oxygenated in acetonitrile by aqueous hydrogen peroxide to 2-rhoda(III)oxetanes with a labile acetonitrile ligand, $[(Rbpa)Rh^{III}(\kappa^2\text{-}C,O\text{-}CH_2CH_2O{-})(MeCN)]^+$, $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$. The rate of elimination of acetaldehyde from $[(Rbpa)Rh^{III}(\kappa^2\text{-}C,O\text{-}CH_2CH_2O{-})(MeCN)]^+$ increases in the order R = Me < R = Bu < R = Bz. Elimination of acetaldehyde from $[(Bzbpa)Rh^{III}(\kappa^2\text{-}C,O\text{-}CH_2CH_2O)(MeCN)]^+$ $[\mathbf{3c}]^+$, in the presence of ethene results in regeneration of ethene complex $[(Bzbpa)Rh^{I}(C_2H_4)]^+$ $[\mathbf{2c}]^+$, and closes a catalytic cycle. In the presence of Z,Z-1,5-cyclooctadiene (cod) the corresponding cod complex $[(Bzbpa)Rh^{I}(cod)]^+$ $[\mathbf{6c}]^+$ is formed. Further oxidation of $[\mathbf{3c}]^+$ by H_2O_2 results in the transient formylmethyl-hydroxy complex $[(Bzbpa)Rh^{III}(OH)\{\kappa^1\text{-}C\text{-}CH_2C(O)H\}]^+$ $[\mathbf{5c}]^+$.

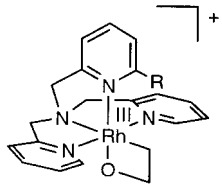
Keywords: alkene ligands · metallaoxetanes · N ligands · oxygenations · rhodium

Introduction

Transition metal catalysed selective oxidation of olefins is of great interest, both in bulk- and in fine-chemical synthesis. Mechanistic proposals for catalytic olefin oxidation with the atom-efficient oxidants dioxygen or hydrogen peroxide are often controversial.

Compared with other transition metals, rhodium and iridium complexes have gained relatively little attention in oxidation chemistry. Nevertheless, their catalytic activity in olefin oxidation by dioxygen or hydroperoxide has been demonstrated and reviewed.[1–3] The mechanistic picture of rhodium-catalysed olefin oxidation is complicated. In oxygenation of olefins by dioxygen five-membered peroxometallacyclic κ^2-*C,O*-β-peroxyalkylrhodium(III) species (3-rhoda-1,2-dioxolanes)[1, 4, 5a, 6a, 7] as well as noncyclic κ^1-*C*-β-hydroperoxyalkylrhodium(III) species[8] have been proposed as initial intermediates. In co-oxygenation of olefins and phosphanes, five-membered peroxometallacyclic κ^2-*C,O*-β-peroxyalkyl rhodium(III) species have been proposed to contract to four-membered oxometallacyclic κ^2-*C,O*-β-oxyalkylrhodium(III) species (2-rhodaoxetanes) by oxygen-atom transfer to phosphane.[1, 4, 5] In some early work, olefin oxidation by peroxorhodium and -iridium complexes was shown to proceed by free-radical pathways.[2, 4, 5, 9].

In an attempt to gain a better mechanistic insight into rhodium catalysed oxidation of olefins we are investigating the stoichiometric oxidation of rhodium(I)-coordinated olefins by O_2 and H_2O_2. We previously described the oxidation of $[Rh^{I}(ethene)]^+$ by H_2O_2 to 2-rhoda(III)oxetanes (1-oxa-2-rhoda(III)cyclobutanes) $[\mathbf{1a}]^+$ and $[\mathbf{1b}]^+$.[10]



$[\mathbf{1a}]^+$: R=H
$[\mathbf{1b}]^+$: R=CH_3

Stabilisation of the 2-rhodaoxetane fragment by the relatively rigid 'N_4' ligands TPA (TPA = tris(pyridin-2-ylmethyl)amine) and MeTPA gave us a first opportunity to study 2-rhodaoxetane reactivity.[10–12] However, for 2-rhodaoxetane moieties to be of synthetic use, their reactivity will have to be increased considerably. We now report the oxidation of the new ethene complexes $[(Rbpa)Rh^{I}(ethene)]^+$ (Rbpa = *N*-alkyl-*N*,*N*-di(2-pyridylmethyl)amine; alkyl = R = Me, Bu, Bz). Reaction of these 'N_3' ligand complexes with aqueous H_2O_2 in acetonitrile results in the formation of the 2-oxyethyl complexes $[(Rbpa)Rh^{III}(\kappa^2\text{-}C,O\text{-}CH_2CH_2O{-})(MeCN)]^+$. In these, the 2-rhodaoxetane

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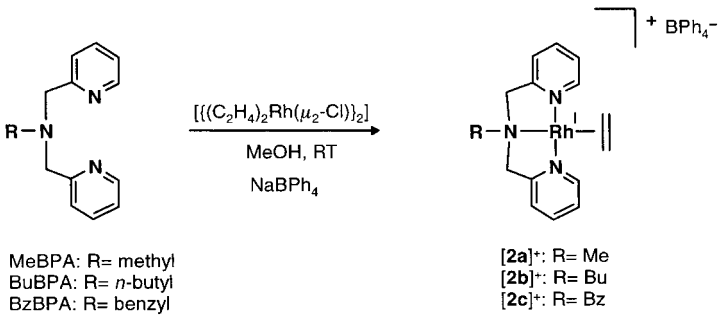
fragment is stabilised by the 'N_3' ligand and one molecule of acetonitrile. Because of the lability of the coordinated acetonitrile, these acetonitrile-stabilised 'N_3'-2-rhodaoxetanes prove to be significantly more reactive than the corresponding 'N_4'-2-rhodaoxetanes $[\mathbf{1a}]^+$ and $[\mathbf{1b}]^+$.

Results and Discussion

Synthesis of [(Rbpa)Rh^{I}(ethene)]$^+$: We synthesised the cationic complexes [(Mebpa)Rh^{I}(C_2H_4)]$^+$ ($[\mathbf{2a}]^+$), [(Bubpa)Rh^{I}-(C_2H_4)]$^+$ ($[\mathbf{2b}]^+$), and [(Bzbpa)Rh^{I}(C_2H_4)]$^+$ ($[\mathbf{2c}]^+$) by the route shown in Scheme 1. Stirring of $[\{(C_2H_4)_2Rh(\mu\text{-Cl})\}_2]$ with the ligands Mebpa, Bubpa, or Bzbpa in MeOH at $-78\,^{\circ}C$ afforded solutions of [**2a**]Cl, [**2b**]Cl, and [**2c**]Cl, respectively. The cations $[\mathbf{2a}]^+$, $[\mathbf{2b}]^+$ and $[\mathbf{2c}]^+$ were isolated as BPh_4 salts by precipitation with $NaBPh_4$.

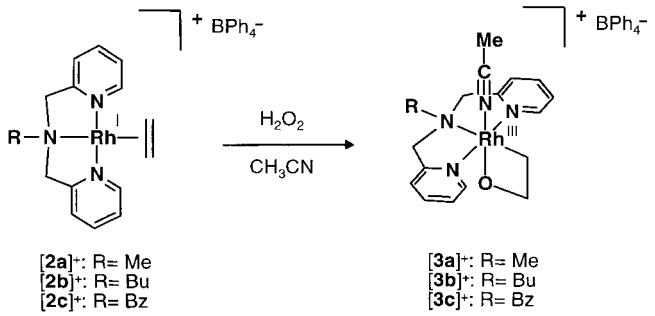


Scheme 1. Preparation of [Rh^{I}(ethene)] complexes $[\mathbf{2a}]^+$–$[\mathbf{2c}]^+$.

The ^{1}H and ^{13}C NMR data of $[\mathbf{2a}]^+$–$[\mathbf{2c}]^+$ show signals for two equivalent pyridine groups. Compared with the free ligands, the Py-H6 signals in the ^{1}H NMR spectrum have shifted almost 1.0 ppm upfield as a result of anisotropic shielding by the coordinated ethene fragment (e.g. Bubpa: $\delta = 8.5$, $[\mathbf{2b}]^+$: $\delta = 7.5$). The diastereotopic protons of the two equivalent NCH_2Py groups give rise to two AB-type doublets. In the ^{1}H and ^{13}C NMR spectra of $[\mathbf{2a}]^+$–$[\mathbf{2c}]^+$, the ethene fragment is observed as a broad singlet at room temperature. The fluxionality of ethene in the 'N_3'-ligand complexes $[\mathbf{2a}]^+$–$[\mathbf{2c}]^+$ parallels that in the 'NP_2'-ligand complex [(pnp)Rh^{I}(C_2H_4)]$^+$ (pnp = 2,6-bis(diphenylphosphanylmethyl)pyridine).[13a]

The ^{1}H NOE patterns of both $[\mathbf{2b}]^+$ and $[\mathbf{2c}]^+$ are characteristic for the *mer* coordination mode of the Bubpa and Bzbpa ligands; clear NOE contacts are observed between the Py-H6 and the ethene protons. Furthermore, clear NOE contacts are observed between $NC_\alpha H_2$ ($[\mathbf{2b}]^+$: N*CH*$_2$Pr; $[\mathbf{2c}]^+$: N*CH*$_2$Ph) and the equatorial NCH_2Py protons[13b] (one of the two AB-type doublets). The latter also show NOE contacts with the Py-H3 protons. The axial NCH_2Py protons[13b] (the other AB-type doublet) do not show NOE contacts with either $NC_\alpha H_2$ or Py-H3.

Oxidation of [(Rbpa)Rh^{I}(ethene)]$^+$ to 2-rhodaoxetanes: The complexes $[\mathbf{2a}]^+$–$[\mathbf{2c}]^+$ are air-sensitive. As shown by ^{1}H NMR spectroscopy, ready displacement of ethylene by O_2 in acetone or acetonitrile results in a complex mixture of compounds. Treatment of acetone solutions of $[\mathbf{2a}]BPh_4$, $[\mathbf{2b}]BPh_4$, and $[\mathbf{2c}]BPh_4$ with aqueous H_2O_2 at room temperature also results a complex mixture of oxidation products. However, in acetonitrile selective and instantaneous oxidation of $[\mathbf{2a}]^+$–$[\mathbf{2c}]^+$ by H_2O_2 is observed. ^{1}H NMR spectroscopy indicates the formation of the 2-rhodaoxetanes $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$ in nearly quantitative yield. They were isolated as $[\mathbf{3a}]BPh_4$, $[\mathbf{3b}]BPh_4$, and $[\mathbf{3c}]BPh_4$ by precipitation with diethyl ether (Scheme 2).



Scheme 2. Oxidation of ethene complexes to acetonitrile-stabilized 'N_3'-2-rhodaoxetanes.

The ^{1}H and ^{13}C NMR data of the rhodium(III) complexes $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$ indicate two equivalent pyridyl fragments, as in the starting rhodium(I) complexes $[\mathbf{2a}]^+$–$[\mathbf{2c}]^+$. The Py-H6 signals of the 2-rhodaoxetanes $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$ have undergone the expected downfield coordination shift relative to those of the free ligands. Signals indicative of the 2-rhodaoxetane fragment Rh^{III}(κ^2-*C,O,*-CH_2CH_2O–) are clearly observed in the ^{1}H-NMR spectra of $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$. In all three complexes $RhCH_2\mathit{CH_2}O$ is observed as a triplet, whereas $Rh\mathit{CH_2}CH_2O$ is observed as a doublet of triplets due to coupling with the rhodium center. In the ^{13}C NMR spectrum of $[\mathbf{3a}]^+$, $Rh\mathit{CH_2}CH_2O$ and $RhCH_2\mathit{CH_2}O$ show a ^1J and ^2J rhodium coupling, respectively. Chemical shifts and coupling constants are summarised in Table 1. Other NMR data for $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$ are very similar to those of the 'N_4'-2-rhodaoxetanes $[\mathbf{1a}]^+$ and $[\mathbf{1b}]^+$.[10c]

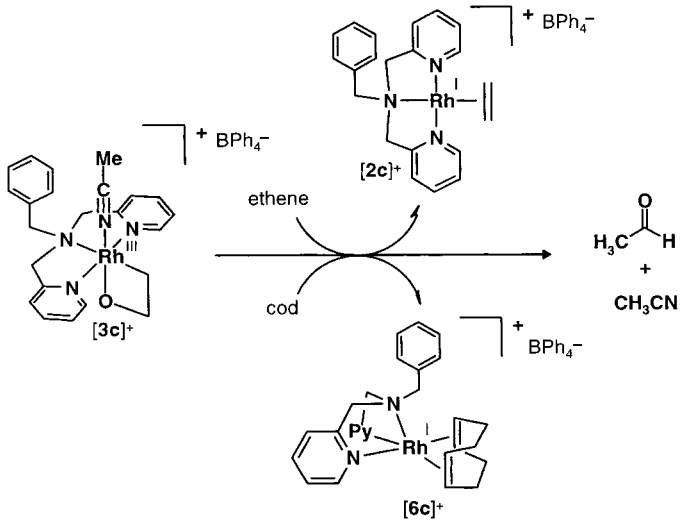
Complex $[\mathbf{3a}]^+$ was fully characterised by ^{1}H and ^{13}C NMR, ^{1}H-NOESY, C,H,N analysis, and FAB and ESI mass spectrometry. The instability of $[\mathbf{3b}]^+$ and $[\mathbf{3c}]^+$ prevented their CHN-analysis and their further characterisation by ^{13}C NMR spectroscopy and ^{1}H-NOESY at room temperature. In the ^{1}H NOESY spectrum of $[\mathbf{3a}]^+$ clear NOE contacts are observed between the Py-H6 protons and $RhC\mathit{H_2}CH_2O$, indicating that $C\mathit{H_2}$ is oriented trans to the tertiary amine nitrogen (N^{amine}_{Me}). Other NOE contacts similar to those for ethene complex $[\mathbf{2b}]^+$ are indicative of the *mer* coordination mode of the Mebpa ligand in $[\mathbf{3a}]^+$.

Decomposition of the 2-rhodaoxetanes in solution: The acetonitrile adducts of the 'N_3'-rhodaoxetanes, $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$, are much less stable than the corresponding 'N_4'-rhodaoxetanes $[\mathbf{1a}]^+$ and $[\mathbf{1b}]^+$, as shown by ^{1}H NMR spectroscopy. In CD_2Cl_2, $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$ eliminate acetaldehyde at room temperature, as indicated by the gradual appearance of ^{1}H NMR signals at $\delta = 9.7$ (q, ^3J(H,H) = 2.9 Hz, 1H; $CH_3C(O)\mathit{H}$) and

Table 1. Chemical shifts (δ) and coupling constants (J, [Hz]) of the 2-rhodaoxetane fragments.

	[**1a**]$^{+}$ [b]	[**1b**]$^{+}$ [b]	[**3a**]$^{+}$ [c]	[**3b**]$^{+}$ [c]	[**3c**]$^{+}$ [c]
^{1}H NMR[a]					
δ (RhCH_2CH$_2$O–)	2.25	2.35	2.21	2.20	2.29
^{2}J(Rh,H)	2.4	2.6	2.4	2.3	2.5
δ RhCH$_2$CH_2O–)	4.98	4.80	4.76	4.65	4.74
^{3}J(H,H)	7.5	0.6	7.5	7.5	7.5
^{13}C NMR[b]					
δ (RhCH_2CH$_2$O–)	1.3	2.5	–1.4	–	–
^{1}J(Rh,C)	18.4	8.0	16.5		
δ (RhCH$_2$CH_2O–)	78.7	0.6	80.5	–	–
^{2}J(Rh,C)	4.0	4.2	3.7		

[a] ^{1}H NMR: CD_2Cl_2. [b] ^{13}C NMR: [D$_6$]acetone. [c] ^{13}C NMR: CD_2Cl_2.



Scheme 3. Elimination of acetaldehyde in the presence of ethene or cod; formation of an ethene or a cod complex.

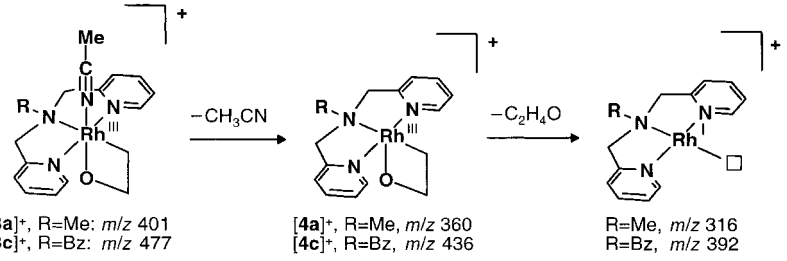
$\delta = 2.1$ (d, ^{3}J(H,H) = 2.9 Hz, 3H; CH_3C(O)H). The methyl homologue [**3a**]$^{+}$ is the least reactive (20% elimination of acetaldehyde in 20 h), the benzyl homologue [**3c**]$^{+}$ is the most reactive (quantitative elimination of acetaldehyde in 2 h). In CD_3CN, [**3a**]$^{+}$ is stable, whereas [**3c**]$^{+}$ eliminates acetaldehyde at a much lower rate than in CD_2Cl_2 (20% elimination in 2 h). Addition of a few drops of CD_3CN to [**3c**]BPh_4 in CD_2Cl_2 results in rapid substitution of CH_3CN by CD_3CN and slows down the elimination of acetaldehyde.

Elimination of acetaldehyde from [**3a**]$^{+}$–[**3c**]$^{+}$ in CD_2Cl_2 generates a complex mixture of Rbpa–rhodium complexes. However, in the presence of ethene or (*Z*,*Z*)-1,5-cyclooctadiene (cod), 2-rhodaoxetane [**3c**]$^{+}$ is converted to the ethene complex [**2c**]$^{+}$ or the cod complex [**6c**]$^{+}$[10d] in nearly quantitative yield (Scheme 3).

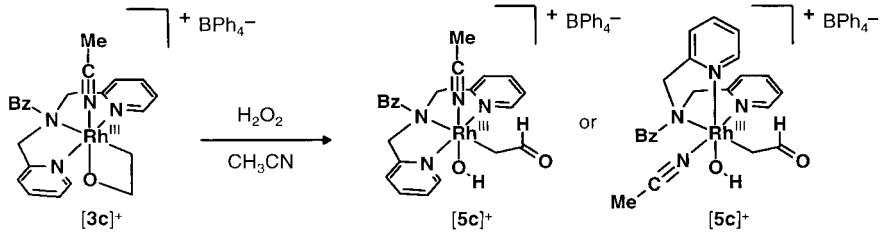
Decomposition of the 2-rhodaoxetanes in the gas phase: Solutions of [**3a**]BPh_4 or [**3c**]BPh_4 generated in situ by dissolving [**2a**]BPh_4 or [**2c**]BPh_4 in acetonitrile in the presence of H_2O_2, were injected into an ESI-MS spectrometer. Signals for [(Rbpa)Rh(C_2H_4O)(MeCN)]$^{+}$ were clearly observed at *m/z* 401 (R = Me) and at *m/z* 477 (R = Bz).(Scheme 4). For both R = Me and R = Bz, daughter-ion spectra (MS/MS) of [(Rbpa)Rh(C_2H_4O)(MeCN)]$^{+}$ showed signals corresponding to [(Rbpa)Rh(C_2H_4O)]$^{+}$, indicating loss of MeCN (41), and [(Rbpa)Rh]$^{+}$, indicating loss of CH_3CN and C_2H_4O (44). Daughter-ion spectra of the [(Rbpa)Rh(C_2H_4O)]$^{+}$ ions showed loss of C_2H_4O. No direct loss of C_2H_4O from [(Rbpa)-Rh(C_2H_4O)(MeCN)]$^{+}$ was observed (Scheme 4).

The above observations indicate that, in the gas-phase, dissociation of MeCN precedes elimination of C_2H_4O. It seems reasonable to assume that the observed elimination of C_2H_4O is elimination of acetaldehyde, as is the case in solution.

Further oxidation of 2-rhodaoxetane [3c]$^{+}$ with H_2O_2: ^{1}H NMR spectroscopy shows that in acetonitrile the 2-rhodaoxetanes [**3a**]$^{+}$ and [**3b**]$^{+}$ are relatively stable towards an excess of H_2O_2 (10 mol mol^{-1}). Remarkably, [**3c**]$^{+}$ no longer eliminates acetaldehyde (vide supra) but instead converts to the transient formylmethyl–hydroxy species [(Bzbpa)Rh^{III}-(OH)(κ^{1}-*C*-CH_2CH(O))(MeCN)]$^{+}$ ([**5c**]$^{+}$, Scheme 5), identified by ^{1}H NMR spectroscopy and ESI mass spectrometry. According to ^{1}H NMR spectroscopy ($\delta = 3.37$ (dd, ^{3}J(H,H) = 5.3 Hz, ^{2}J(Rh,H) = 2.9 Hz, 2H; RhCH_2C(O)H) and $\delta = 10.3$ (t, ^{3}J(H,H) = 5.3 Hz, 1H; RhCH$_2$C(O)H)), [**5c**]$^{+}$ reached its maximum intensity after approximately 4 h. After 12 h, the ^{1}H NMR signals of [**5c**]$^{+}$ had disappeared, and a complex mixture of Bzbpa rhodium complexes was observed. The rate



Scheme 4. Fragmentation of [**3a**]$^{+}$ and [**3c**]$^{+}$ in the gas phase (ESI-MS).



Scheme 5. Oxidation of 2-rhodaoxetane [**3c**]$^{+}$ to formylmethyl–hydroxy complex [**5c**]$^{+}$.

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of formation of $[\mathbf{5c}]^+$ roughly equalled the rate of elimination of acetaldehyde from $[\mathbf{3c}]^+$ in the absence of H_2O_2.

Further evidence for the formation of $[\mathbf{5c}]^+$ comes from ESI-MS: dissolution of $[\mathbf{2c}]BPh_4$ in acetonitrile in the presence of an excess of 35% aqueous H_2O_2 results in oxidation to $[\mathbf{3c}]^+$ (indicated by a signal at m/z 477), followed by slow oxidation to $[\mathbf{5c}]^+$ (indicated by a transient signal at m/z 493). A daughter-ion spectrum (MS/MS) of m/z 493 showed a signal at m/z 452 (indicating loss of MeCN) and a signal at m/z 434 (indicating loss of both MeCN and H_2O), consistent with formulation of $[\mathbf{5c}]^+$ as a formylmethyl–hydroxy complex.

Elimination of acetaldehyde: The observed elimination of acetaldehyde from $[\mathbf{3c}]^+$, and the accompanying formation of ethene complex $[\mathbf{2c}]^+$ in the presence of ethene (Scheme 3), show that the Rh^I oxidation state is accessible from a 2-rhoda(III)oxetane, even with "hard", non-π-acceptor, nitrogen donor ligands.

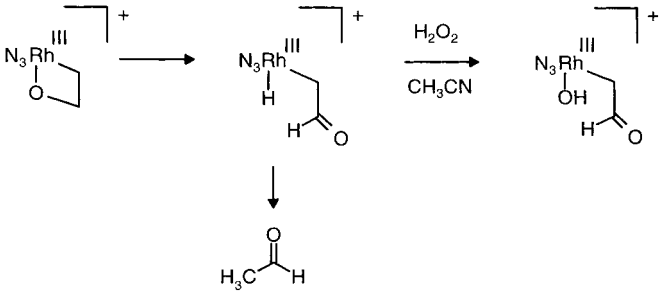
Our ^1H NMR studies of the acetonitrile-stabilised 'N_3'-2-rhodaoxetanes $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$ reveal ready elimination of acetaldehyde at room temperature, whereas such elimination from the 'N_4'-2-rhodaoxetanes $[\mathbf{1a}]^+$ and $[\mathbf{1b}]^+$ requires temperatures in excess of 80°C. The change from the non-labile 'N_4' ligand system in $[\mathbf{1a}]^+$ and $[\mathbf{1b}]^+$ to the more labile MeCN/'N_3' ligand system in $[\mathbf{3a}]^+$–$[\mathbf{3c}]^+$ clearly increases the reactivity of the 2-rhodaoxetane fragment.

The observed suppression of acetaldehyde elimination from $[\mathbf{3c}]^+$ in CD_2Cl_2 upon addition of acetonitrile (vide supra) suggests elimination of acetaldehyde in solution from a coordinatively unsaturated 16-electron rhodium(III) species, which we propose to be $[(Rbpa)Rh^{III}(\kappa^2\text{-}C,O\text{-}CH_2CH_2O-)]^+$, $[\mathbf{4c}]^+$(Scheme 4). This formation of $[\mathbf{4c}]^+$ through dissociation of acetonitrile would be analogous to that observed in the gas phase by ESI-MS. Generation of a species through dissociation of a 2-methyl pyridyl arm of Bzbpa, through heterolytic dissociation of the 2-rhodaoxetane Rh–O bond[14], or through dissociation of the 2-rhodaoxetane Rh–O bond after protonation of the rhodaoxetane oxygen[10c, 15] are all considered less likely. In the presence of ethene, the 14-electron species $[(Bzbpa)Rh]^+$ formed upon acetaldehyde elimination from $[\mathbf{4c}]^+$ is trapped as the 16-electron ethene complex $[(Bzbpa)Rh^I(C_2H_4)]^+$ $[\mathbf{2c}]^+$ (Scheme 3).

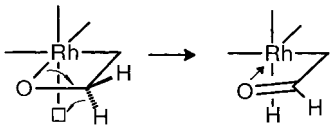
For the elimination of acetaldehyde from $[\mathbf{4c}]^+$ it seems reasonable to propose formation a cis-formylmethylhydridorhodium(III) complex via a β-hydride shift and reductive elimination of a C–H bond (Scheme 6).

In accord with this mechanism, a *cis*-formylmethylhydridoiridium(III) complex has been obtained by reaction of ethylene oxide with $[Ir^I(C_8H_{14})(PMe_3)_3(Cl)]$.[14a] The proposed β-hydride shift in $[\mathbf{4c}]^+$ (Scheme 7) requires a prior *mer*–*fac* rearrangement of the Bzbpa ligand to generate a *cis*-C, *cis*-O vacant site. The β-hydride shift to this site (Scheme 7) would be analogous to that in the formation of a π-allyl-hydridoiridium(III) complex from the irida(III)cyclobutane $[Cp^*Ir^{III}(\kappa^2\text{-}C,C\text{-}CH_2CH_2CH_2)(dmso)]$ (dmso = dimethyl sulfoxide) upon dissociation of a *cis,cis*-dmso ligand.[17]

The steric hindrance at N_R^{amine} of Rbpa in $[(Rbpa)Rh^{III}(\kappa^2\text{-}C,O\text{-}CH_2CH_2O-)(MeCN)]^+$ increases in the order R = Me < R = Bu < R = Bz.The rate of acetaldehyde elimination from $[(Rbpa)Rh^{III}(\kappa^2\text{-}C,O\text{-}CH_2CH_2O-)(MeCN)]^+$ follows the same order. This could reflect the steric influence of R on the dissociation of acetonitrile, but could also reflect a steric influence of R on the rate of reductive elimination of acetaldehyde from the resulting unsaturated 2-rhodaoxetane $[(Rbpa)Rh^{III}(\kappa^2\text{-}C,O\text{-}CH_2CH_2O-)]^+$: the increasingly hindered coordination of N_R^{amine} to Rh^{III} on going from R = Me to R = Bu to R = Bz reduces the effective donor capacity of N_R^{amine}[10d] and thereby increases the rate of elimination of acetaldehyde.



Scheme 6. Proposed formylmethyl–hydrido intermediate in elimination of acetaldehyde and oxidation to formylmethyl–hydroxide complex.



Scheme 7. β-Hydride shift to *cis*-C, *cis*-O vacant site.

Elimination of acetaldehyde versus oxidation by H_2O_2: In acetonitrile the rate at which $[\mathbf{3c}]^+$ eliminates acetaldehyde is comparable to its rate of oxidation by H_2O_2. Complex $[\mathbf{3a}]^+$ does not eliminate acetaldehyde in acetonitrile and is not oxidised by H_2O_2. Therefore, it is tempting to assume that elimination of acetaldehyde from $[\mathbf{3c}]^+$ and oxidation of $[\mathbf{3c}]^+$ to the formylmethyl–hydroxide complex $[\mathbf{5c}]^+$ proceed via one and the same *cis*-formylmethyl–hydrido intermediate (Scheme 6). Whereas acetaldehyde results from reductive elimination of a C–H bond, formylmethyl–hydroxy complex $[\mathbf{5c}]^+$ results from oxidation of the formylmethyl–hydrido intermediate by H_2O_2.

Conclusion

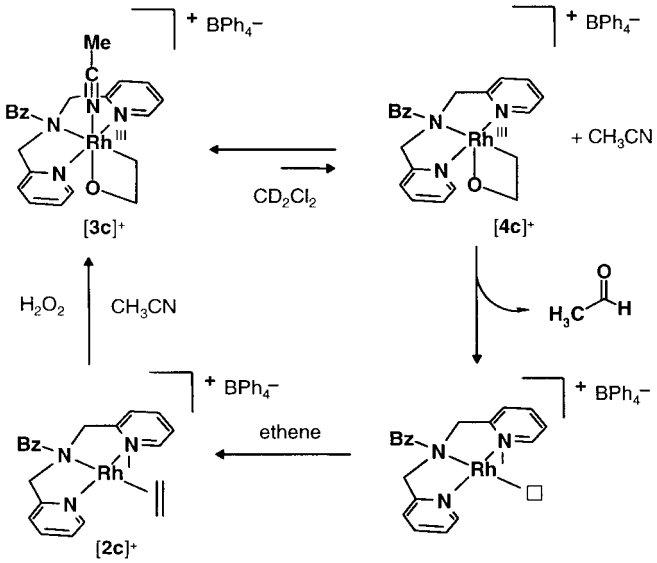
Selective oxidation of $[Rh^I(ethene)]^+$ by H_2O_2 to stable 2-rhoda(III)oxetanes is not limited to [('N_4' ligand) Rh^I(ethene)]$^+$. In acetonitrile the complexes [('N_3' ligand)Rh^I(ethene)]$^+$ have been selectively oxidised to labile acetonitrile adducts of the corresponding 'N_3'-rhodaoxetanes. The rate of elimination of acetaldehyde from these adducts is found to be significantly higher than for the corresponding 'N_4'-rhodaoxetanes.

The elimination of acetaldehyde is proposed to involve generation of a vacant site through dissociation of acetonitrile, followed by a β-hydride shift from the κ^2-*C,O*-2-oxyethyl fragment to the Rh^{III} center of the 2-rhodaoxetane moiety.

The reactivity of $[\mathbf{3a}]^+$ – $[\mathbf{3c}]^+$ strongly depends on the Rbpa ligand: the rate of acetaldehyde elimination increases in the order R = Me < Bu < Bz, probably for steric reasons.

The most labile 2-rhodaoxetane, $[\mathbf{3c}]^+$, is further oxidised by H_2O_2 in acetonitrile to the transient formylmethyl – hydroxy complex $[\mathbf{5c}]^+$. Such reactivity is not observed for $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$. We propose that elimination of acetaldehyde from $[\mathbf{3c}]^+$, and oxidation of $[\mathbf{3c}]^+$ to formylmethyl – hydroxy complex $[\mathbf{5c}]^+$, proceed via the same *cis*-formylmethylhydrido intermediate.

The generation of ethene complex $[\mathbf{2c}]^+$ upon decomposition of 2-rhodaoxetane $[\mathbf{3c}]^+$ in CH_2Cl_2, in the presence of ethene, closes a catalytic cycle (Scheme 8). However, we did



Scheme 8. Catalytic oxidation of ethene to acetaldehyde.

not find any indications for "one-pot" catalytic behaviour of $[\mathbf{3c}]^+$ in the presence of H_2O_2 and ethene in any of the solvents tried. Probably the "naked" $[(Bzbpa)Rh^I]^+$ that results from reductive elimination reacts faster with H_2O_2 than with ethene, poisoning the potential catalyst. Another reason for the failure of $[\mathbf{3c}]^+$ to catalytically generate acetaldehyde from ethene could be the further oxidation of $[\mathbf{3c}]^+$ by H_2O_2 to formylmethyl – hydroxy complex $[\mathbf{5c}]^+$.

Our attempts to oxygenate the newly prepared ethene complexes with O_2 failed as the olefin was displaced by the incoming O_2. In closing a catalytic cycle for oxygenation of ethene by H_2O_2 we have, however, unequivocally demonstrated the conversion of a 2-rhoda(III)oxetane and ethene to a rhodium(I)ethene complex and acetaldehyde. This is the final step in the mechanistic scheme proposed for rhodium catalysed co-oxygenation of olefins and phosphanes, which involves contraction of a five-membered peroxometallacyclic β-peroxyalkylrhodium(III) intermediate to a four-membered oxometallacyclic β-oxyalkylrhodium(III) intermediate by atom transfer to phosphane as a prior step.[4] Recently the conversion of $[(bpa)Rh^I(cod)]^+$ (bpa = *N,N*-di(2-pyridylmethyl)amine)[10d] and $[(P_3O_9)Ir^I(cod)]^{2-}$; $P_3O_9^{3-}$ = trimetaphosphate)[11a] to corresponding 2-metallaoxetanes, through monooxygenation of one of the coordinated cod double bonds by O_2, has been reported. Together with our present results, these findings prompt us to search for N donor ligands that would allow isolation of peroxygenated or oxygenated intermediates in the reaction of Rh(ethene)$]^+$ or [Rh(propene)$]^+$ with O_2.

Experimental Section

General: All procedures were performed under N_2 using standard Schlenk techniques. Solvents (p.a.) were deoxygenated by bubbling through a stream of N_2 or by the freeze-pump-thaw method. The temperature indication of room temperature corresponds to approximately 20 °C. NMR experiments were carried out on a Bruker DPX200 (200 MHz and 50 MHz for ^{1}H and ^{13}C respectively), a Bruker AC300 (300 MHz and 75 MHz for ^{1}H and ^{13}C respectively), and a Bruker AM-500 (500 MHz and 125 MHz for ^{1}H and ^{13}C, respectively). Solvent shift reference for ^{1}H NMR spectroscopy: [D$_6$]acetone: $\delta_H = 2.05$, CD_3CN $\delta_H = 1.98$, CD_2Cl_2 $\delta_H = 5.31$. For ^{13}C NMR: [D$_6$]acetone $\delta_C = 29.50$, CD_3CN $\delta_C = 1.28$, CD_2Cl_2 $\delta_C = 54.20$. Elemental analyses (C,H,N) were carried out on a Carlo Erba NCSO-analyser. Fast atom bombardment (FAB) ionisation mass spectra were recorded on a VG 7070 mass spectrometer. Electrospray ionisation (ESI) mass spectra were performed on a slightly modified Finnigan MAT TSQ7000 electrospray tandem mass spectrometer described in our previous reports on the gas-phase chemistry of $[CpIr^{III}(PMe_3)(CH_3)]^+$[18] and $[O{=}Mn^V(salen)]^+$ (salen = *N,N*′-bis(salicylidene)-4,5-dimethylphenylenediamine dianion)[19] (octopole, quadrupole, octopole, quadrupole setup). The first octopole was fitted with an open cylindrical sheet around the rods into which a collision gas could be bled for thermalisation or reaction pressures up to 20 mTorr. Daughter-ion spectra were recorded in daughter-ion mode; that is, the first quadrupole is used to mass select ions of a single mass, which are then collided with target gas in the second octopole. The second quadrupole is operated in scanning mode and serves to detect the ionic collision fragments. The incoming ions were thermalised in the first octopole with argon at a pressure of ≈10 mTorr and at a temperature of 70 °C. The tube lens was typically operated at 70 V (referenced to *m*/*z* 500).
$[\{(C_2H_4)_2Rh(\mu\text{-}Cl)\}_2]$ was prepared according to a literature procedure.[20] The synthesis and characterisation of the ligands Bubpa and Bzbpa, and compound $[(Bzbpa)Rh^I(cod)]PF_6$, $[\mathbf{6c}]PF_6$, have been described previously.[10d] All other chemicals are commercially available and were used without further purification, unless stated otherwise.

***N*-methyl-*N,N*-di(2-pyridylmethyl)amine (Mebpa)**: bpa (1.01 g, 5.09 mmol) and methyl iodide (0.74 g, 5.21 mmol) were dissolved in acetonitrile (100 mL). Na_2CO_3 (approximately 10 g) was added. The solution was refluxed for 3 d under a nitrogen atmosphere. Subsequently, the Na_2CO_3 was removed by filtration, and the solvent was evaporated under vacuum. The resulting oil was stirred for 1 h in a mixture of water and Na_2CO_3. The mixture was extracted with diethyl ether. The combined diethyl ether layers were evaporated and a red oil was obtained. The product was purified by chromatography on a silica column with 10% methanol in chloroform. ^{1}H NMR (200.13 MHz, $CDCl_3$, 300 K): $\delta = 8.56$ (dq, $^3J(H,H) = 4.7$ Hz, 2H; Py-H6), 7.67 (m, 2H; Py-H4), 7.53 (m, 2H; Py-H3), 7.17 (m, 2H; Py-H5), 3.79 (s, 4H; N-CH_2-Py), 2.33 (s, 3H; N-CH_3); ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$, 300 K): $\delta = 159.0$ (Py-C2), 148.8 (Py-C6), 136.2 (Py-C4), 122.8 (Py-C3), 121.8 (Py-C5), 63.4 (N–CH_2–Py), 42.5 (N–CH_3); FAB$^+$-MS (*m*/*z*): 213 $[M]^+$, 198 $[M - CH_3]^+$.

(η^2-Ethene)(κ^3-*N*-methyl-*N,N*-di(2-pyridylmethyl)amine)rhodium(I) tetraphenylborate ([2a]BPh$_4$): $[\{(C_2H_4)_2Rh^I(\mu_2\text{-}Cl)\}_2]$ (0.22 g, 1.11 mmol) was added to a solution of Mebpa (0.24 g, 1.11 mmol) in methanol (50 mL). After stirring for 1 h at −78 °C, $NaBPh_4$ (0.18 g, 1.11 mmol) was added. A yellow powder precipitated which was collected by filtration. The product was washed with methanol and dried under vacuum, yielding 0.85 g (77%). ^{1}H NMR (200.13 MHz, [D$_6$]acetone, 300 K): $\delta = 7.92$ (dt, $^3J(H,H) = 7.8$ Hz, $^3J(H,H) = 7.8$ Hz, $^4J(H,H) = 1.5$ Hz, 2H; Py-H4), 7.66 (dddd, $^3J(H,H) = 5.6$ Hz, $^4J(H,H) = 1.5$ Hz, $J = 1.5$ Hz, $J = 0.6$ Hz, 2H; Py-H6), 7.50 (dd, br, $^3J(H,H) = 7.8$ Hz, $J = 0.4$ Hz, 2H; Py-H3), 7.4 – 7.3 (m, 2H; Py-H5), 7.34 (m, 8H; BAr-H2), 6.93 (t, $^3J(H,H) = 7.4$ Hz, 8H; BAr-H3), 6.77 (t, $^3J(H,H) = 7.4$ Hz, 4H; BAr-H4), 5.00 (d[AB], $^3J(H,H) = 15.7$ Hz, 2H; NCH_2Py), 4.36 (dd[AB], $^3J(H,H) = 15.7$ Hz, $^3J(Rh,H) = 1.3$ Hz; NCH_2Py), 3.48 (s, 4H;

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CH_2=CH_2), 2.92 (s, 3H, NCH_3); $^{13}C\{^1H\}$ NMR (50.32 MHz, [D$_6$]acetone, 300 K): $\delta = 165.4$ (q, ^1J(B,C) = 49.6 Hz; BAr-C1), 165.1 (Py-C2), 150.2 (Py-C6), 138.9 (Py-C4), 125.9 (Py-C3), 124.3 (Py-C5), 137.5 (BAr-C2), 126.5 (BAr-C3), 122.8 (BAr-C4), 67.6 (NCH_2Py), 57.7 (br, CH_2=CH_2), 47.33 (NCH_3); FAB$^+$-MS: (*m*/*z*): 344 $[M]^+$, 316 $[M - C_2H_4]^+$, 300 $[M - C_2H_4 - CH_3 - H]^+$; elemental analysis (%) calcd for $C_{39}H_{39}N_3BRh$: C 70.60, H 5.93, N 6.33; found: C 70.65, H 5.81, N 6.23.

(η^2-Ethene)-(κ^3-*N*-butyl-*N*,*N*-di(2-pyridylmethyl)amine)rhodium(I) tetraphenylborate ([2b]BPh$_4$): $[\{(C_2H_4)_2Rh^I(\mu_2\text{-}Cl)\}_2]$ (0,76 g, 3.92 mmol) was added to a solution of Bubpa (1.00 g, 3.92 mmol) in methanol (50 mL). After stirring for 1 h at $-78\,^\circ$C, $NaBPh_4$ (1.33 g, 3.92 mmol) was added. A yellow powder precipitated, which was collected by filtration, washed with methanol, and dried under vacuum, yieding 2.10 g (76%). ^{1}H NMR (200.13 MHz, [D$_6$]acetone, 298 K): $\delta = 7.97$ (ddd, ^3J(H,H) = 7.7 Hz, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.6 Hz, 2H; Py-H4), 7.70 (dddd, ^3J(H,H) = 5.6 Hz, ^3J(H,H) = 1.6 Hz, J = 1.6 Hz, J = 0.7 Hz, 2H; Py-H6), 7.57 (dd, ^3J(H,H) = 7.7 Hz, 2H; Py-H3), 7.5–7.4 (m, 2H; Py-H5), 7.37 (m, 8H; BAr-H2), 6.95 (t, ^3J(H,H) = 7.4 Hz, 8H; BAr-H3), 6.80 (t, ^3J(H,H) = 7.4 Hz, 4H; BAr-H4), 5.13 (d[AB], ^2J(H,H) = 16.1 Hz, 2H; N-C*H*HPy), 4.60 (dd[AB], ^2J(H,H) = 16.1 Hz, ^3J(Rh,H) = 1.3 Hz, 2H; NCH_2Py), 3.51 (s, br, 4H; CH_2=CH_2), 3.13 (m, 2H; $NCH_2CH_2CH_2CH_3$), 1.81 (m, 2H; $NCH_2CH_2CH_2CH_3$), 1.39 (m, 2H; $NCH_2CH_2CH_2CH_3$), 0.79 (t, $^3J(H,H)$ = 7.37 Hz, 3H; $NCH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (50.32 MHz, [D$_6$]acetone, 300 K): $\delta = 165.4$ (Py-C2), 164.9 (q ^1J(C,B) = 49.6 Hz; BAr-C1), 149.4 (Py-C6), 138.5 (Py-C4), 137.0 (BAr-C2), 126.1 (BAr-C3), 125.3 (Py-C3), 123.1 (Py-C5), 122.3 (BAr-C4), 66.6 (NCH_2Py), 62.8 ($NCH_2CH_2CH_2CH_3$), 56.7 (br, CH_2=CH_2), 31.3 ($NCH_2CH_2CH_2CH_3$), 21.2 ($NCH_2CH_2CH_2CH_3$), 13.9 ($NCH_2CH_2CH_2CH_3$); FAB$^+$-MS (*m*/*z*): 386 $[M]^+$, 356 $[M - C_2H_4 - 2H]^+$, 329 $[M - Bu]^+$, 300 $[M - C_2H_4 - Bu - H]^+$; elemental analysis (%) calcd for $C_{42}H_{45}N_3BRh$: C 71.50, H 6.43, N 5.96; found: C 71.40, H 6.13, N 6.05.

(η^2-Ethene)-(κ^3-*N*-benzyl-*N*,*N*-di(2-pyridylmethyl)amine)rhodium(I) tetraphenylborate ([2c]BPh$_4$): [**2c**]BPh$_4$ was prepared by a procedure similar to those of [**2a**]BPh$_4$ and [**2b**]BPh$_4$, using the ligand Bzbpa. The yield was 0.60 g (78%). ^{1}H NMR (200.13 MHz, [D$_6$]acetone, 298 K): $\delta = 8.03$ (m, ^3J(H,H) = 7.6 Hz, 2H; Ph-H2), 7.79 (ddd, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.5 Hz, 2H; Py-H4), 7.51 (dddd, ^3J(H,H) = 5.7 Hz, ^4J(H,H) = 1.5 Hz, J = 1.5 Hz, J = 0.7 Hz, 2H; Py-H6), 7.30–7.00 (m, 5H; Py-H3, Ph-H3, and Ph-H4), 7.36 (m, 8H; BAr-H2), 7.22 (m, 2H; Py-H5), 6.95 (t, ^3J(H,H) = 7.4 Hz, 8H; BAr-H3), 6.78 (t, ^3J(H,H) = 7.4 Hz, 4H; BAr-H4), 5.08 (d[AB], ^2J(H,H) = 15.8 Hz, 2H; NCH_2Py), 4.64 (dd[AB], ^2J(H,H) = 15.8 Hz, ^3J(Rh,H) = 1.2 Hz, 2H; NCH_2Py), 4.32 (s, 2H; NCH_2Ph), 3.39 (s, br, 4H; CH_2=CH_2); $^{13}C\{^1H\}$ NMR (75.47 MHz, [D$_6$]acetone, 298 K): $\delta = 156.2$ (Py-C2), 155.9 (q, ^1J(B,C) = 49.5 Hz; BAr-C1), 140.1 (Py-C6), 129.1 (Py-C4), 128.0 (BAr-C2), 124.8 (Ph-C1), 124.6 (Ph-C2), 120.5 (Ph-C3), 119.75 (Ph-C4), 117.1 (BAr-C3), 115.9 (Py-C3), 114.2 (Py-C5), 113.2 (BAr-C4), 57.6 (NCH_2Py), 57.3 (NCH_2Ph), The CH_2=CH_2 signal is too broad to be observed; FAB$^+$-MS (*m*/*z*): 420 $[M]^+$, 391 $[M - C_2H_4 - H]^+$, 300 $[M - C_2H_4 - Bz - H]^+$; elemental analysis (%) calcd for $C_{45}H_{43}N_3BRh$: C 73.08, H 5.86, N 5.68; found: C 73.40, H 5.98, N 5.81.

(κ^2-O,C-2-Oxyethyl)(κ^3-*N*-methyl-*N*,*N*-di(2-pyridylmethyl)amine)rhodium(III) tetraphenylborate ([3a]BPh$_4$): [**2a**]BPh$_4$ (0.24 g) was dissolved in a mixture of aqueous H_2O_2 (0.1 mL 35%) and acetonitrile (5 mL). The solution was stirred for 1 h. Subsequently diethyl ether (50 mL) was added. A pale yellow powder precipitated, which was filtered and dried under vacuum pressure, yielding 0.15 g (61%); ^{1}H NMR (200.13 MHz, CD_2Cl_2, 300 K): $\delta = 8.71$ (d, ^3J(H,H) = 5.3 Hz, 2H; Py-H6), 7.88 (ddd, ^3J(H,H) = 7.7 Hz, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.5 Hz, 2H; Py-H4), 7.6–7.3 (m, 4H; Py-H3 and Py-H5), 7.32 (m, 8H; BAr-H2), 6.99 (t, ^3J(H,H) = 7.4 Hz, 8H; BAr-H3), 6.84 (t , ^3J(H,H) = 7.4 Hz, 4H; BAr-H4), 4.76 (m, 4H; $RhCH_2CH_2O$ and NCH_2Py), 4.13 (d[AB], ^2J(H,H) = 15.0 Hz, 2H; NCH_2Py), 2.65 (s, 3H; NCH_3), 2.21 (dt, ^3J(H,H) = 7.5 Hz, ^2J(Rh,H) = 2.4 Hz, 2H; $RhCH_2CH_2O$), 1.73 (s, $NCCH_3$); $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2+drop CD_3CN, 300 K): $\delta = 165.2$ (Py-C2), 164.6 (q, ^1J(B,C) = 49.0 Hz; BAr-C1), 152.6 (Py-C6), 139.65 (Py-C4), 136.6 (BAr-C2), 126.4 (BAr-C3), 126.2 (Py-C3), 124.7 (Py-C5), 122.8 (BAr-C4), 80.5 (d, ^3J(Rh,H) = 3.7 Hz; $RhCH_2CH_2O$), 65.82 (s, 2C; NCH_2Py), 46.2 (s, 1C; NCH_3), 3.60 ($RhNCCH_3$), −1.38 (d, ^2J(Rh,H) = 16.5 Hz, $RhCH_2CH_2O$), the Rh-NCCH_3 signal was not observed; FAB$^+$-MS (*m*/*z*): 401 $[M]^+$, 374 $[M–CH_3CN]^+$, 316 $[M - CH_3CN - C_2H_4O]^+$; elemental analysis (%) calcd for $C_{41}H_{42}N_4OBRh$: C 68.35, H 5.88, N 7.78; found: C 68.20 H 5.76 N 7.76.

(κ^2-O,C-2-Oxyethyl)(κ^3-*N*-butyl-*N*,*N*-di(2-pyridylmethyl)amine)rhodium(III) tetraphenylborate ([3b]BPh$_4$): [**3b**]BPh$_4$ was prepared by a procedure similar to that for [**3a**]BPh$_4$, using [**2b**]BPh$_4$. ^{1}H NMR (200.13 MHz, CD_2Cl_2, 300 K): $\delta = 8.66$ (d, ^3J(H,H) = 5.3 Hz, 2H; Py-H6), 7.84 (ddd, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.6 Hz, 2H; Py-H4), 7.5–7.3 (m, 4H; Py-H3 and Py-H5), 7.33 (m, 8H; BAr-H2), 7.00 (t, ^3J(H,H) = 7.4 Hz, 8H; BAr-H3), 6.85 (t, ^3J(H,H) = 7.4 Hz, 4H; BAr-H4), 4.65 (m, 4H; NCH_2Py and $RhCH_2CH_2O$), 4.29 (d{AB], ^2J(H,H) = 15.0 Hz, 2H; NCH_2Py), 2.84 (m, 2H; $NCH_2CH_2CH_2CH_3$), 2.22 (dt, ^3J(H,H) = 7.5 Hz, ^2J(Rh,H) = 2.3 Hz, 2H; $RhCH_2CH_2O$), 1.70 (m, 2H; $NCH_2CH_2CH_2CH_3$), 1.63 (s, 3H; $RhNCCH_3$), 1.44 (m, 2H; $NCH_2CH_2CH_2CH_3$), 0.83 (t, ^3J(H,H) = 7.2 Hz, 3H; $NCH_2CH_2CH_2CH_3$).

(κ^2-O,C-2-Oxyethyl)(κ^3-*N*-benzyl-*N*,*N*-di(2-pyridylmethyl)amine)rhodium(III) tetraphenylborate ([3c]BPh$_4$): [**3c**]BPh$_4$ was prepared by a procedure similar to that for [**3a**]BPh$_4$, using [**2c**]BPh$_4$. The only difference is that the reaction was performed at a temperature of $-20\,^\circ$C. The yield was 35%. ^{1}H NMR (200.13 MHz, CD_2Cl_2, 298 K): $\delta = 8.74$ (d, ^3J(H,H) = 5.6 Hz, 2H; Py-H6), 7.92 (ddd, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.4 Hz, 2H; Py-H4), 7.6–7.4 (m, 4H; Py-H5 and Py-H3), 7.0–7.5 (m, 5H; Ph), 7.29 (m, 8H; BAr-H2), 6.96 (t, ^3J(H,H) = 7.4 Hz, 8H; BAr-H3), 6.82 (t, ^3J(H,H) = 7.4 Hz, 4H; BAr-H4), 4.74 (t, ^3J(H,H) = 7.5 Hz, 2H; $RhCH_2CH_2O$), 4.45 (d[AB], ^2J(H,H) = 16.6 Hz, 2H; NCH_2Py), 4.39 (d[AB], ^2J(H,H) = 16.6 Hz, 2H; NCH_2Py), 3.86 (s, 2H; NCH_2Bz), 2.29 (dt, ^3J(H,H) = 7.5 Hz, ^2J(Rh,H) = 2.5 Hz, 2H; $RhCH_2CH_2O$), 1.65 (s, 3H; CH_3CN); FAB$^+$-MS (*m*/*z*): 477 $[M]^+$, 391 $[M - C_2H_4O - CH_3CN - H]^+$.

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