Aqueous rhodium(III) hydrides and mononuclear rhodium(II) complexes

Andreja Bakac*

In aqueous solutions, as in organic solvents, rhodium hydrides display the chemistry of one of the three limiting forms, *i.e.* {$Rh^I + H^+$}, {$Rh^{II} + H^•$}, and {$Rh^{III} + H^-$}. A number of intermediates and oxidation states have been generated and explored in kinetic and mechanistic studies. Monomeric macrocyclic rhodium(II) complexes, such as $L(H_2O)Rh^{2+}$ (L = L^1 = [14]aneN$_4$, or L^2 = *meso*-Me$_6$[14]aneN$_4$) can be generated from the hydride precursors by photochemical means or in reactions with hydrogen atom abstracting agents. These rhodium(II) complexes are oxidized rapidly with alkyl hydroperoxides to give alkylrhodium(III) complexes. Reactions of Rh(II) with organic and inorganic radicals and with molecular oxygen are fast and produce long-lived intermediates, such as alkyl, superoxo and hydroperoxo complexes, all of which display rich and complex chemistry of their own. In alkaline solutions of rhodium hydrides, the existence of Rh(I) complexes is implied by rapid hydrogen exchange between the hydride and solvent water. The acidity of the hydrides is too low, however, to allow the build-up of observable quantities of Rh(I). Deuterium kinetic isotope effects for hydride transfer to a macrocyclic Cr(V) complex are comparable to those for hydrogen atom transfer to various substrates.

1 Introduction

Rhodium hydrides are key species in a large number of industrial processes and laboratory reactions that rely on rhodium and its compounds as catalysts. The most prominent examples of such reactions include the hydrogenation of organic substrates and of carbon dioxide, hydroformylation of olefins, hydrodesulfurization, carbonylation of methanol, and several industrially important asymmetric catalytic hydrogenation and hydroformylation reactions.[1-4] Most of the investigations and commercial applications are carried out in organic solvents, but aqueous and semiaqueous media have been steadily gaining importance.[1,3,5-8]

Ames Laboratory, Iowa State University, Ames, IA, 50011, USA

Andreja Bakac is a Senior Chemist at the Ames Laboratory and Adjunct Professor of Chemistry at Iowa State University. Her interests are in the kinetics and mechanisms of thermal and photochemical reactions of transition metal complexes, especially in the area of oxygen activation and catalysis.
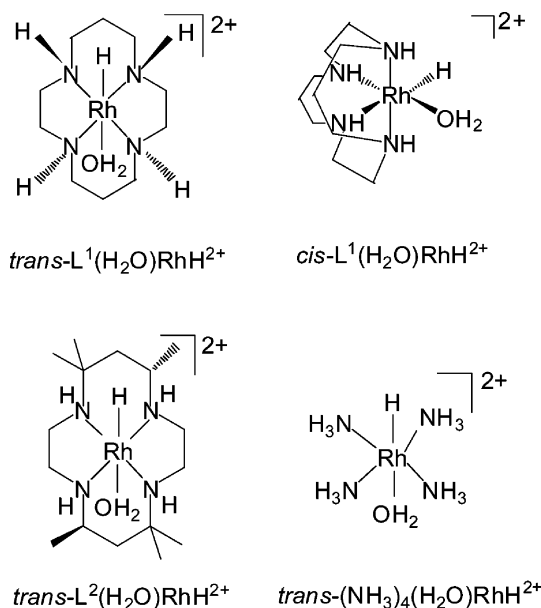

Andreja Bakac

The Ruhrchemie–Rhone–Poulenc process for the hydroformylation of propene, for example, utilizes a water-soluble rhodium hydride catalyst in an aqueous/organic biphasic medium.[3] This shift toward aqueous chemistry is driven in part by the need to reduce the use of organic solvents as a cost-cutting measure and to protect the workforce and the environment from the harmful effects of such solvents. From the practical point of view, the use of aqueous biphasic media in organic synthesis is ideal because it places the products and catalysts into separate, immiscible phases.[9] Equally important are the beneficial effects of water on some reactions,[10] notably those that involve metal hydrides as intermediates, or that have polar and/or ionic transition states. A strong case for aqueous media was presented in a recent study which demonstrated that the reactions of water-soluble $(TSPP)RhD^{4-}$ with substrates (CO, aldehydes, olefins) in D_2O are significantly faster than the reactions of the corresponding non-sulfonated rhodium hydride, (TPP)RhH, in benzene despite the comparable thermodynamics in the two solvents.[11-13]

This article focuses on the kinetic and mechanistic issues of aqueous chemistry of rhodium hydrides. In their reactions with substrates, these species often generate intermediates, such as monomeric rhodium(II) and rhodium(IV) complexes. The chemistry of several such species also will be discussed. Our recent work in this area utilized several cationic ammine and macrocyclic rhodium hydrides shown in Chart 1. All the kinetic data are given at 25 °C.

2 Rh–H bond

With very few exceptions, the Rh(III)–H bond length falls in the range 1.5 ± 0.1 Å. Some representative data are shown in Table 1. Older work has been summarized earlier.[14] The complex $(NH_3)_5RhH(ClO_4)_2$ seems to be an exception, having a Rh–H bond distance of 1.82 ± 0.17 Å.[15] Even after the rather large standard deviation is taken into account, the value still falls outside the

trans-L^1(H$_2$O)RhH^{2+} *cis*-L^1(H$_2$O)RhH^{2+}

trans-L^2(H$_2$O)RhH^{2+} *trans*-(NH$_3$)$_4$(H$_2$O)RhH^{2+}

Chart 1

range defined by the remainder of the complexes in Table 1. The Rh–H stretching vibration, $v_{\text{Rh–H}}$, for (NH$_3$)$_5$RhH(ClO$_4$)$_2$ (2126 cm^{-1})[16] on the other hand, is comparable to $v_{\text{Rh–H}}$ for a number of other rhodium hydrides.[17,18]

The typical Rh(III)–H bond dissociation energy of approximately 60 kcal mol^{-1} makes these complexes reasonably stable, in both the kinetic and thermodynamic sense, in the absence of external substrates. The formation of the hydrides from Rh(II) and molecular hydrogen is close to thermoneutral or moderately downhill, depending on the energy of the Rh–Rh bond when the starting Rh(II) is dimeric. This is shown for the porphyrin complexes in eqn (1), which forms the basis for one of the preparative methods for rhodium hydrides. In eqn (1), Por stands for any of a number of porphyrins that have been utilized in

Table 2 Bond dissociation energies of Rh–H and Rh–Rh bonds[a]

| Complex	BDE (Rh–H)	BDE[b] (Rh–Rh)	Ref.
H$_2$RhCl[P(4-tolyl)$_3$)]$_3$	58[c]	[d]	32
(TMP)RhH	60	∼0	33,34
(OEP)RhH	62	15.5	34
(TXP)RhH	60	12	34
(TPP)RhH	53[e,f]	[d]	12
(TPP)RhD	54[e,f]	[d]	12
(TSPP)(D$_2$O)Rh–H	59[e,g]	12	12
(TSPP)(D$_2$O)Rh–D	60[e,g]	[d]	12

[a] BDE in kcal mol^{-1}. [b] BDE for the Rh–Rh bond in Rh(II) dimer. [c] Mean BDE. [d] Not determined. [e] BDFE (change in free energy for dissociation of Rh–D or Rh–H bond). [f] In C$_6$D$_6$. [g] In D$_2$O.

rhodium chemistry, and BDEs are given in kcal mol^{-1}. Some of the typical Rh–H and Rh–Rh BDEs are listed in Table 2.

$$\text{H-H} + (\text{Por})\text{Rh-Rh}(\text{Por}) \rightleftharpoons 2\ (\text{Por})\text{Rh-H}$$
BDE: 104   ≤16   ∼60
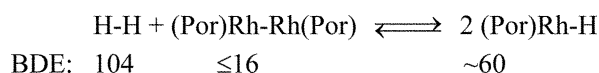
$$\Delta H^0 \leq 0\ \text{kcal/mol} \quad (1)$$

Similarly, heterolytic splitting of H$_2$ by Rh(III) also leads to rhodium hydrides.[2]

$$\text{H}_2 + \text{Rh(III)} \rightarrow \text{Rh}^{\text{III}}(\text{H}^-) + \text{H}^+ \quad (2)$$
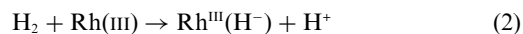
Hydride exhibits a strong *trans*-labilizing effect, as shown by the long *trans*-ligand–metal bonds and large substitution rates for the *trans*-ligands.[27] The replacement of H$_2$O in *trans*-L^1(H$_2$O)RhH^{2+} by SCN$^-$, for example, is complete upon mixing. The binding of SCN$^-$ in the resulting complex is strong, $K = 1.49 \times 10^3$ M^{-1}, so that there is no exchange between SCN$^-$ and solvent water on the NMR time scale at SCN$^-$ concentrations of 10–20 mM. The case for *trans*-effect in this particular reaction is weakened somewhat by the observation that a similarly rapid reaction takes place between SCN$^-$ and the *cis* analog. Apparently, steric crowding in *cis*-L^1(H$_2$O)RhH^{2+} strongly labilizes the position *cis* to the

Table 1 Terminal rhodium–hydrogen bond lengths as determined by X-ray crystallography

Complex	Rh–H Distance[a]/Å	Ref.
[(NP$_3$)Rh(H)(CCH)]BPh$_4$·1.5C$_4$H$_8$O [b]	1.4(1)	19
[Rh(Tp*)(H)(SnPh$_3$)(PPh$_3$)](CH$_2$Cl)	1.42(2)	20
Rh(H)$_2$(O$_2$COH)(P(*i*-Pr)$_3$)$_2$	1.44(4)	21
cis,*trans*,*trans*-[Rh(H)$_2$(PPh$_3$)$_2$(pdz)$_2$]ClO$_4$·2CH$_2$Cl$_2$	1.44(4)	22
cis,*trans*,*cis*-[Rh(H)$_2$(PPh$_3$)$_2$(NH$_2$CH$_2$Ph)$_2$]PF$_6$	1.47(3)	23
trans,*trans*-[Rh(H)Cl(PPh$_3$)$_2$(im)$_2$]ClO$_4$·CH$_2$Cl$_2$	1.47(6)	22
trans-[Rh(Cl)(H)(BPin)(P(*i*-Pr$_3$)$_2$]	1.47(2)	24
Rh(Tp*)(H)(COC$_6$H$_4$NO$_2$)(PPh$_3$)	1.49(2)	20
(triphos)RhH(η^2-C$_{60}$)	1.5(2)	25
cis,*trans*,*trans*-[Rh(H)$_2$(PPh$_3$)$_2$(im)$_2$]ClO$_4$·2CH$_2$Cl$_2$	1.50(4)	22
cis-Rh(PMe$_3$)$_4$(H)(CCCH$_2$CH$_2$OH)]Cl	1.506(28)	26
cis-[L^{1}ClRhH](ClO$_4$)	1.52(4)	27
RhH$_3$(triphos-I)	1.52(5)	28
[(dippe)Rh(H)]$_2$(μ-η^2-H–SiMe$_2$)$_2$	1.52(4)	29
[Rh(H)(PPh$_3$)$_2$(C$_6$H$_4$(CH$_3$)C=N–N(H)C(O)NH$_2$]PF$_6$	1.52(4)	30
[{Rh(dipp)H}$_2$(μ-H)$_2$(μ-ClO$_4$)]ClO$_4$	1.57(9)	31
cis,*trans*-[Rh(H)$_2$(PPh$_3$)$_2$(tbz)]ClO$_4$	1.58(8)	22
[(NH$_3$)$_5$RhH](ClO$_4$)$_2$	1.82(17)	15

[a] In molecules with two or more equivalent hydrides, the mean value is quoted. Numbers in parentheses represent one standard deviation of the last significant figure. [b] NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$.

hydride. The halide ions (Cl⁻, Br⁻ and I⁻) exchange with H_2O in *trans*-$L^1(H_2O)RhH^{2+}$ in an equilibrium process that causes NMR line broadening at room temperature. The process is slowed down considerably at 2 °C, as shown by sharp NMR signals, Fig. 1.
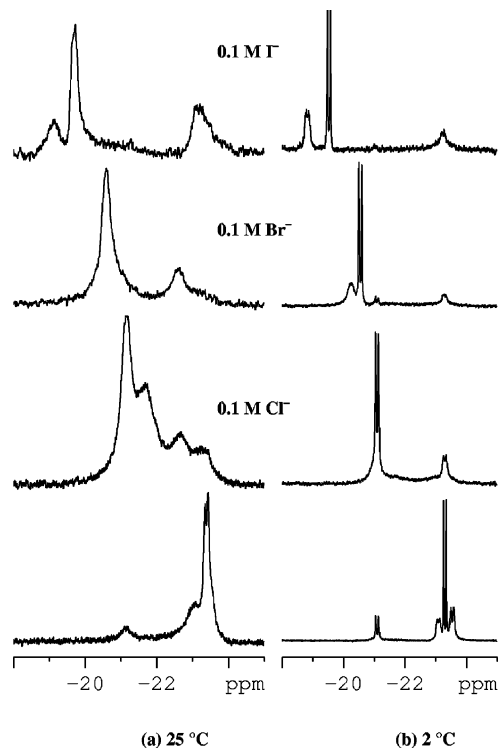

Fig. 1 ¹H NMR spectra of the products of the reaction of *trans*-$L^1(D_2O)RhH^{2+}$ (12–20 mM) with 0.1 M X⁻ (X = Cl, Br or I) in air-free D_2O at 25 °C (left panel) and 2 °C (right panel). Solutions of *trans*-$L^1(D_2O)RhH^{2+}$ in the bottom spectra contained small amounts of *trans*-L^1ClRhH^+ which appears at −21.1 ppm. Reproduced with permission from ref. 27. © 2003, American Chemical Society.

3 Hydrogen atom abstraction from rhodium hydrides

In general, all the methods for the formation of rhodium–hydrogen bonds, and all the reactions of the rhodium–hydrogen bonds, can be classified as involving rhodium in the oxidation states I, II or III, and hydrogen in the form of hydrogen ion, hydrogen atom, or hydride anion,[35,36] eqn (3).

$$(Rh^I + H^+) \text{ or } (Rh^{II} + H^\bullet) \text{ or } (Rh^{III} + H^-) \rightleftharpoons Rh^{III}H \quad (3)$$
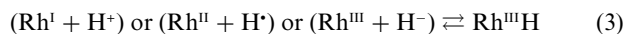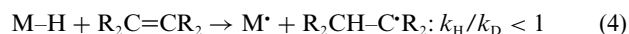
Probably the most explored reaction of metal hydrides is hydrogen atom abstraction by both radical and non-radical species. Most of this chemistry, with some exceptions,[37] was carried out in nonaqueous media. The older work has been summarized in several reviews.[36,38–40] Briefly, the kinetics of the reactions of metal hydrides with carbon-centered radicals were measured either directly or by use of radical clocks.[36,38,39,41–46] Steric effects were found to be dominant, so that the rates decrease dramatically with increased crowding at the metal–hydrogen site.[36] Also, these reactions exhibit normal kinetic isotope effects, $k_H/k_D > 1$.[36,38,39] Hydrogen transfer from metal hydrides to olefins, on the other hand, responds mainly to the energy of the M–H bond and often exhibits an inverse kinetic isotope effect, $k_H/k_D < 1$.[36,38,39,47]

Table 3 Kinetics of hydrogen atom abstraction from rhodium hydrides by radicals in aqueous solution

RhH[a]	Radical	k/M^{-1} s^{-1}	Ref.
$(NH_3)_4(H_2O)RhH^{2+}$	$HO_2^\bullet$	$\leq 4 \times 10^7$	48
$(NH_3)_4(H_2O)RhH^{2+}$	$Cr_{aq}OO^{2+}$	1.35×10^2	49
$L^1(H_2O)RhH^{2+}$	$H^\bullet$	$>3 \times 10^8$	18
$L^1(H_2O)RhH^{2+}$	$CH_3^\bullet$	1.0×10^9	50
$L^1(H_2O)RhH^{2+}$	$Cr_{aq}OO^{2+}$	1.29×10^2	49
$L^1(H_2O)RhD^{2+}$	$Cr_{aq}OO^{2+}$	1.7×10^1	49
$L^2(H_2O)RhH^{2+}$	$CH_3^\bullet$	1.4×10^8	49
$L^2(H_2O)RhH^{2+}$	$Cr_{aq}OO^{2+}$	2.4×10^1	49

[a] All *trans* isomers.

Both reactions take part in free-radical hydrogenation of alkenes, eqn. (4) and (5).

$$M-H + R_2C=CR_2 \rightarrow M^\bullet + R_2CH-C^\bullet R_2: k_H/k_D < 1 \quad (4)$$

$$M-H + R_2CH-C^\bullet R_2 \rightarrow M^\bullet + R_2CH-CHR_2: k_H/k_D > 1 \quad (5)$$

As expected, hydrogen abstraction by methyl radicals from the tetraamine complexes in aqueous solution according to eqn (6) is extremely rapid, Table 3, and sensitive to steric effects. The bulkier *trans*-L^2 complex reacts close to an order of magnitude more slowly than the L^1 analog.

$$CH_3^\bullet + L(H_2O)RhH^{2+}$$
$$\rightarrow CH_4 + L(H_2O)Rh^{2+} (L = L^1, L^2, (NH_3)_4) \quad (6)$$
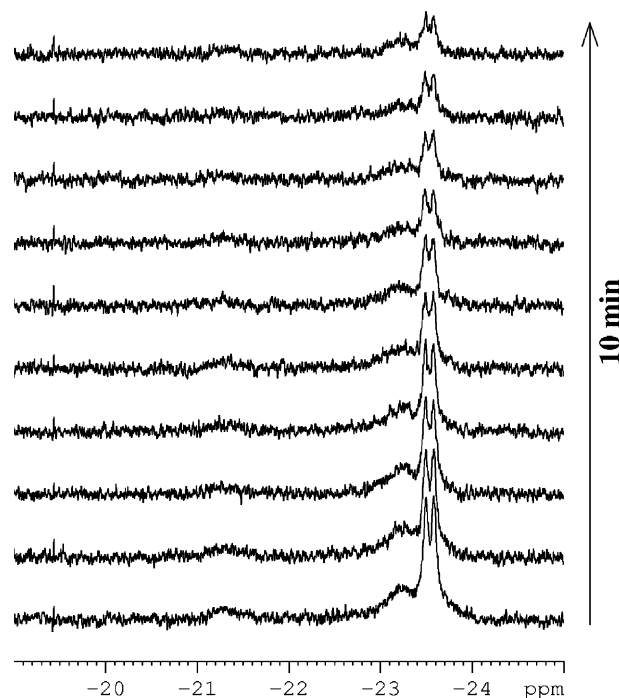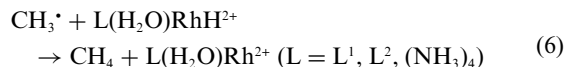
Fig. 2 Disappearance of the hydride peak in *trans*-$L^1(D_2O)RhH^{2+}$ as a result of H/D exchange in D_2O at pD 8.96 and 25 °C. Spectra collected over the first 10 min of reaction are displayed. Reproduced with permission from ref. 27. © 2003, American Chemical Society.

For the very fast reaction with hydrogen atoms, only a lower limit of $>3 \times 10^8$ M^{-1} s^{-1} could be established. This reaction is responsible for the formation of the second mole of

L(H$_2$O)Rh^{2+} in the process of photochemical cleavage of the hydride, eqn (7) and (8).

$$L(H_2O)RhH^{2+} \xrightarrow{h\nu} L(H_2O)Rh^{2+} + H^{\bullet} \qquad (7)$$

$$H^{\bullet} + L(H_2O)RhH^{2+} \rightarrow H_2 + L(H_2O)Rh^{2+} \qquad (8)$$

$$Net: 2\,L(H_2O)RhH^{2+} \xrightarrow{h\nu} H_2 + 2\,L(H_2O)Rh^{2+}$$
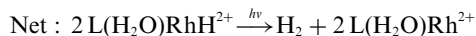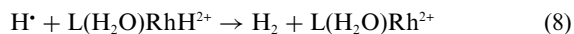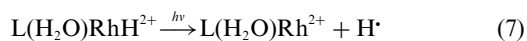
Similarly, the reaction with HO$_2$$^{\bullet}$ is involved in the photochemical process in the presence of O$_2$, reaction (7) followed by eqn (9)–(11). The upper limit for the rate constant for the HO$_2$$^{\bullet}$/(NH$_3$)$_4$(H$_2$O)RhH^{2+} reaction was estimated as $k \leq 4 \times 10^7$ M^{-1} s^{-1}.[48]

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \qquad (9)$$

$$HO_2^{\bullet} + L(H_2O)RhH^{2+} \rightarrow H_2O_2 + L(H_2O)Rh^{2+} \qquad (10)$$

$$L(H_2O)Rh^{2+} + O_2 \rightleftarrows L(H_2O)RhOO^{2+} \qquad (11)$$

$$Net: 2\,L(H_2O)RhH^{2+} + 3\,O_2 \xrightarrow{h\nu} H_2O_2 + 2\,L(H_2O)RhOO^{2+}$$
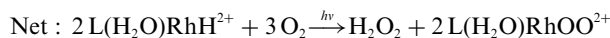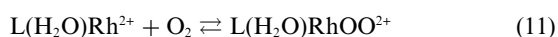
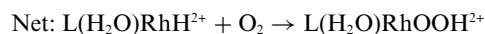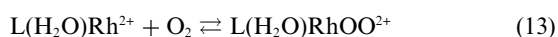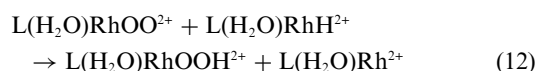Hydrogen atom abstraction from rhodium hydrides by small radicals resulting in strong element–hydrogen bonds,[51] such as CH$_3$–H (BDE = 105 kcal mol^{-1}) H–H (104) and H–O$_2$H (87.8), should not come as a surprise, given that both thermodynamic and steric factors are favorable.

More intriguing was the observation that even superoxometal complexes, including those of rhodium, engaged in H-atom abstraction from rhodium hydrides. These reactions take place as shown in eqn (12) and exhibit large kinetic isotope effects, Table 4. When central metals and the remaining ligands in the hydrido and superoxo complexes are identical, the reaction is catalytic in the presence of molecular oxygen. The chemistry shown in eqn (12) and (13) forms the basis of a convenient method for the generation of the hydroperoxo complexes of rhodium(III).

$$L(H_2O)RhOO^{2+} + L(H_2O)RhH^{2+}$$
$$\rightarrow L(H_2O)RhOOH^{2+} + L(H_2O)Rh^{2+} \qquad (12)$$

$$L(H_2O)Rh^{2+} + O_2 \rightleftarrows L(H_2O)RhOO^{2+} \qquad (13)$$

Net: L(H$_2$O)RhH^{2+} + O$_2$ → L(H$_2$O)RhOOH^{2+}

The reaction becomes stoichiometric when the metals, or ligands bound to the hydrido and superoxo complexes, are different, as shown in eqn (14). Clearly, a mixture of pathways begins to operate later in the reaction as the products build up.

$$L^1(H_2O)RhH^{2+} + L^2(H_2O)RhOO^{2+}$$
$$\xrightarrow{O_2} L^1(H_2O)RhOO^{2+} + L^2(H_2O)RhOO^{2+} \qquad (14)$$
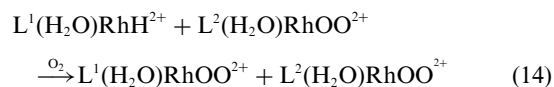
The kinetics of hydrogen atom abstraction by superoxometal complexes exhibit a pronounced sensitivity to steric effects, as shown by a decrease in the rate constant as monodentate ligands are replaced by saturated macrocycles, Table 4. The effect, however, becomes severe only when both reactants carry macrocyclic ligands.

Absolute values of the rate constants for the reactions with superoxometal complexes are much smaller than those for the radicals in Table 3. The difference originates mostly in the smaller driving force for the reaction with the superoxo complexes, although a direct comparison is possible only for one set of reagents, HO$_2$$^{\bullet}$ and Cr$_{aq}$OO^{2+}. On the basis of the 11 kcal mol^{-1} difference in O–H bond dissociation energies for the products HO$_2$–H (90 kcal mol^{-1}) and Cr$_{aq}$OO–H^{2+} (79 kcal mol^{-1}),[49] one would expect the rate constant for the HO$_2$$^{\bullet}$ reaction to be about 10^4 times greater than that for the Cr$_{aq}$OO^{2+} reaction. The observed factor is $\leq 3 \times 10^5$. The remaining difference probably can be attributed to steric effects.

Even the non-radical aquachromyl(IV) ion, Cr$_{aq}$O^{2+}, reacts by hydrogen atom abstraction. These reactions, summarized in Table 5, also exhibit a substantial normal KIE.

4 Proton dissociation from rhodium hydrides

Even though acid dissociation constants have been determined for a number of metal hydrides, such data are available for only a handful of rhodium complexes. As expected, the values vary widely with the ligand environment, Table 6. Specifically, the acidity is reduced by hard ligands;[54] there is no spectroscopic evidence for the deprotonation of L^1(H$_2$O)RhH^{2+} and related N$_4$-complexes even in alkaline solutions (pH $\leq$ 12).[27]

Table 5 Kinetics data (10^3 M^{-1} s^{-1}) for hydrogen atom abstraction from rhodium hydrides by Cr$_{aq}$O^{2+} ion[a]

Rh hydride	$10^{-3}k$/M^{-1} s^{-1}	KIE
trans-L^1(H$_2$O)RhH^{2+}	~10	
trans-L^1(H$_2$O)RhD^{2+}	2.7	~3
trans-L^2(H$_2$O)RhH^{2+}	1.12	
trans-L^2(H$_2$O)RhD^{2+}	0.34	3.3

[a] Data from ref. 49.

Table 4 Rate constants for hydrogen atom transfer from rhodium hydrides to superoxometal complexes[a]

| Complex	Cr$_{aq}$OO^{2+}	(NH$_3$)$_4$(H$_2$O)RhOO^{2+}	L^1(H$_2$O)RhOO^{2+}	L^1(H$_2$O)CrOO^{2+}
(NH$_3$)$_4$(H$_2$O)RhH^{2+}	135	32.7, 93.8[b]	27.6[b]	3
trans-L^1(H$_2$O)RhH$^{2+\,c}$	129[c]	22.8	0.4[d]	<1
cis-L^1(H$_2$O)RhH^{2+}	123	[e]	[e]	[e]
trans-L^2(H$_2$O)RhH^{2+}	24	[e]	[e]	[e]

[a] In O$_2$-saturated acidic aqueous solutions: L^1 = [14]aneN$_4$: L^2 = Me$_6$[14]aneN$_4$; data from ref. 52 and 53. [b] Argon atmosphere. [c] For deuterated complex, k = 17.0 M^{-1} s^{-1}. [d] For deuterated complex, k = 0.06 M^{-1} s^{-1}. [e] Not determined.

Table 6 Acidity constants of rhodium hydrides

Rh hydride	pK_a	Solvent	Ref.
$HRh(dppe)(CH_3OH)_2$	1.0	CH_3OH	35
$HRh(CO)Cl(PPh_3)_2^+$	1.8	CH_3OH	35
$Rh(CNR)_4(H_2O)H$	<0	H_2O	54
$(TSPP)(D_2O)RhD^{2+}$	7.1	D_2O	13
$HRh(dmgH)_2(PPh_3)$	9.5	H_2O	35
$Rh(bpy)_2(H_2O)H^{2+}$	9.5	H_2O	54
$Rh(NH_3)_4(H_2O)H^{2+}$	>14	H_2O	54

Table 7 Rate constants for hydride transfer from rhodium hydrides to $(salen)CrO^+$ in acidic aqueous solutions[a]

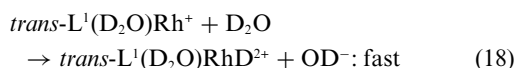| Rh hydride	$10^{-3}k/M^{-1}\ s^{-1}$	KIE
$trans\text{-}L^1(H_2O)RhH^{2+}$	8.8	
$trans\text{-}L^1(H_2O)RhD^{2+}$	1.6	5.4
$trans\text{-}(NH_3)_4(H_2O)RhH^{2+}$	2.5	
$trans\text{-}L^2(H_2O)RhH^{2+}$	1.0	
$trans\text{-}L^2(H_2O)RhD^{2+}$	0.16	6.2

[a] Data from ref. 49.

None the less, small amounts of Rh(I) present at pH > 8 provide a mechanism for hydride exchange between $trans\text{-}L^1(H_2O)RhH^{2+}$ and solvent water in an HO^--dependent process.[27] The exchange is much slower for the *cis*-isomer under comparable conditions.

The kinetics of the exchange were studied by observing the hydride NMR shift of $trans\text{-}L^1(D_2O)RhH^{2+}$ in D_2O.[27] Under the conditions in Fig. 2 (pD 9.0, D_2O), the intensity of the hydride resonance steadily decreases with time. Over the same period of time, the characteristic UV maximum of rhodium hydride at 287 nm remains unchanged. The NMR changes are thus clearly associated with the H/D exchange reaction of eqn (15). The reverse of reaction 15 was made negligible by use of D_2O as solvent, *i.e.* $[HDO]/[D_2O] \ll 0.01$.

$$trans\text{-}L^1(D_2O)RhH^{2+} + D_2O$$
$$\xrightarrow{OD^-} trans\text{-}L^1(D_2O)RhD^{2+} + HDO \quad (15)$$
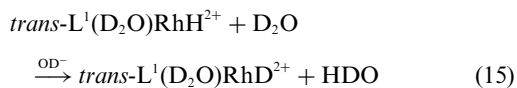
The kinetics followed a mixed second-order rate law, eqn (16), suggesting a bimolecular deprotonation of the Rh–H bond followed by the reaction of the newly formed Rh(I) with D_2O, eqn (17) and (18), as the most likely exchange mechanism.

$$-d[trans\text{-}L^1(D_2O)RhH^{2+}]/dt$$
$$= 1.45 \times 10^3 [trans\text{-}L^1(D_2O)RhH^{2+}][OD^-] \quad (16)$$

$$trans\text{-}L^1(D_2O)RhH^{2+} + OD^-$$
$$\rightarrow trans\text{-}L^1(D_2O)Rh^+ + HDO: 1.45 \times 10^3\ M^{-1}\ s^{-1} \quad (17)$$

$$trans\text{-}L^1(D_2O)Rh^+ + D_2O$$
$$\rightarrow trans\text{-}L^1(D_2O)RhD^{2+} + OD^-: fast \quad (18)$$

Other commonly accepted mechanisms for hydride exchange, such as transient formation of a H_2-complex or dihydride are ruled out by the rate law and by the stability of the complex in acidic solutions.[27]

The scheme in eqn (17) and (18) requires the rate constants k_{18} (and k_{-17}) to be much greater than the product $k_{16}[OH^-]$. From the data at the highest $[OD^-]$ studied (pD 9), one obtains a limit, $k_{18} \gg 10^{-3}\ s^{-1}$, in qualitative agreement with the available kinetic data for another rhodium hydride, $HRh(dmgH)_2PPh_3$, which is generated from H_2O and $Rh(dmgH)_2PPh_3^-$ with $k = 0.023\ s^{-1}$.[55]

5 Hydride transfer reactions

The most common and straightforward reaction in this category is the protonation of the hydride to generate Rh(III) and H_2. An example of such chemistry in aqueous methanol is provided by the reactions of $HRh(dmgH)_2PPh_3$ with H_2O ($k = 4 \times 10^{-5}\ s^{-1}$) and with H^+. In the latter case, the protonation takes place at one of the oxime oxygens (K_H) followed by intramolecular elimination of H_2 (k_H). The overall rate constant for the reaction with H^+ is $K_H k_H = 0.24\ M^{-1}\ s^{-1}$.[55] The complex $Rh^{III}(bpy)_2H^{2+}$ does not react with H_2O/H^+, but the one-electron reduced species reacts efficiently.[56,57]

As one would predict on the basis of thermodynamics, the reaction between the cationic rhodium hydrides $(N_4)(H_2O)RhH^{2+}$ ($N_4 = (NH_3)_4$, L^1, L^2) and $(salen)Cr^VO^+$ takes place by hydride transfer,[49] eqn (19).

$$(N_4)(H_2O)RhH^{2+} + (salen)Cr^VO^+$$
$$\xrightarrow{H^+, H_2O} (N_4)Rh(H_2O)_2^{3+} + (salen)Cr^{III}(H_2O)_2^+ \quad (19)$$
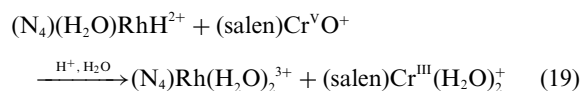
The reactions exhibit a significant deuterium KIE, Table 7, which rules out electron transfer. The failure to detect $(N_4)Rh(H_2O)^{2+}$ or the product of its reaction with O_2, $(N_4)(H_2O)RhOO^{2+}$, was taken as definitive evidence against hydrogen atom abstraction.

For reasons of both solubility and reactivity, hydride transfer to acceptors other than hydrogen ion is much more common in nonaqueous media, although rhodium hydrides received only scant attention under any conditions. The most commonly used hydride acceptors in kinetic studies, which include KIEs, are triphenylmethyl cation and substituted analogs.[58–60] In a particularly detailed study of a large number of metal hydrides, the rate constants covered a range of over seven orders of magnitude which provided a useful scale of kinetic hydricity.[58] More recently, the thermodynamic hydride donor abilities (ΔG_{H^-}) of metal hydrides in acetonitrile have been determined[60–63] directly by calorimetric and equilibrium methods. The value for the water-soluble $(TSPP)(D_2O)RhD^{4-}$ ($\Delta G_{H^-} \sim 54.9$ kcal mol^{-1})[13] places this hydride approximately in the middle of the current hydricity scale for metal hydrides.

6 Rhodium(II)

Hydrogen atom abstraction from rhodium hydrides generates rhodium(II), which dimerizes unless steric hindrance prevents the Rh–Rh bond formation. Indeed, the list of monomeric Rh(II) complexes is steadily growing.[18,64–72] Reactions with dimeric rhodium(II) are kinetically somewhat more complex because of the monomer–dimer equilibrium, but in most cases this presents no major problem in data collection or analysis.

What makes the study of rhodium(II) chemistry much more challenging, especially in aqueous solutions, is the lack of convenient preparative methods. Early transition metal complexes that are widely used in coordination chemistry can be easily prepared in the reduced state (*i.e.* Cr_{aq}^{2+}, V_{aq}^{2+}, Ti_{aq}^{3+}, $Ru(NH_3)_6^{2+}$, *etc*) in large concentrations by chemical or electrochemical reduction of a

higher oxidation state. In the rhodium case, however, this approach usually yields the hydride complex. In fact, zinc reduction of $(N_4)Rh(H_2O)_2^{3+}$ ($N_4 = (NH_3)_4$, L^1, L^2) is the best preparative route to rhodium hydrides.[16,18]

Instead, solutions of $(N_4)(H_2O)Rh^{2+}$ must be prepared in chemical reactions, such as hydrogen atom abstraction from the hydride. Thus, by necessity and design, solutions of Rh(II) are not pure; they contain various added reagents and their products. Another option is the photochemical cleavage of the Rh–H bond described above. In both cases, extraordinary precautions have to be taken to ensure that no hydride remains in solution. This is not an easy task, especially in the photochemical approach given that the product Rh(II) absorbs UV light more intensely than the hydride does.[50] Finally, the concentrations of Rh(II) that can be obtained by these methods are quite low, typically below millimolar. In view of these limitations, the number of kinetic and mechanistic studies with Rh(II) complexes in aqueous solutions is not overwhelming, but some reliable data have been obtained.

Often competing with the productive chemistry of transient Rh(II) species are dimerization and ligand substitution reactions. As expected for the dimerization of 17e radicals, and shown in Table 8, such Rh–Rh bond forming reactions are fast.

Table 8 Kinetics of dimerization of some Rh(II) complexes

Complex	k/M^{-1} s^{-1}	Conditions	Ref.
$Rh(NH_3)_4^{2+}$	1.4×10^7	H_2O, pH 1	73
$Rh(bpy)_2^{2+}$	1.7×10^8	H_2O, pH 8.9[a]	74
$Rh(dmgH)_2PPh_3$	2.1×10^8	CH_3CN	75
	2.3×10^8	EtOH–H_2O, 95 : 5 (v/v)	76
	3.8×10^8	EtOH or C_6H_6	77
$Rh(ttbs)$	6×10^9 [b]	Toluene	78

[a] Dominant species at this pH are $Rh(bpy)_2(H_2O)_2^{2+}$ ($pK_a = 8.6$) and $Rh(bpy)_2(H_2O)(OH)^+$ ($pK_a = 11.1$). [b] Reverse reaction has $k = 6.7 \times 10^5$ s^{-1}.

The dissociation of ammonia from the ammine complexes is slower for the rhodium than for the corresponding cobalt(II) complexes, Table 9. The reasonably long lifetime of the chemically or photochemically generated tetrammine rhodium complex (about 3 ms) makes bimolecular reactions of this species possible. This includes the reaction with molecular oxygen to generate the superoxo complex, $(NH_3)_4RhOO^{2+}$, even in the absence of free NH_3 to stabilize the Rh(II) ammine complex.[48,52] Large excess of NH_3 is required in reactions of $Co(NH_3)_n^{2+}$ ($n = 4$ or 5).

The monomeric macrocyclic complexes $LRh(H_2O)^{2+}$ ($L = L^1$, L^2) are reasonably stable in aqueous solutions at room temperature, and several of their reactions have been examined. In every case, the L^1 complex is more reactive, Table 10, possibly because steric hindrance is less severe than for the L^2 analogs.

The reaction between $L^1Rh(H_2O)^{2+}$ and *tert*-BuOOH generates methyl radicals,[50] which can be scavenged by excess Rh(II) to generate the methyl complex,[81] eqn (20)–(22). Because of the small available concentrations of $L^1Rh(H_2O)^{2+}$, see above, this method is of limited utility. Another potential approach to the preparation of alkylrhodium(III) complexes, *i.e.* alkene insertion into the Rh–H bond,[16,82] obviously is not useful for the preparation of the methyl complex.

$$L^1Rh(H_2O)^{2+} + (CH_3)_3COOH$$
$$\rightarrow L^1(H_2O)RhOH^{2+} + (CH_3)_3CO^{\bullet} \qquad (20)$$

$$(CH_3)_3CO^{\bullet} \rightarrow CH_3^{\bullet} + (CH_3)_2CO: \text{fast} \qquad (21)$$

$$CH_3^{\bullet} + L^1Rh(H_2O)^{2+} \rightarrow L^1(H_2O)RhCH_3^{2+} \qquad (22)$$

The rate constants for reactions 20 ($>4 \times 10^4$ M^{-1} s^{-1}) and 22 (1×10^9 M^{-1} s^{-1}) are large in their respective categories, showing that $LRh(H_2O)^{2+}$ complexes are good reductants in addition to being substitutionally labile. Also, the rhodium complexes are significantly more reactive than their cobalt analogs.

Table 9 Ligand substitution at mononuclear rhodium(II) centers[a]

Reaction	k/s^{-1} (M = Rh)	k/s^{-1} (M = Co)	Ref.
$M(NH_3)_4^{2+} \rightarrow M(NH_3)_3^{2+} + NH_3$	350	$>10^6$	73,79
$M(NH_3)_3^{2+} \rightarrow M(NH_3)_2^{2+} + NH_3$	40	6×10^4	73,79
$M(NH_3)_2^{2+} \rightarrow M(NH_3)^{2+} + NH_3$	[b]	9×10^3	79
$M(NH_3)^{2+} \rightarrow M^{2+} + NH_3$	[b]	1×10^3	79
$M(bpy)_3^{2+} \rightarrow M(bpy)_2^{2+} + bpy$	0.45 (pH 4.2)		56
	0.6 (pH 8.8)		74

[a] The remaining coordination sites in these (presumably) five- or six-coordinated complexes are occupied by molecules of H_2O. [b] Not determined.

Table 10 Kinetic data for the reactions of *trans*-macrocyclic rhodium and cobalt complexes in aqueous solutions[a]
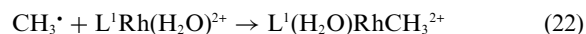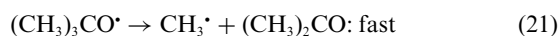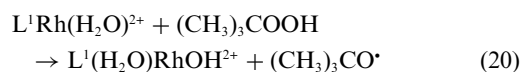
Reaction	k/M^{-1} s^{-1} (M = Rh)	k/M^{-1} s^{-1} (M = Co)	Ref.
$^{\bullet}CH_3 + L^1(H_2O)M^{2+}$	8.6×10^8	1.6×10^7	50,80
$^{\bullet}CH_3 + L^2(H_2O)M^{2+}$	[b]	4.2×10^7	50
$O_2 + (NH_3)_4(H_2O)M^{2+}$	3.1×10^8	[b]	73
$O_2 + L^1(H_2O)M^{2+}$	2.1×10^8	1.2×10^7	53
$O_2 + L^2(H_2O)M^{2+}$	8.2×10^7	5.0×10^6	53
$Fe_{aq}^{3+} + L^1(H_2O)M^{2+}$	9×10^4 [c]	4.10×10^3 [c]	50
$Fe_{aq}^{3+} + L^2(H_2O)M^{2+}$	1.6×10^4 [c]	2.74×10^2 [c]	50
tert-BuOOH + $L^1(H_2O)M^{2+}$	$>4 \times 10^4$	52.0	50
tert-BuOOH + $L^2(H_2O)M^{2+}$	4×10^3	11.4	50

[a] $L^1 = $ [14]aneN$_4$, $L^2 = $ *meso*-Me$_6$[14]aneN$_4$. [b] Not determined. [c] The rate constant is acid-dependent. The value quoted is at 0.10 M HClO$_4$.

Table 11 Relative rate constants for the reactions of $(NH_3)_4(H_2O)Rh^{IV}O^{2+}$

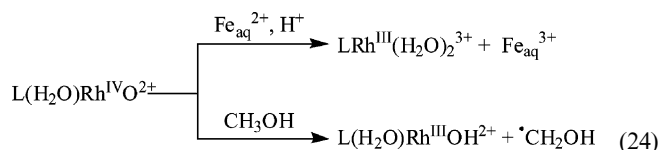| Substrate	$k_{Substrate}/k_{MeOH}$
CH_3OH	(1)
CD_3OH	0.2
C_2H_5OH	2.7
$2\text{-}C_3H_7OH$	3.4
$2\text{-}C_3D_7OH$	1
C_2H_5CHO	45
$(NH_3)_4(H_2O)RhH^{2+}$	125

Data from ref. 83.

7 Rhodium(IV)

Ammine and macrocyclic complexes of this unusual oxidation state were generated in Fenton-like reactions between the hydroperoxo complexes and Fe_{aq}^{2+}, eqn (23).[83] The rate constants for reaction 23 (30 M^{-1} s^{-1} for L = $(NH_3)_4$, 31 M^{-1} s^{-1} for L = L^2) are comparable to those for other metal hydroperoxides and for H_2O_2 itself.[53,84] The rhodium(IV) intermediate is short-lived, and its chemical composition or structure have not been determined. The notation used, $L(H_2O)RhO^{2+}$, is adopted from our chromium and iron chemistry.[85–87]

$$L(H_2O)RhOOH^{2+} + Fe_{aq}^{2+} \rightarrow L(H_2O)RhO^{2+} + Fe_{aq}OH^{2+} \quad (23)$$
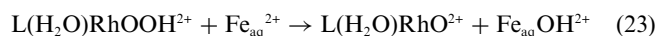
$L(H_2O)RhO^{2+}$ rapidly oxidizes alcohols, aldehydes, and rhodium hydrides in competition with the oxidation of the second equivalent of Fe_{aq}^{2+} in the Fenton scheme, eqn (24).

$$L(H_2O)Rh^{IV}O^{2\pm} \begin{cases} \xrightarrow{Fe_{aq}^{2+},\ H^+} LRh^{III}(H_2O)_2^{3+} + Fe_{aq}^{3+} \\ \xrightarrow{CH_3OH} L(H_2O)Rh^{III}OH^{2+} + {}^\bullet CH_2OH \end{cases} \quad (24)$$

The deviations from the ideal 2 : 1 ($[Fe_{aq}^{2+}]$: $[L(H_2O)RhOOH^{2+}]$) stoichiometry in the presence of added substrates formed the basis for the kinetic analysis and yielded the relative rate constant in Table 11. In the reactions with alcohols, the rate constants increase in the order $CH_3 < 1° < 2°$, *i.e.* in the order of increasing radical stability. This reactivity order, and the kinetic isotope effects, are most consistent with hydrogen atom abstraction from the α-carbon.

8 Conclusions

In their reactions with various substrates, rhodium hydrides generate an array of reactive intermediates. Even though the number of studies in aqueous solutions is limited, it is already obvious that such conditions bring out some novel chemistry and lead to interesting new species. For example, the chemistry of all of the oxidation states in the range Rh(I)–Rh(IV) has been observed in aqueous solutions. Admittedly, two of these oxidation states, Rh(I) and Rh(IV), have not been observed directly, but kinetic studies have shown Rh(I) to be responsible for the ready hydride exchange in $L^1(H_2O)RhH^{2+}$ with solvent water in alkaline solutions. The spectroscopically undetected Rh(IV) has been shown to react with alcohols and aldehydes. The kinetic data, including deuterium kinetic isotope effects, are most consistent

with these reactions taking place by hydrogen atom transfer. In the presence of molecular oxygen, the hydride serves as a thermal and photochemical source of the persistent hydroperoxo and superoxo complexes, both of which engage in rich chemistry of their own and serve as a source of additional intermediates.

Abbreviations

BDE = bond dissociation energy; BDFE = bond dissociation free energy; dipp = $(Me_2CH)_2P(CH_2)_3P(CHMe_2)_2$; dmgH = dimethylglyoxime anion; dppe = diphenylphosphinoethane; HBpin = pinacolborane; im = imidazole; pdz = pyridazine; tbz = 2-(4-thiazolyl)benzimidazole; TMP = tetramesitylporphyrin; Tp* = hydrotris(3,5-dimethylpyrazolyl)borate anion; TPP = tetraphenylporphyrin; triphos = $CH_3C(CH_2PPh_2)_3$; triphos-I = $C_2H_5C(CH_2PPh_2)_3$; TSPP = tetra(*para*-sulfonatophenyl)porphyrin; ttbs = *N*,*N*′-ethylenebis(3,5-di-*tert*-butylsalicyl-aldiminato); TXP = tetraxylylporphyrin

References

1 *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, vol. 1 & 2.
2 J. Halpern, *Chem. Eng. News*, 2003, **81**, 114.
3 K. Weissermel and H.-J. Arpe, *Industrial Organic Chemistry. Third, completely revised edition*, VCH-Wiley, Weinheim, 1997.
4 J. Halpern, *Science*, 1982, **217**, 401–407.
5 *Aqueous Phase Organometallic Catalysis–Concepts and Applications*, Wiley-VCH, Weinheim, 2nd edn, 2004.
6 *Aqueous Organometallic Chemistry and Catalysis*, ed. I. T. Horvath and F. Joo, Kluwer, Dordrecht, 1995.
7 F. Joo, *Acc. Chem. Res.*, 2002, **35**, 738–745.
8 D. J. Darensbourg, F. Joo, M. Kannisto, A. Katho and J. H. Reibenspies, *J. Chem. Soc., Chem. Commun.*, 1992, 1990–1993.
9 I. T. Horvath and F. Joo, In *Aqueous organometallic chemistry and catalysis*, ed. I. T. Horvath and F. Joo, Kluwer, Dordrecht, 1995, pp. 1–13.
10 J. P. Collman and R. Boulatov, *Inorg. Chem.*, 2001, **40**, 2461–2464.
11 X. Fu, L. Basickes and B. B. Wayland, *Chem. Commun.*, 2003, 520–521.
12 X. Fu and B. B. Wayland, *J. Am. Chem. Soc.*, 2004, **126**, 2623–2631.
13 X. Fu and B. B. Wayland, *J. Am. Chem. Soc.*, 2005, **127**, 16460–16467.
14 R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 1–82.
15 B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1105–1109.
16 K. Thomas, J. A. Osborn, A. R. Powell and G. Wilkinson, *J. Chem. Soc. A*, 1968, 1801–1806.
17 M. Moszner, E. Kwaskowska-Chec and J. J. Ziolkowski, *Inorg. Chim. Acta*, 2004, **357**, 2483–2493.
18 A. Bakac and L. M. Thomas, *Inorg. Chem.*, 1996, **35**, 5880–5884.
19 C. Bianchini, C. Mealli, M. Peruzzini, F. Vizza and F. Zanobini, *J. Organomet. Chem.*, 1988, **346**, C53–C57.
20 V. Circu, M. A. Fernandes and L. Carlton, *Inorg. Chem.*, 2002, **41**, 3859–3865.
21 T. Yoshida, D. L. Thorn, T. Okano, J. A. Ibers and S. Otsuka, *J. Am. Chem. Soc.*, 1979, **101**, 4212–4221.
22 X.-Y. Yu, M. Maekawa, T. Morita, H.-C. Chang, S. Kitagawa and G.-X. Jin, *Polyhedron*, 2002, **21**, 1613–1620.
23 P. Marcazzan, B. O. Patrick and B. R. James, *Inorg. Chem.*, 2004, **43**, 6838–6841.
24 S. Shimada, A. S. Batsanov, J. A. K. Howard and T. B. Marder, *Angew. Chem., Int. Ed.*, 2001, **40**, 2168–2171.

25 H. Song, K. Lee, J. T. Park and I.-H. Suh, *J. Organomet. Chem.*, 1999, **584**, 361–365.

26 T. B. Marder, D. Zargarian, J. C. Calabrese, T. H. Herskovitz and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1484–1485.

27 K. Lemma, A. Ellern and A. Bakac, *Inorg. Chem.*, 2003, **42**, 3662–3669.

28 J. Ott, L. M. Venanzi, C. A. Ghilardi, S. Midollini and A. Orlandini, *J. Organomet. Chem.*, 1985, **291**, 89–100.

29 L. Rosenberg, M. D. Fryzuk and S. J. Rettig, *Organometallics*, 1999, **18**, 958–969.

30 M. B. Ezhova, B. O. Patrick, B. R. James, M. E. Ford and F. J. Wallerb, *Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2707–2714.

31 K. Tani, T. Yamagata, Y. Tatsuno, T. Saito, Y. Yamagata and N. Yasuoka, *J. Chem. Soc., Chem. Commun.*, 1986, 494–495.

32 R. S. Drago, J. G. Miller, M. A. Hoselton, R. D. Farris and M. J. Desmond, *J. Am. Chem. Soc.*, 1983, **105**, 444–449.

33 X.-X. Zhang and B. B. Wayland, *J. Am. Chem. Soc.*, 1994, **116**, 7897–7898.

34 B. B. Wayland, S. Ba and A. E. Sherry, *J. Am. Chem. Soc.*, 1991, **113**, 5305–5311.

35 R. G. Pearson, *Chem. Rev.*, 1985, **85**, 41–49.

36 R. M. Bullock, *Comments Inorg. Chem.*, 1991, **12**, 1–33.

37 D. E. Cabelli, F. Shafiq, C. Creutz and R. M. Bullock, *Organometallics*, 2001, **20**, 3729–3737.

38 R. M. Bullock, in *Transition Metal Hydrides*, ed. A. Dedieu, VCH, New York, 1992, pp. 263–307.

39 D. C. Eisenberg and J. R. Norton, *Isr. J. Chem.*, 1991, **31**, 55–66.

40 S. S. Kristjansdottir and J. R. Norton, in *Transition Metal Hydrides*, ed. A. Dedieu, VCH, New York, 1992, pp. 309–359.

41 R. M. Bullock and E. G. Samsel, *J. Am. Chem. Soc.*, 1990, **112**, 6886–6898.

42 C. E. Ash, P. W. Hurd, M. Y. Darensbourg and M. Newcomb, *J. Am. Chem. Soc.*, 1987, **109**, 3313–3317.

43 D. C. Eisenberg, C. J. C. Lawrie, A. E. Moody and J. R. Norton, *J. Am. Chem. Soc.*, 1991, **113**, 4888–4895.

44 J. A. Franz, D. S. Kolwaite, J. C. Linehan and E. Rosenberg, *Organometallics*, 2004, **23**, 441–445.

45 J. A. Franz, D. S. Kolwaite, J. C. Linehan, K. I. Goldberg and J. L. Look, in *220th ACS National Meeting*, American Chemical Society, Washington, DC, 2000.

46 J. A. Franz, J. C. Linehan, J. C. Birnbaum, K. W. Hicks and M. S. Alnajjar, *J. Am. Chem. Soc.*, 1999, **121**, 9824–9830.

47 L. Tang, E. T. Papish, G. P. Abramo, J. R. Norton, M. H. Baik, R. A. Friesner and A. Rappe, *J. Am. Chem. Soc.*, 2003, **125**, 10093–10102.

48 J. F. Endicott, C.-L. Wong, T. Inoue and P. Natarajan, *Inorg. Chem.*, 1979, **18**, 450–454.

49 A. Bakac and I. A. Guzei, *Inorg. Chem.*, 2000, **39**, 736–740.

50 A. Bakac, *Inorg. Chem.*, 1998, **37**, 3548–3552.

51 S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.*, 2003, **36**, 255–263.

52 A. Bakac, *J. Am. Chem. Soc.*, 1997, **119**, 10726–10731.

53 A. Bakac, *Adv. Inorg. Chem.*, 2004, **55**, 1–59.

54 R. G. Pearson, in *Bonding Energetics in Organometallic Compounds*, ed. T.J. Marks, American Chemical Society, Washington, DC, 1990, pp. 251–262.

55 T. Ramasami and J. H. Espenson, *Inorg. Chem.*, 1980, **19**, 1846–1852.

56 Q. G. Mulazzani, M. Venturi and M. Z. Hoffman, *J. Phys. Chem.*, 1982, **86**, 242–247.

57 N. Sutin, C. Creutz and E. Fujita, *Comments Inorg. Chem.*, 1997, **19**, 67–92.

58 T. Y. Cheng, B. S. Brunschwig and R. M. Bullock, *J. Am. Chem. Soc.*, 1998, **120**, 13121–13137.

59 T. Y. Cheng and R. M. Bullock, *J. Am. Chem. Soc.*, 1999, **121**, 3150–3155.

60 N. Sarker and J. W. Bruno, *J. Am. Chem. Soc.*, 1999, **121**, 2174–2180.

61 W. W. Ellis, A. Miedaner, C. J. Curtis, D. H. Gibson and D. L. DuBois, *J. Am. Chem. Soc.*, 2002, **124**, 1926–1932.

62 W. W. Ellis, J. W. Raebiger, C. J. Curtis, J. W. Bruno and D. L. DuBois, *J. Am. Chem. Soc.*, 2004, **126**, 2738–2743.

63 W. W. Ellis, R. Ciancanelli, S. M. Miller, J. W. Raebiger, M. Rakowski DuBois and D. L. DuBois, *J. Am. Chem. Soc.*, 2003, **125**, 12230–12236.

64 T. R. Felthouse, *Prog. Inorg. Chem.*, 1982, **29**, 73–166.

65 D. G. DeWit, *Coord. Chem. Rev.*, 1996, **147**, 209–246.

66 M. P. Garcia, M. V. Jimenez, A. Cuesta, C. Siurana, L. A. Oro, F. J. Lahoz, J. A. Lopez and M. P. Catalan, *Organometallics*, 1997, **16**, 1026–1036.

67 B. B. Wayland, A. E. Sherry, G. Poszmik and A. G. Bunn, *J. Am. Chem. Soc.*, 1992, **114**, 1673–1681.

68 K. R. Dunbar, S. C. Haefner and L. E. Pence, *J. Am. Chem. Soc.*, 1989, **111**, 5504–5506.

69 S. R. Cooper, S. C. Rawle, R. Yagbasan and D. J. Watkin, *J. Am. Chem. Soc.*, 1991, **113**, 1600–1604.

70 N. G. Connelly, D. J. H. Emslie, B. Metz, A. G. Orpen and M. J. Quayle, *Chem. Commun.*, 1996, 2289–2290.

71 S. C. Rawle, R. Yagbasan, K. Prout and S. R. Cooper, *J. Am. Chem. Soc.*, 1987, **109**, 6181–6182.

72 M. Gerisch, J. R. Krumper, R. G. Bergman and T. D. Tilley, *J. Am. Chem. Soc.*, 2001, **123**, 5818–5819.

73 J. Lilie, M. G. Simic and J. F. Endicott, *Inorg. Chem.*, 1975, **14**, 2129–2133.

74 H. A. Schwartz and C. Creutz, *Inorg. Chem.*, 1983, **22**, 707–713.

75 S. L. Scott, W.-J. Chen, A. Bakac and J. H. Espenson, *J. Phys. Chem.*, 1993, **97**, 6710–6714.

76 K. R. Howes, A. Bakac and J. H. Espenson, *Inorg. Chem.*, 1988, **27**, 3147–3151.

77 U. Tinner and J. H. Espenson, *J. Am. Chem. Soc.*, 1981, **103**, 2120–2121.

78 A. G. Bunn, Y. Ni, M. Wei and B. B. Wayland, *Inorg. Chem.*, 2000, **39**, 5576–5578.

79 J. Lilie, N. Shinohara and M. G. Simic, *J. Am. Chem.Soc.*, 1976, **98**, 6516–6520.

80 A. Bakac and J. H. Espenson, *Inorg. Chem.*, 1989, **28**, 3901–3904.

81 A. Bakac, unpublished data.

82 R. S. Paonessa, N. C. Thomas and J. Halpern, *J. Am. Chem. Soc.*, 1985, **107**, 4333–4335.

83 O. Pestovsky and A. Bakac, *Inorg. Chem.*, 2002, **41**, 3975–3982.

84 A. Bakac, *Prog. Inorg. Chem.*, 1995, **43**, 267–351.

85 O. Pestovsky, S. Stoian, E. L. Bominaar, X. Shan, E. Münck, L. J. Que and A. Bakac, *Angew. Chem., Int. Ed.*, 2005, **44**, 6871–6874.

86 O. Pestovsky and A. Bakac, *J. Am. Chem. Soc.*, 2004, **126**, 13757–13764.

87 M. Hung and A. Bakac, *Inorg. Chem.*, 2005, **44**, 9293–9298.