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Reactivity of mononuclear rhodium(II) compounds

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Contents

Abstract

Mononuclear rhodium(II) compounds reported in the literature are tabulated, classified according to functionality and placed in one of four stability categories. The reactions reported

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for mononuclear Rh(II) compounds are presented and grouped according to reactivity type: adduct formation, ligand dissociation and substitution, dimerization, disproportionation, oxidation and reduction. Observed reactivity is rationalized on the basis of the factors that influence stability. Ligands that are sufficiently bulky can protect the metal from external attack by all but the smallest reagent molecules. Polydentate ligands can protect the metal from external attack or can impose coordination environments that destabilize Rh(I) or Rh(III). Electronic features of ligands that withdraw electron density or delocalize the unpaired electron from the metal promote stability. Reactivity can also depend on whether the Rh(II) complex is four coordinate (15 electron), five coordinate (17 electron) or six coordinate (19 electron). Because conventional two-electron oxidative addition and reductive elimination processes are not possible for Rh(II), redox behavior is of special interest. Mechanisms proposed for unusual oxidation and C–H activation behavior in some Rh(II) systems are presented. Factors giving rise to differences in reactivity between different classes of Rh(II) compounds are evaluated.

Keywords: Reactivity; Mononuclear Rhodium(II) compounds; Mechanisms.

Abbreviations

$BHpz_3^-$	hydridotris(1-pyrazolyl)borate monoanion
bipy	bipyridine
s-bqdi$^-$	semi-benzoquinonediimine monoanion
^{n}Bu	*n*-butyl
^{t}Bu	*tert*-butyl
COD	1,5-cyclooctadiene
cy	cyclohexyl
3,5-DBcat^{2-}	3,5-di-*tert*-butylcatecholate dianion
s-disn$^-$	semi-diiminosuccinonitrile monanion
DMA	*N*,*N*-dimethylacetamide
dmgH$^-$	dimethylglyoximate monanion
DMSO	dimethyl sulfoxide
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Et	ethyl
Me	methyl
mnt^{2-}	maleonitriledithiolate dianion
NBD	norbornadiene
np_3	tris(2-diphenylphosphinoethyl)amine
OEP^{2-}	octaethylporphyrinate dianion
OETAP^{2-}	octaethyltetraazaporphyrinate dianion
pc^{2-}	phthalocyanine dianion
PDABP	polymeric dialkylbenzylphosphine (on a polystyrene backbone, with some cross-linking by divinylbenzene)
PDPBP	polymeric diphenylbenzylphosphine (on a polystyrene backbone)

Ph	phenyl
phen	1,10-phenanthroline
pp_3	tris(2-diphenylphosphinoethyl)phosphine
$PPDOBF_2^-$	BF_2-bridged 2,2′-[1,3-propanediylbis(nitrilo)]bis[3-pentanoneoximato] monanion
^iPr	isopropyl
^nPr	*n*-propyl
py	pyridine
9S3	1,4,7-trithiacyclononane
12S3	1,5,9-trithiacyclododecane
$salen^{2-}$	ethylenebis(salicylideneiminato) dianion
$saloph^{2-}$	*ortho*-phenylenebis(salicylideneiminato) dianion
sep	1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane
tfa^-	1,1,1-trifluoracetylacetonate monanion
THF	tetrahydrofuran
tht	tetrahydrothiophene
TMP^{2-}	*meso*-tetra(mesityl)porphyrinato dianion
TMPP	tris(2,4,6-trimethoxyphenyl)phosphine
^{o}tol	*ortho*-tolyl
TPP^{2-}	*meso*-tetraphenylporphyrinato dianion
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
$ttbsalen^{-2}$	*N*,*N*′-ethylenebis(3,5-di-*tert*-butylsalicylaldiminato) dianion
$ttbsaloph^{-2}$	*N*,*N*′-phenylenebis(3,5-di-*tert*-butylsalicylaldiminato) dianion
$TTEPP^{2-}$	*meso*-tetrakis(2,4,6-triethylphenyl)porphyrinato dianion
$TTiPP^{2-}$	*meso*-tetrakis(2,4,6-triisopropylphenyl)porphyrinato dianion
TXP^{2-}	*meso*-tetrakis(3,5-dimethylphenyl)porphyrinato dianion

1. Introduction

The coordination chemistry of rhodium has been extensively investigated for many years. The chemistry of rhodium is understandably dominated by its +1 ($4d^8$) and +3 ($4d^6$) oxidation states, and the interconversion between these states by oxidative addition and reductive elimination processes is a central theme in an account of its reactivity. Because of the greater substitutional lability of many Rh complexes in comparison with 3d and 5d analogues and because both oxidative addition and reductive elimination reactions are often readily feasible, rhodium complexes have been widely used in the design of catalytic systems [1–3].

As expected, the chemistry of Rh(II) ($4d^7$) has been much less extensively studied. In the group 9 triad, Rh(II) compounds are far less prevalent than Co(II) compounds but much more common than those of Ir(II). Among known Rh(II) compounds, diamagnetic dimers with Rh—Rh bonds are most common, and the nature of the metal–metal bond has been the subject of several early studies [4–6]. A review of Rh(II) carboxylates, which are nearly all dimeric, appeared more than 10 years ago

[7]. A more general review of Rh(II) compounds appeared in 1982 [8], and mononuclear examples were far outweighed by binuclear and polynuclear ones. Research in the intervening years has produced many more examples of paramagnetic mononuclear Rh(II) compounds as chemists have begun to understand how to frustrate Rh—Rh bond formation and to stabilize mononuclear species. Predictable patterns of reactivity have begun simultaneously to emerge. Of particular interest are redox reactions that are often non-complementary (e.g. one-electron oxidations by two-electron oxidizing agents) and ligand addition–dissociation behavior of 15-electron (four-coordinate), 17-electron (five-coordinate) or 19-electron (six-coordinate) Rh(II) systems.

A review of mononuclear d^7 compounds of the platinum metals that included Rh(II) examples appeared in 1992 [9], but a complete and systematic treatment of stability factors and reactivity patterns of the Rh(II) compounds was not done.

This article reviews and categorizes the reactions that have been reported for mononuclear Rh(II) compounds and summarizes factors that influence stability and reactivity. Mononuclear Rh(II) compounds reported in the literature are placed in four broad categories according to stability: (A) those that are reportedly isolable or are persistent species in solution; (B) transient species with sufficient longevity in solution for spectra, chemical reactivity or electrochemical activity to be observed; (C) highly reactive photolysis or radiolysis transients with observable rates of decay; and (D) species which are postulated (but undetected) intermediates in known reactions. Widely varying degrees of stability surely exist within each of these categories. In category B some species are conveniently observed at ambient temperature while others are sufficiently long lived only at low temperatures. Some species placed in category D could possibly have been detected in solution had the appropriate experiment been performed and could thus be as stable as some of the species in category B or C. In any case the essential stabilizing features of mononuclear Rh(II) complexes become apparent in spite of the crudeness of these classifications.

To assist in seeing patterns, the compounds are further grouped, in so far as possible, according to predominant functionality. Also, observed reactivity is organized according to a number of reaction categories: adduct formation, ligand dissociation and substitution, dimerization (by both metal–metal bond formation and ligand coupling), disproportionation to Rh(I) and Rh(III), one-electron oxidation or reduction and catalytic activity. For the most part these are the reactivity patterns expected for complexes of a divalent d^7 metal center.

Magnetic and spectral data as well as other physical properties of these complexes are not reviewed here unless directly relevant to specific reactivity discussed. Prior reviews [8,9] have included satisfactory summaries of such data for many Rh(II) compounds.

2. Relative stabilities of mononuclear rhodium(II) compounds

Mononuclear Rh(II) compounds that have been reported in the literature appear in Table 1 (see Section 4). Note that compounds in this table have been grouped

according to type: porphyrin-containing compounds; phosphine complexes that contain two or more phosphine donor atoms; organometallics; sulfur donor complexes; complexes with N, O or halide donor ligands; and Rh^{2+} complexes trapped in diamagnetic host lattices. In cases where compounds possess the characteristics of more than one group, classification is based on a judgment of predominant functionality.

The Rh(II) species in diamagnetic host lattices are of interest primarily for their electron paramagnetic resonance (EPR) spectra and were discussed in previous reviews [8,9]; they will not be considered further in this article.

Some compounds cited in earlier reviews have not been included in Table 1. The diamagnetic Rh(III) complex $[Rh(\eta^5\text{-}C_5Me_5)(BHpz_3)]PF_6$ was originally identified in the literature as an Rh(II) complex [10]. Paramagnetism in solutions of $Rh_2(H_2O)_{10}^{2+}$ was originally ascribed to a small amount of dissociation to mononuclear $Rh(aq)^{2+}$ [11], but this interpretation was later withdrawn based on assignment of the observed paramagnetism in this and similar dimers to temperature induced paramagnetism (TIP) [12].

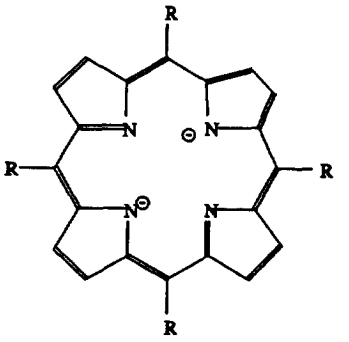
With one exception, dioxygen complexes have not been included in Table 1. Considerable ambiguity concerning Rh oxidation state assignments has appeared in the literature, with interpretation of structural and spectroscopic data ranging from $Rh(I)/O_2$ to $Rh(II)/O_2^-$ to $Rh(III)/O_2^{2-}$. For example, $RhCl(O_2)(PPh_3)_2$, prepared from interaction of $RhCl(PPh_3)_3$ and molecular oxygen in benzene, showed an EPR spectrum said to be characteristic of an $Rh(II)/O_2^-$ complex [13], but this was unconfirmed by other workers [14,15]. The same compound prepared in CH_2Cl_2 was subsequently shown to be an O_2-bridged diamagnetic dimer containing Rh(III) [16–18]. Similarly, the product of O_2 reacting with $[RhCl(Pcy_3)_2]_n$ in the solid state contains an EPR-active component suggested to be an $Rh(II)/O_2^-$ species [19]. On the other hand, $RhCl(O_2)(Pcy_3)_2$, prepared from $RhCl(Pcy_3)_2 + O_2$ in benzene, was characterized as an Rh(I) complex of η^2-O_2 on the basis of an unusually high O—O stretching frequency (993 cm^{-1}) [20]. Similarly, an X-ray crystal structure of $RhCl(O_2)(P^iPr_3)_2$ was interpreted as a planar Rh(I) complex with *trans* phosphines and η^2-O_2, but despite being "essentially diamagnetic", the sample showed a weak EPR signal indicative of the presence of Rh(II) [21]. Other O_2 complexes with potentially ambiguous oxidation states are $RhCl(O_2)(AsPh_3)_2$ [22], $RhCl(O_2)(PPh_3)_3$ [23–25], $RhCl(O_2)(RCH{=}CH_2)(EPh_3)_2$ (E≡P, As) [26] and $Rh(O_2)(AsPh_3)_4^+$ [27].

Table 1 assigns each complex according to a "stability category" (A, B, C or D). Although the stability range within each category is wide and the distinction between categories poorly resolved, it is possible to identify general structural and electronic features of ligands that affect the stability and reactivity of mononuclear Rh(II) complexes.

2.1. *Structural effects of ligands*

2.1.1. *Porphyrin-containing compounds*

The effect of sterically demanding ligands is clearly evident in the series of Rh(II) porphyrins in which the meso positions of the porphyrin ligand ring system (**I**)



R
2,4,6-$^{i}Pr_3C_6H_2$= TTiPP
2,4,6-$Et_3C_6H_2$= TTEPP
2,4,6-$Me_3C_6H_2$= TMP
3,5-$Me_2C_6H_3$= TXP
C_6H_5= TPP

I

are substituted. In addition, the β-pyrrole positions can be substituted as in octaethylporphyrin (OEP). In this series, steric bulk decreases in the order TTiPP > TTEPP > TMP > TXP > TPP > OEP, and the nature and chemical behavior of the Rh(II) complexes of these species vary accordingly. Whereas $[Rh(OEP)]_2$ [28,29] and $[Rh(TPP)]_2$ [30–33] are primarily Rh—Rh bonded dimers in solution, Rh(TTiPP) [34,35], Rh(TTEPP) [35,36] and Rh(TMP) [35,37–39] occur as monomers in benzene and toluene solutions. (The EPR evidence that led to an early claim for monomeric Rh(TPP) [40] seems better interpreted as being due to Rh(III)(TPP)(O_2^-) [30].) Measured bond energies are 16.5 kcal mol^{-1} for $[Rh(OEP)]_2$ [28,29] and 12 kcal mol^{-1} for $[Rh(TXP)]_2$ [39], implying a gradual weakening of the Rh—Rh interaction as the bulk of the R substituents on the porphyrin increases.

Stabilities of Lewis base adducts of the Rh(II) porphyrins also depend on the steric demands of the porphyrin ligand. The adduct Rh(TTiPP)(CO), containing the bulkiest porphyrin, is entirely monomeric [34], but Rh(TMP)(CO) exists in equilibrium with a greater amount of a dimeric species [34,41,42] (see Section 3). The species Rh(TXP)(CO) [34,42,43] and Rh(OEP)(CO) [42,44–46], containing still less sterically demanding porphpyrins, are proposed transients in some reactions but exist as CO-bridged dirhodium species in their ground states. For the ligand C_2H_4, the monomeric adduct Rh(TTiPP)(C_2H_4) can be stabilized at 90 K, but dimerization occurs at higher temperature [35,36]. No monomeric C_2H_4 adducts can be observed for less bulky members of the series; for example, only C_2H_4-bridged dirhodium species are observed for (TTEPP)Rh and (TMP)Rh [35,36]. Clearly, the formation of monomeric complexes is facilitated by steric hindrance. Even when bridged binuclear species occur, the number of bridging units (—C(=O)— or $-CH_2CH_2-$) increases as the steric demands of the porphyrin increase (see Section 3). A series of monomeric adducts Rh(TMP)L (L ≡ NEt_3, $NHEt_2$, py, 2,6-Me_2py, PEt_3, PPh_3, $AsPh_3$, CNR) have been stabilized at 90 K [35,45], but they decompose in various ways at higher temperatures. For example, the resistance of the isocyanide adducts

toward further reaction (cleavage of CN—R) decreases as the steric bulk of R in CNR decreases: 2,6-$Me_2C_6H_3$ > ^{t}Bu > Me (see Section 3).

2.1.2. Phosphine compounds

In the series of complexes $RhX_2(PR_3)_2$ (X ≡ halide), steric demands of the monodentate phosphines are readily evaluated by comparing cone angles [47–49], e.g. $P^o tol_3$ (194°) > $P^t Bu_3$ (182°) > P(neopentyl)$_3$ (about 180°) > Pcy_3 (179°) > $P^i Pr_3$ (160°) > PPh_3 (145°) > $P^n Bu_3 \approx P^n Pr_3 \approx PEt_3$ (132°) > PMe_3 (118°). Thus *trans*-$RhCl_2(P^o tol_3)_2$ has been isolated and characterized [50,51]. Likewise, $RhCl_2[PPh(^o tol)_2]_2$ has been prepared [51], but low values of μ_{eff} (0.8–1.1) suggest that some Rh—Rh interaction may be occurring. Attempts to isolate and characterize $RhCl_2(PPh^o_2tol)_2$ were unsuccessful [51]. In view of this apparent decline in stability as ^{o}tol is replaced in the phosphine by the less bulky Ph, the report of the isolation and structural characterization of $RhCl_2(PPh_3)_2$ [52] seems surprising and anomalous. In fact, a recent structural study presents convincing evidence that this material is actually $RhCl(CO)(PPh_3)_2$, with disordered CO and Cl ligands [53].

A series of compounds *trans*-$RhCl_2(PR^t Bu_2)_2$ have been prepared. For R ≡ Me, Et, and ^{n}Pr [54,55], the values of μ_{eff} are below spin-only values in the solid state and considerable Rh—Rh interaction is inferred [55]; in CH_2Cl_2 solution, however, μ_{eff} = 2.12 for R ≡ Me. Attempts to prepare analogous Rh(II) complexes with fewer than two ^{t}Bu groups per phosphine (e.g. $P^n Pr_2{}^t Bu$) and with several other less bulky phosphines (PEt_3, PMe_2Ph, PEt_2Ph, $P^n Pr_2Ph$, $P^n Bu_2Ph$, $P^n Bu_3$) were unsuccessful [55]. For $PR^t Bu_2$ complexes with R ≡ $CH_2CH_2CO_2Et$ [56] $CH_2CH_2CH_2CO_2Et$ [56], and CH_2(2-MeO-5-MeC_6H_3) [57], stable monomers are obtained. With R ≡ 2-$MeOC_6H_4$, demethylation, ring closure and replacement of Cl^- occur to give *trans*-$Rh[\eta^2\text{-}P^t Bu_2(^oC_6H_4O-)]_2$ [58].

The steric bulk of $P(CH_2SiMe_3)_3$ (compare P(neopentyl)$_3$) allows the isolation of monomeric $RhBr_2[P(CH_2SiMe_3)_3]_2$, although the chloride analogue appears to be the paramagnetic bridged dimer $\{RhCl(\mu\text{-}Cl)[P(CH_2SiMe_3)_3]_2\}_2$ with essentially non-interacting Rh atoms [59].

$RhCl_2(Pcy_3)_2$ and $RhBr_2(Pcy_3)_2$ can be prepared from RhX_3 and Pcy_3 in ^{i}PrOH [60]. Significantly, addition of Cl_2 or Br_2 to $RhX(Pcy)_2$ (X ≡ Cl, Br, I) gives $RhCl_2(Pcy_3)_2$, $RhClBr(Pcy_3)_2$, $RhClI(Pcy_3)_2$, and $RhBr_2(Pcy_3)_2$ rather than the Rh(III) products $RhX_3(Pcy_3)_2$ that might be expected [61]. The reluctance to form $RhX_3(Pcy_3)_2$, presumably due to steric barriers, is consistent with the observed reluctance of $RhX_2(Pcy_3)_2$ to disproportionate [61].

$RhCl_2(P^i Pr_3)_2$ has been independently prepared and structurally characterized by two groups using different methods of synthesis: reaction of $RhCl(N_2)(P^i Pr_3)_2$ with *N*-chlorosuccinimide in THF [62] and reaction of $[RhCl(P^i Pr_3)_2]_n$ with CCl_4 in pentane [63].

Polydentate ligands have also been employed to stabilize monomeric Rh(II) complexes, where, in addition to the usual chelate effect stabilization, the ligand backbone protects a portion of the periphery of the complex from external attack. The complex $[Rh(TMPP)_2](BF_4)_2$ containing the bulky phosphine ligand P[2,4,6-$(MeO)_3C_6H_2$]$_3$ (TMPP) has been isolated and structurally characterized

[64,65]. The phosphorus atoms of the two TMPP ligands are mutually *cis*, with two of the three trimethoxyphenyl groups of each TMPP coordinated to Rh through an *ortho*-methoxy group. Thus the complex is essentially six coordinate and sterically protected, with elongated and relatively labile *trans*-methoxy bonds to Rh. Attempts at forming adducts with CO resulted only in disproportionation to Rh(I) and Rh(III) products containing TMPP and CO [65,66], but reaction with CN^tBu and CN^iPr gave the stable, structurally characterized four-coordinate Rh(II) products *trans*-$[Rh(\eta^1\text{-TMPP})_2(CNR)_2](BX_4)_2$ (X≡F, Ph) [67]. A similar reaction with the less bulky isocyanide CNMe leads to disproportionation [67]. Thus sterically demanding R groups stabilize Rh(II) isocyanide products.

Other polydentate phosphine ligands provide similar stabilization. The complex $[Rh(np_3)(-C{\equiv}CPh)]BPh_4$ containing the tetradentate ligand $N(CH_2CH_2PPh_2)_3$ (np_3) has been isolated and spectroscopically characterized [68]. The related complex $Rh(np_3)(CN)^+$ has been prepared electrochemically in solution but has not been isolated [69]; a stability difference could be attributed in part to the greater steric demand of −C≡CPh as compared with −CN. The tridentate ligand $CH_3C(CH_2PPh_2)_3$ (triphos) contributes to the stability of Rh(triphos)($S_2C{=}O$) and Rh(triphos)($Se_2C{=}O$) [70]. The steric protection of the bidentate phosphine ligand dppe is sufficient to allow isolation of the complex *cis*-$RhCl_2$(dppe) in the reaction of $RhCl_2$(2-methylallyl) with dppe in 96% ethanol [71].

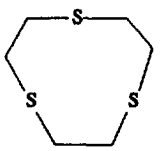
2.1.3. Other compounds

The influence of ligand structure on stability is evident in a number of organometallic compounds. The σ-diaryl complex $Rh(2,4,6\text{-}^iPr_3C_6H_2)_2(tht)_2$ has been isolated and structurally characterized [72]. The complex is trans planar with respect to the donor atoms, but the four ring systems are tilted relative to the molecular plane forming a propeller-like array that somewhat shields the metal above and below the plane. It is significant that attempts to prepare analogous products with less bulky aryl R groups (e.g., $2,4,6\text{-}Me_3C_6H_2$) produce only Rh(III) and Rh(I) products [72].

The compound $Rh(C_6Cl_5)_2(COD)$ can be prepared in situ and a variety of derivatives $Rh(C_6Cl_5)_2L_2$ ($L_2 \equiv [P(OMe)_3]_2$, $[P(OPh)_3]_2$, $(PPh_3)_2$, py_2, dppe, dppm) can be prepared by substitution of COD [73]. Of these, $Rh(C_6Cl_5)_2[P(OPh)_3]_2$ has been structurally characterized and is trans-planar, with the C_6Cl_5 rings perpendicular to the molecular plane [73]. As with the related $Rh(aryl)_2(tht)_2$ system, steric effects of the aryl ligands contribute to the stability of these compounds, very probably complemented by the electronic influence of the electron-withdrawing C_6Cl_5 groups.

The isolable sandwich complex $[Rh(C_6Me_6)_2](AlX_4)_2$ (X≡Cl, Br) [74] is an example of the stabilizing steric protection of π-bonded arene ligands.

The conformational properties of crown thioethers such as the tridentate ligand 9S3 (**II**) are believed to contribute to the stabilization of $Rh(9S3)_2^{2+}$ [75–77]. Although a salt of this cation has not been isolated, disporportionation of the ion is found to be very unfavorable in solution ($K \approx 1 \times 10^{-7}$) [75]. The six-coordinate structure is believed to disfavor Rh(I), which normally prefers four coordination, and to provide steric shielding that inhibits dimerization and hinders access by



II

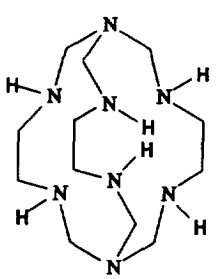
reagents to the metal center. A similar effect (without the electronic benefits of sulfur donor atoms) is seen for the hexadentate nitrogen donor ligand "sep" (**III**), which helps to stabilize $Rh(sep)^{2+}$ in solution [78]. This complex, although a highly reactive reductant, is more stable than analogues with less constrained nitrogen donor ligands.

The ability of the tetradentate Schiff base "salen" (**IV**) to twist away from a planar geometry allows the mononuclear complex Rh(salen) to exist in equilibrium with its dimer $[Rh(salen)]_2$ in the solid state [79]. The more rigid "saloph" ligand (**V**) gives planar "Rh(saloph)", unprotected above and below the molecular plane, and the compound is entirely dimeric [79]. The Rh(II) complex of ttbsalen (salen with *tert*-butyl groups in the 3 and 5 positions on each ring) is dimeric below 233 K, but dissociates partially in benzene to give the persistent monomer radical Rh(ttbsalen) at higher temperature (243–393 K) [79a,b]. The steric bulk of the *t*-butyl groups undoubtedly contributes to the stability of this monomer, but electronic factors have also been identified [79a] (see Section 2.2).

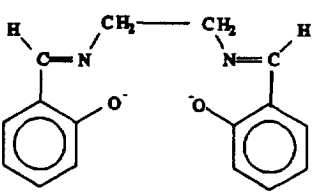
2.2. *Electronic effects of ligands*

Electronic properties of ligands that could influence the stability of Rh(II) complexes include the σ donor and π donor–acceptor capabilities of the ligand, the hardness or softness of the ligand donor atoms and the presence of a delocalized π system in the ligand backbone. A combination of such factors could affect the energy of the metal orbital containing the unpaired electron (usually the d_{z^2} orbital in four-coordinate planar systems), the stability of Rh(II) relative to Rh(I) and Rh(III) or the extent of delocalization of unpaired electron density on to the ligand.

A careful EPR study of a series of monoadducts of the porphyrin complex



III



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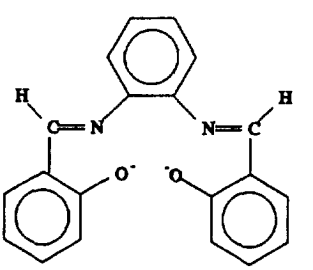
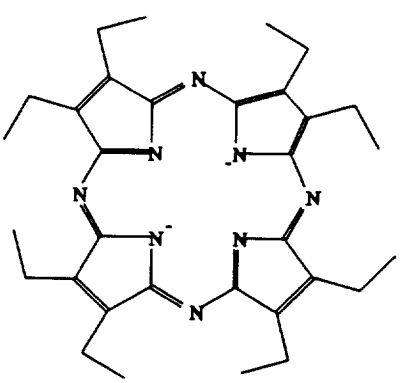


V

Rh(TMP) with a variety of ligands L has elucidated the role of the electronic properties of L in affecting the stability of Rh(TMP)L [35]. Strong σ donors such as py and $NHEt_2$ favor disproportionation to $Rh(TMP)^-$ and $Rh(TMP)L_2^+$, presumably because strong interaction of L on the *z* axis destabilizes the unpaired electron in the d_{z^2} orbital to such an extent that electron transfer occurs to lower energy porphyrin π* orbitals, forming an $Rh(III)(TMP^{\cdot 3-})$ intermediate [35]. Such a species has actually been identified in the reaction of py with the octaethyltetraazaporphyrinato ($OETAP^{2-}$) (**VI**) complex of rhodium(II) giving the persistent radical anion complex $Rh(III)(OETAP^{\cdot 3-})py_2$ [80]. Good π acids such as CO, PPh_3, CNR and C_2H_4 give adducts that are generally more stable toward disproportionation, since delocalization of unpaired spin density on to the ligand is facilitated and d_{xz} and d_{yz} orbitals are stabilized by π back bonding. In Rh(TMP)(CO), for example, EPR evidence suggests that the carbonyl carbon is partially rehybridized toward sp^2 with bent Rh–C–O and a significant spin density on C (a value of 0.3 or more was determined for Rh(TTiPP)(CO)) [34,35,41]. Not surprisingly, some of the π acid adducts are unstable relative to coupling products such as (TMP)Rh−C(=O)−C(=O)−Rh(TMP) [34,41] and (TMP)Rh−CH_2CH_2−Rh(TMP) [35,36], where coupling occurs through ligand atoms bearing unpaired electron spin density.

Stabilization of the monomeric substituted salen (**IV**) complex Rh(ttbsalen) relative to its dimer has an electronic origin in addition to a steric one [79a]. An analysis of the EPR spectrum of the monomer indicates the unpaired electron to be in the d_{yz} orbital of Rh. Dimerization requires a reorganization energy (estimated to be less than 8 kcal mol^{-1}) in order to utilize the d_{z^2} orbital in making the Rh−Rh bond. This unfavorable contribution is responsible for the relatively weak Rh−Rh bond (13 kcal mol^{-1}) in the dimer [79a].

The stability of the crown thioether complexes such as $Rh(9S3)^{2+}$ is attributed both to conformational constraints of the ligands (see above) and to the electronic properties of its sulfur donor atoms [75,76]. As weak σ donors and strong π acceptors ("soft" Lewis bases), the sulfur atoms tend to destabilize Rh(III) relative



VI

to its lower oxidation states and help to delocalize the unpaired spin density. Thus the combination of both steric and electronic factors stabilizes these complexes against oxidation and disproportionation.

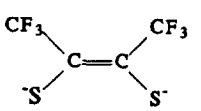
The electronic properties of sulfur donor atoms presumably confer a similar stabilizing influence on Rh(cysteine)$_2$, Rh(cysteine methylester)$_2$, and Rh(penicillamine)$_2$, which are believed to coordinate in a bidentate fashion through $-NH_2$ and $-S^-$ [81].

In Rh(η^5-C_5H_5)[$S_2C_2(CF_3)_2$]$^-$ [82,83], the π acid character of the sulfur donor atoms in the $S_2C_2(CF_3)_2^{2-}$ ligand (**VII**) is enhanced by the electron-withdrawing CF_3 groups.

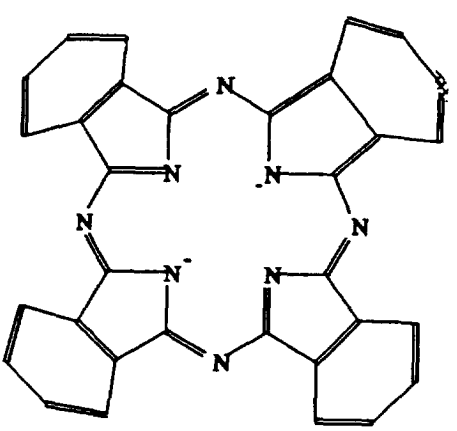
The electronic effects of S and Se in the complexes Rh(triphos)($S_2C{=}O$) and Rh(triphos)($Se_2C{=}O$) undoubtedly complement the conformational benefits of the polydentate triphos ligand [70].

Many of the "stable" mononuclear Rh(II) complexes in Table 1 have ligands with structures that are highly conducive to delocalization of the unpaired electron away from rhodium. A notoriously non-innocent ligand in this regard is NO, as in $RhCl_3(NO)(PPh_3)_2$ [84]. On the basis of a very low N—O stretching frequency (1660 cm^{-1}), it is tempting to regard $RhCl_3(NO)(PPh_3)_2$ as a complex of Rh(IV) (d^5) and NO^- in which the unpaired electron has been completely transferred to the NO, but this interpretation was ruled out in favor of Rh(II)/NO^+ on the basis of EPR spectral data [84]. In any case, NO must surely exert a considerable electron-delocalizing influence in this compound.

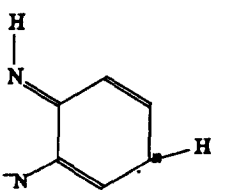
Many of the complexes in Table 1 have ligands containing several multiple bonds,



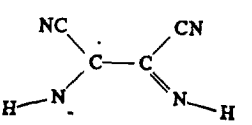
VII



VIII



IX



X

often conjugated, which allow the stabilizing contribution of resonance structures with ligand-centered unpaired electrons. This is obviously true of the porphyrins in the Rh(por) complexes. An extreme example of delocalization of an unpaired electron on to a porphyrin-like ligand is the octaethyltetraazaporphyrinato (**VI**) complex, $Rh(OETAP)py_2$, shown to be an Rh(III) complex containing the persistent radical anion $OETAP^{\cdot 3-}$ [80]. A similar species occurs upon electrochemical reduction of the phthalocyanine (pc) (**VIII**) complex $Rh(pc)(CN)_2^-$, where the added electron enters a ligand-centered lowest unoccupied molecular orbital (LUMO) to give $Rh(III)/pc^{\cdot 3-}$ in $Rh(pc)(CN)_2^{2-}$ [85].

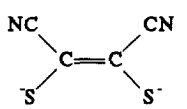
Several other ligands possess a potential for delocalization: salen (**IV**) in Rh(salen) [79], ttbsalen in Rh(ttbsalen) [79a,b], *s*-bqdi$^-$ (**IX**) in $RhCl(s\text{-bqdi})(PPh_3)_2$ [86], and *s*-disn$^-$ (**X**) in $RhCl(s\text{-disn})(PPh_3)_2$ [86].

All the organometallic Rh(II) complexes in Table 1 contain aromatic ligands that facilitate unpaired electron delocalization: $Rh(C_6Cl_5)_2L_2$ ($L \equiv PPh_3$, $P(OR)_3$, py, etc.) [73], $Rh(2,4,6\text{-}^iPr_3C_6H_2)_2(tht)_2$ [72], $[Rh(\eta^6\text{-}C_6Me_6)_2](AlX_4)_2$ [74], $Rh(\eta^5\text{-}C_9H_7)(CH_3)[Ph_2CH(CH_3)CH_2PPh_2]$ [87], $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2^+$ [88], $Rh(\eta^5\text{-}C_5Me_5)_2$ [89], $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)$ [89], $Rh(\eta^5\text{-}C_5H_5)_2$ [90–92], and $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)$ [89,93]. The last two cases offer compelling evidence for delocalization of unpaired electron density on to the ligand. Although monomeric $Rh(\eta^5\text{-}C_5H_5)_2$ [90,92] and $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)$ [89,93] can be detected at low temperatures, both complexes readily dimerize to the thermodynamically favored Rh(I) products **XI** at room temperature, formed by the coupling of ligand-centered radicals [89,90,92]. The related Rh(II) indenyl complex $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)$ does not dimerize and is quite stable in THF solution, even at 25 °C C [89], apparently a result of the greater delocalizing ability of $\eta^5\text{-}C_9H_7$ relative to $\eta^5\text{-}C_5R_5$ ($R \equiv H$, Me).

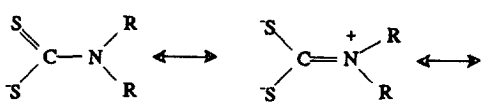
Certain of the complexes of sulfur donor ligands enjoy not only the stabilizing electronic influence of the sulfur atoms (see above) but also the delocalizing effect of unsaturation in the ligand structure. This is true of mnt^{2-} (**XII**) in $(Bu_4)_2[Rh(mnt)_2]$ [94], of the dithiolate $S_2C_2(CF_3)_2^{2-}$ (**VII**) in $Rh(\eta^5\text{-}C_5H_5)[S_2C_2(CF_3)_2]^-$ [82,83], and of the dithiocarbamates (**XIII**) in $Rh(S_2CNR_2)_2$ and $Rh(S_2CNR_2)_2(PPh_3)$ ($R \equiv$ Me, Et) [95].

Although $Rh(bipy)_3^{2+}$ and $Rh(phen)_3^{2+}$ are relatively unstable compared with many

XI



XII



XIII

of the other compounds in Table 1, the π-delocalized ligands bipy and phen are expected to impart more stability to RhN_6^{2+} complexes than would saturated analogues such as ethylenediamine. In a study of the electrochemical reduction of $Rh(bipy)_3^{3+}$ and $Rh(phen)_3^{3+}$, it is assumed that the unpaired electron density in the products $Rh(bipy)_3^{2+}$ and $Rh(phen)_3^{2+}$ resides primarily in ligand molecular orbitals [96,97].

Delocalization of unpaired electron density on to ligands is expected to be particularly important for complexes with more than 18 valence electrons seeking accommodation in metal orbitals. This applies to several of the compounds mentioned above, which are formally 19-electron complexes, e.g. $RhCl_3(NO)(PPh_3)_2$, $Rh(OETAP)py_2$, $Rh(C_6Me_6)_2^{2+}$, $Rh(\eta^5\text{-}C_9H_7)(CH_3)[PPh_2CH(CH_3)CH_2PPh_2]$, $Rh(\eta^5\text{-}C_5H_5)_2$, $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}L)$ ($L \equiv C_5H_5$, C_5Me_5, C_9H_7), $Rh(bipy)_3^{2+}$, and $Rh(phen)_3^{2+}$.

3. Reactions of mononuclear rhodium(II) compounds

3.1. Adduct formation

Several of the complexes in Table 1 are Lewis base adducts of known four-coordinate mononuclear Rh(II) complexes. Four-coordinate, 15-electron complexes are especially susceptible to attack by one or two ligands to produce 17- or 19-electron adducts. An added Lewis base perturbs electronic energy levels in the complex (e.g. destabilizes the unpaired electron), thereby promoting subsequent reactivity. Some of these effects have been discussed in Section 2, but specific reactions of adducts will be discussed in the appropriate sections below.

Exposure of the porphyrin complexes Rh(TTiPP) and Rh(TMP) in toluene solution to CO (0.1–1.0 atm) produces the adducts Rh(TTIPP)(CO) and Rh(TMP)(CO) [34].

The ethylene adduct $Rh(TTiPP)(\eta^2\text{-}C_2H_4)$, has been observed when Rh(TTiPP) is treated with C_2H_4 (0.3 atm in C_6H_6) [35,36], but adducts of complexes with less bulky porphyrins undergo rapid coupling reactions (see below) and have not been detected.

A series of adducts Rh(TMP)L ($L \equiv NEt_3$, $NHEt_2$, py, 2,6-Me_2py, PEt_3, PPh_3, $AsPh_3$, CNR) have been stabilized at 90 K in toluene or methyl cyclohexane [35]. Cleavage of Lewis bases CNR and $P(OMe)_3$ by Rh(II) porphyrins at higher temperatures (e.g. Eqs. (20) and (21)) is assumed to occur by prior formation of such adduct intermediates [35,80].

When the mononuclear transient Rh(TPP) is electrochemically generated in the presence of $RC{\equiv}CH$ ($R \equiv {}^n\text{Pr}$, ${}^n\text{Bu}$), an adduct intermediate $Rh(TPP)(\eta^2\text{-}RC{\equiv}CH)$ is formed that undergoes a subsequent intramolecular cleavage reaction (Eq. (26)) [98].

Treatment of $RhCl_2(Pcy_3)_2$ with CO in the solid state produces $RhCl_2(Pcy_3)_2(CO)$, which is marginally stable in the solid state but very unstable in solution [99].

Reaction of $Rh(TMPP)_2^{2+}$ with bulky isocyanides CNR ($R \equiv {}^t\text{Bu}$, ${}^i\text{Pr}$) gives the stable complexes (apparent adducts) $Rh(TMPP)_2(CNR)_2^{2+}$, but this reaction is

accompanied by dissociation of TMPP methoxy groups (η^3-TMPP in the reactant to η^1-TMPP in the product) and might be better classified as a substitution reaction [67].

Reaction of $Rh(TMPP)_2^{2+}$ with CO leads to CO-containing Rh(I) and Rh(III) products, but the Rh(II) "adducts" $Rh(TMPP)_2(CO)_n^{2+}$ ($n=1$ or 2) are very probably intermediates [65,66].

When $Rh(2,4,6\text{-}^iPr_3C_6H_2)_2(tht)_2$ is treated with excess CO in hexane, spectroscopic evidence is observed for a mixture of adducts $Rh(2,4,6\text{-}^iPr_3C_6H_2)_2(tht)_2(CO)_n$ ($n=1$, 2), but none were successfully isolated [72].

The dithiocarbamate complexes $Rh(S_2CNR_2)_2$ and $Rh(S_2CNR_2)_2(PPh_3)$ (R ≡ Me, Et) are both stable [95], but direct reaction of $Rh(S_2CNR_2)_2$ with PPh_3 to give the adduct $Rh(S_2CNR_2)_2(PPh_3)$ was not reported.

The salen (**IV**) derivative Rh(ttbsalen) (ttbsalen ≡ tetra-^{t}butyl-substituted salen) forms the phosphine adduct Rh(ttbsalen)(PPh_3). Epr data show that the effect of the PPh_3 is to raise the energy of the d_{z^2} orbital relative to d_{yz}, thereby moving the unpaired electron from d_{yz} to d_{z^2} [79a].

3.2. Ligand dissociation and substitution

Mononuclear Rh(II) complexes possess structural and electronic features that make them generally susceptible to ligand substitution reactions. Four-coordinate (15-electron) Rh(II) complexes are normally planar with axial sites potentially open to attack by incoming ligands (depending on the extent of steric hindrance by coordinated ligands), making these systems vulnerable to associative substitution. Five-coordinate Rh(II) complexes possess the 17-electron configuration often linked to substitutional lability and, depending on the steric demands of coordinated ligands, may be vulnerable to associative attack at the vacant site. Six-coordinate (19-electron) Rh(II) complexes are expected to be labile, both because of the Jahn–Teller effect and because dissociation of a ligand removes antibonding electron density by reducing the valence electron count at Rh to less than 18.

The four-coordinate complex $Rh(C_6Cl_5)_2(COD)$ readily loses COD by substitution with L ≡ $P(OPh)_3$, $P(OMe)_3$, PPh_3, py, dppe/2 or dppm/2 [73]:

$$Rh(C_6H_5)_2(COD)+2L\rightarrow Rh(C_6Cl_5)_2L_2+COD \quad (1)$$

Reaction of ^{t}BuNC with $Rh(2,4,6\text{-}^iPr_3C_6H_2)_2(tht)_2$ involves reduction to Rh(I) and formation of an imidoacyl ligand:

$$Rh(R)_2(tht)_2+4CN^tBu\rightarrow 2tht+Rh(CN^tBu)_3[C(=N^tBu)R]+R^{\cdot} \quad (2)$$

but the reaction (R ≡ 2,4,6-^{i}Pr$_3$C$_6$H$_2$) undoubtedly begins with simple substitution of tht by isocyanide [72].

The complex $Rh(NH_3)_4^{2+}$, produced by pulse radiolysis of a series of Rh(III) ammine complexes, is observed to aquate in two substitution steps, giving $Rh(NH_3)_3(H_2O)^{2+}$ and finally $Rh(NH_3)_2(H_2O)_2^{2+}$ [100].

Several six-coordinate (19-electron) Rh(II) complexes are observed to undergo ligand dissociation reactions. $Rh(\eta^3\text{-TMPP})_2^{2+}$ adds CNR (R ≡ ^{t}Bu, ^{i}Pr) to give the

complex $Rh(\eta^1\text{-TMPP})_2(CNR)_2^{2+}$ in a reaction where loss of four methoxy groups accompanies coordination of two isocyanide ligands [67].

$Rh(NH_3)_5(H_2O)^{2+}$, $Rh(NH_3)_5Cl^+$, and $Rh(NH_3)_4Br_2$, formed by photolysis [101] or pulse radiolysis [100] of Rh(III) ammine complexes, rapidly lose two ligands to form the reactive intermediate $Rh(NH_4)_4^{2+}$.

Electrochemically generated $Rh(py)_4Cl_2$ rapidly loses py and Cl^- to form $Rh(py)_3Cl^+$ prior to dimerization [102].

Photolytically produced $Rh(bipy)_3^{2+}$ rapidly loses bipy to give the reactive intermediate $Rh(bipy)_2^{2+}$ [103]. When $Rh(N{-}N)_3^{2+}$ (N—N ≡ bipy, phen) is electrochemically produced in the presence of MeCN or Cl^-, rapid substitution reactions

$$Rh(N{-}N)_3^{2+} + MeCN \rightarrow N{-}N + Rh(N{-}N)_2(MeCN)^{2+} \quad (3)$$

$$Rh(N{-}N)_3^{2+} + Cl^- \rightarrow N{-}N + Rh(N{-}N)_2Cl^+ \quad (4)$$

occur to form 17-electron products [96,97]. Similarly, electrochemically generated $Rh(N{-}N)_2Cl_2$ quickly loses Cl^- to give $Rh(N{-}N)_2Cl^+$ [96,97].

$RhCl_3(NO)(PPh_3)_2$ is prepared by displacing ethanol from $RhCl_3(NO)(EtOH)_n$ ($n=1$ or 2) with excess PPh_3 [84].

The phthalocyanine (pc) (**VIII**) complexes $Rh(pc)Cl(L)^-$ (L ≡ py, DMSO), formed by electrochemical reduction of Rh(pc)(L)Cl, dissociate L and Cl^- to form Rh(pc) prior to rapid dimerization [85].

3.3. Dimerization

Given the unpaired electron in mononuclear rhodium(II) ($4d^7$) compounds, dimerization is expected to be an important and in many cases a favored process. Indeed, the vast majority of stable Rh(II) compounds are diamagnetic dimers with four-coordinate or five-coordinate monomer units joined by Rh—Rh bonds [7,8]. Dimerization may also occur by ligand atom coupling if the unpaired electron is sufficiently delocalized into relatively high energy ligand-centered orbitals.

The ground state structures of Rh(II) porphyrin compounds with relatively unencumbered porphyrin ligands are dimeric, e.g. $[Rh(OEP)]_2$, $[Rh(TPP)]_2$, $[Rh(TXP)]_2$. Complexes of porphyrin ligands with very bulky substituents are monomeric in solution, e.g. Rh(TMP), Rh(TTEPP), Rh(TTiPP). Line broadening in ^1H nuclear magnetic resonance (NMR) spectra of $[Rh(TXP)]_2$ solutions gives evidence for a monomer–dimer equilibrium

$$2Rh(TXP) \rightleftharpoons [Rh(TXP)]_2 \quad (5)$$

and an Rh—Rh bond energy of 12 kcal mol^{-1} was estimated from a temperature dependence study [39]. A similar study of $[Rh(OEP)]_2$ predicted an Rh—Rh bond energy of 16.5 kcal mol^{-1} [28,29], confirming that the dimeric product (e.g. Eq. (5)) becomes more favored for less bulky porphyrins.

Rh(TPP), generated by photolysis of $[Rh(TPP)]_2$ at 77 K in 2-Me-THF [31], by flash photolysis of $(\mu\text{-TPP})[Rh(CO)_2]_2$ in benzene [31,32] or by electrochemical

reduction of $Rh(TPP)(NHMe_2)_2^+$ in THF [33,98,104], dimerizes rapidly in the absence of other reagents to $[Rh(TPP)]_2$.

Reaction of Rh(TMP) with CO gives Rh(TMP)(CO) which partially dimerizes [34,41,42]:

$$2Rh(TMP)(CO) \rightleftharpoons (TMP)Rh-C(=O)-C(=O)-Rh(TMP) \quad (6)$$

When CO reacts with $[Rh(TXP)]_2$, the analogous diketone product is formed completely and the presumed intermediate Rh(TXP)(CO) is not detected [34,42,43]. For the less bulky porphyrin OEP, the presumed intermediate Rh(OEP)(CO) gives primarily the monoketone product (OEP)Rh−C(=O)−Rh(OEP) [42,44–46]. The delocalization of unpaired spin density on to the CO ligand observed in EPR studies [35] is consistent with formation of these CO-coupled dimers.

Similarly, reaction of the bulky Rh(TTiPP) with C_2H_4 (0.3 atm) at 90 K gives a monomer adduct which dimerizes slowly by ligand coupling [35,36]:

$$2Rh(TTiPP)(C_2H_4) \rightarrow (TTiPP)Rh-(CH_2)_4-Rh(TTiPP) \quad (7)$$

The same reaction with the less encumbered Rh(TTEPP) gives rapid formation of the μ-$(CH_2)_4$ dimer, while the still less encumbered Rh(TMP) gives the μ-$(CH_2)_2$ dimer (TMP)Rh−CH_2CH_2−Rh(TMP). The monomer adducts $Rh(TTEPP)(C_2H_4)$ and $Rh(TMP)(C_2H_4)$ are not detected [35,36]. Clearly, for both CO and C_2H_4, the formation of monomeric complexes is facilitated by increased steric hindrance. Even when bridged binuclear complexes occur, the number of bridging units (−C(=O)− or $-CH_2CH_2-$) increases as the steric demands of the porphyrin increase.

The tetra-^{t}butyl-substituted salen (**IV**) complex Rh(ttbsalen) reacts with CO and C_2H_4 in a manner similar to that of the less bulky porphyrin complexes. Reaction with CO in benzene produces the monoketone (ttbsalen)Rh−C(=O)−Rh(ttbsalen), while reaction with C_2H_2 gives (ttbsalen)Rh−CH_2CH_2−Rh(ttbsalen) [79a].

The phosphine complexes $RhX_2(PR_3)_2$ (X≡halide) show evidence of Rh−Rh interaction as the steric bulk of PR_3 decreases. Thus $RhCl_2(P^o tol_3)_2$ appears to be entirely monomeric, but $RhCl_2(PPh^o tol_2)_2$ has μ_{eff} well below the spin-only value for a single unpaired electron [51]. The complexes $RhCl_2(PR^t Bu_2)_2$ (R≡Me, Et, Pr) also have low μ_{eff} values in the solid state [54,55], but $RhCl_2(PMe^t Bu_2)_2$ has $\mu_{eff} \equiv 2.12$ and appears monomeric in CH_2Cl_2 solution [55].

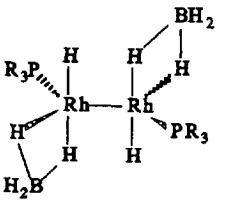
$RhCl_2(P^o tol_3)_2$ reacts with excess $NaBH_4$ in the presence of one equivalent of $P^o tol_3$ in EtOH to give the diamagnetic dimer $[RhH(BH_4)(P^o tol_3)]_2$, believed to have structure **XIV** or **XV** [105].

Both complexes $Rh(\eta^5-C_5H_5)_2$ and $Rh(\eta^5-C_5Me_5)(\eta^5-C_5H_5)$ dimerize at room temperature to give the ligand-coupled Rh(I) species **XI** (Section 2.2) [89,90,92,93].

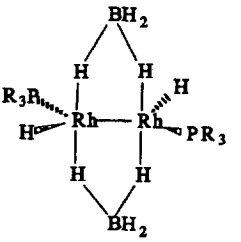
The conformational and electronic properties of the crown thioether ligand 9S3 stabilize the complex $Rh(9S3)^{2+}$, but dimerization is observed to occur slowly (eq 8) [75]:

$$2Rh(933)^{2+} \rightleftharpoons [Rh(9S3)]_2^{4+} \quad (8)$$

The complex $Rh(12S3)^{2+}$ is somewhat more reactive, presumably because the larger chelate rings allow less restricted access to the metal [76].



XIV



XV

$Rh(dmgH)_2(PPh_3)$, produced by flash photolysis of $Rh(^iPr)(dmgH)_2(PPh_3)$, is observed to dimerize rapidly ($k \approx 2 \times 10^7$ l/mol^{-1} s^{-1}) to $[Rh(dmgH)_2(PPh_3)]_2$ [106,107].

The phthalocyanine complex Rh(pc), produced by electrochemical reduction of Rh(pc)Cl(py) or Rh(pc)Cl(DMSO) followed by dissociation of Cl^- and py or DMSO, dimerizes rapidly to $[Rh(pc)]_2$ [85].

Solid state EPR and magnetic moment data suggest that $[Rh(salen)]_2$ is partially dissociated into the monomer Rh(salen) [79]:

$$2Rh(salen) \rightleftharpoons [Rh(salen)]_2 \tag{9}$$

A similar dimerization equilibrium occurs for the tetra-^{t}butyl-substituted salen complex Rh(ttbsalen) in benzene solution [79a,b].

$Rh(py)_4Cl_2$, generated electrochemically from $Rh(py)_4Cl_2^+$, can lose py and Cl^- sequentially to give the presumed intermediate $Rh(py)_3Cl^+$, which rapidly dimerizes to $[Rh(py)_3Cl]_2^{2+}$ in solution [102].

3.4. Disproportionation

In view of the preponderance of stable Rh(I) and Rh(III) compounds, disproportionation of mononuclear Rh(II) complexes is expected to occur readily unless particular features of the ligands stabilize Rh(II) or destabilize Rh(I) and/or Rh(III).

The adducts Rh(TMP)L, prepared in solution at 90 K [35], disproportionate especially readily according to

$$2Rh(TMP)L \rightarrow Rh(TMP)^- + Rh(TMP)L_2^+ \tag{10}$$

when L is a strong σ donor ligand (e.g. py), because L repels and destabilizes the unpaired electron in the d_{z^2} orbital to such an extent that electron transfer occurs via lower energy porphyrin ligand molecular orbitals [35]. Analogous products occur when py reacts with the dimer $[Rh(OEP)]_2$ [108], but in this case attack of py at an axial site of the dimer to induce cleavage of the Rh—Rh bond is probably an important step in the mechanism [80].

Thermolysis of $RhCl_2(P^otol_3)_2$ in $MeOCH_2CH_2OH$ produces a set of products

that can be rationalized in terms of a preliminary disproportionation reaction [51]

$$2RhCl_2(P^otol_3)_2 \rightarrow RhCl(P^otol_3)_2 + RhCl_3(P^otol_3) + P^otol_3 \quad (11)$$

The unsaturated product "$RhCl_3(P^otol_3)$" loses HCl to form the cyclometallated trimer $\{RhCl_2[\eta^2-CH_2C_6H_4P(^otol_2)]\}_3$, while the unsaturated product "$RhCl(P^otol_3)_2$" can either be trapped by CO to give $RhCl(CO)(P^otol_3)_2$ or lose H_2 to give the stilbene complex $RhCl[\eta^4\text{-}^otol_2P(C_6H_4CH{=}CHC_6H_4)P^otol_2]$ [51].

The complex $RhCl_2(CO)(Pcy_3)_2$, prepared in the solid state by treatment of $RhCl_2(Pcy_3)_2$ with CO, disproportionates readily according to the proposed reaction [99]

$$2RhCl_2(CO)(Pcy_3)_2 \rightarrow RhCl(CO)(Pcy_3)_2 + RhCl_3(CO)(Pcy_3)_2 \quad (12)$$

However, the formulation given for the Rh(III) product in this reaction seems inconsistent with observation of an apparent steric barrier to forming $RhX_3(Pcy_3)_2$ in another study [61]. Formation of the Rh(III) product with loss of Pcy_3, giving $RhCl_3(CO)(Pcy_3)$, seems more plausible.

Reaction of the stable complex $Rh(TMPP)_2^{2+}$ with CO in CH_2Cl_2 leads to disproportionation, presumably from the unstable intermediate $Rh(TMPP)_2(CO)_2^{2+}$ [65,66]:

$$Rh(TMPP)_2(CO)_2^{2+} + Rh(TMPP)_2^{2+} \rightarrow Rh(TMPP)_2(CO)_2^{+} + Rh(TMPP)_2^{3+} \quad (13)$$

The Rh(I) product $Rh(TMPP)_2(CO)_2^+$ has been structurally characterized and contains *trans*-η^1-TMPP ligands, but this material loses one CO to give the more stable product $[Rh(\eta^2\text{-TMPP})(\eta^1\text{-TMPP})(CO)]^+$, which has *trans*-phosphorus atoms [65].

In contrast, when $Rh(TMPP)_2^{2+}$ is reacted with the bulky isocyanides CN^tBu or CN^iPr, a stable Rh(II) product $Rh(TMPP)_2(CNR)_2^{2+}$ is formed [67]. Reaction with the less bulky CNMe results in disproportionation as is observed for CO (Eq. 13).

$RhH(CO)(PPh)_3^+$, generated electrochemically from $RhH(CO)(PPh_3)_3$ in the presence of excess PPh_3 at −35 °C, disproportionates in MeCN according to [109]:

$$2RhH(CO)(PPh_3)_3^+ + MeCN + PPh_3 \rightarrow RhH(CO)(PPh_3)_3 + RhH(PPh_3)_4(MeCN)^{2+} + CO \quad (14)$$

Loss of CO is consistent with the high C—O stretching frequency (2060 cm^{-1}) observed in the IR spectrum of the Rh(II) compound.

Disproportionation of $Rh(bipy)_3^{2+}$, formed either from photolysis of $Rh(bipy)_3^{3+}$ in the presence of $Ru(bipy)_3^{2+}$ [103] or by pulse radiolysis of $Rh(bipy)_3^{3+}$ in aqueous solution [110], is believed to be triggered by preliminary loss of bipy from $Rh(bipy)_3^{2+}$, producing $Rh(bipy)_2^{2+}$ and the four-coordinate environment favored by Rh(I) [103,110]:

$$Rh(bipy)_2^{2+} + Rh(bipy)_3^{2+} \rightarrow Rh(bipy)_2^{+} + Rh(bipy)_3^{3+} \quad (15)$$

Pulse radiolysis of $Rh(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5(H_2O)^{3+}$, or $Rh(NH_3)_4Br_2^+$ in water

produces $Rh(NH_3)_4^{2+}$, which reacts in a variety of ways, one of which is rapid ($k \approx 1.4 \times 10^7$) disproportionation [100]:

$$2Rh(NH_3)_4^{2+} + 2H_2O \rightarrow Rh(NH_3)_4^{+} + Rh(NH_3)_4(H_2O)_2^{3+} \quad (16)$$

3.5. One-electron oxidation or reduction

The stability of Rh(III) ($4d^6$) or Rh(I) ($4d^8$) relative to Rh(II) often allows facile one-electron oxidation or reduction reactions of Rh(II) compounds to occur. Thus redox reactions of Rh(II) compounds with conventional two-electron oxidative addition reagents are non-complementary and unusual redox mechanisms might be expected for Rh(II) compounds. In addition to reactions with chemical oxidants and reductants, an increasing number of Rh(II) oxidation and reduction reactions have been carried out electrochemically, as cyclic voltammetry has gained popularity among coordination chemists.

3.5.1. Oxidation by radical abstraction

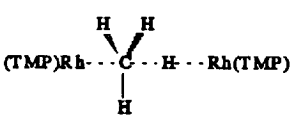
The presence of the unpaired electron in a sufficiently high energy orbital lends a strong radical character to many Rh(II) compounds. Radical abstraction by Rh(II) would accomplish its formal oxidation to Rh(III). Oxidation reactions of Rh(II) complexes with products that appear to have resulted from homolytic bond cleavage are included in this category. In many cases, however, the mechanistic details of the reactions have not been experimentally verified, and those reactions are safely regarded as "radical abstractions" only in a formal sense.

3.5.1.1 Porphyrin complexes. Reactions of metalloradical porphyrin complexes with organic substrates have been studied extensively. Rh(TMP) is found to activate CH_4 (1–10 atm) in C_6H_6 (296–393 K) according to [38,39]

$$2Rh(TMP) + CH_4 \rightarrow Rh(H)(TMP) + Rh(CH_3)(TMP) \quad (17)$$

The reaction is found to be second-order in Rh(TMP) and first order in CH_4, with a small $\Delta H^{\ddagger}$ (7 kcal mol^{-1}), a large negative $\Delta S^{\ddagger}$ (−39 e.u.) and a pronounced isotope effect ($k_H/k_D = 8.6$ at 298 K). On the basis of these results a termolecular four-center transition state (**XVI**) is proposed [38,39].

It is significant that aromatic hydrogen atoms of the solvent benzene are not activated in this reaction, presumably because of the kinetic barrier to forming the very sterically hindered transition state that would be required. Reaction with toluene



XVI

further illustrates the selectivity for aliphatic C—H activation [39]:

$$2Rh(TMP)+CH_3C_6H_5 \rightarrow Rh(H)(TMP)+Rh(CH_2C_6H_5)(TMP) \quad (18)$$

A study of the reaction of Rh(TMP) with H_2 (0.2–1.0 atm) in benzene (296–373 K) acording to

$$2Rh(TMP)+H_2 \rightarrow 2Rh(H)(TMP) \quad (19)$$

led to similar results and mechanistic conclusions, i.e. a proposed termolecular, four-center transition state (TMP)Rh··H··H··Rh(TMP) [37].

Additional support for this mechanism is provided by a study of the reactivity of the rhodium(II) bimetalloradical biporphyrin complex ·Rh(por—$O(CH_2)_6$-O—por)Rh· (por≡*meso*-tris(mesityl)mono(phenyl)porphyrinato, where the oxygen atoms of the $O(CH_2)_6O$ tether attach to each *meso*-phenyl group in the 4 position) [111]. The biporphyrin ligand has essentially the same steric requirements as TMP, so that Rh(II)—Rh(II) bonding is prohibited. Reaction of this biradical with H_2 (296 K, 0.7 atm) in benzene produces HRh(por—$O(CH_2)_6O$—por)RhH, while reaction with CH_4 (296 K, 1 atm) gives HRh(por—$O(CH_2)_6O$—por)Rh—CH_3 as the sole product. The rates of these reactions are greatly enhanced relative to reaction with monomeric Rh(TMP): 670 times faster for reaction with H_2 and 130 times faster for CH_4. The pronounced rate enhancements, the nature of the products and the fact that the reactions are first order in bimetalloradical complex (second-order overall with $k=0.93\ M^{-1}\ s^{-1}$ for H_2 and $k=8.6\times10^{-3}$ for CH_4) argue for bimolecular formation of a four-center transition state similar to **XVI**. The unfavorable termolecular process is avoided by preorganizing the two metalloradical units within one molecule [111].

Reaction of Rh(TMP) with isocyanides illustrates the influence of crowding in the transition state [35,45]. Whereas cleavage of the CH_3—N bond of methyl isocyanide occurs rapidly at room temperature according to

$$2Rh(TMP)+CNCH_3 \rightarrow Rh(CN)(TMP)+Rh(CH_3)(TMP) \quad (20)$$

reaction with CN^{t}Bu is markedly slower, and cleavage of CN(2,6-$Me_2C_6H_3$) does not occur at all.

Rh(TMP) cleaves CH_3 from $P(OMe)_3$ according to

$$2Rh(TMP)+P(OMe)_3 \rightarrow Rh(CH_3)(TMP) + Rh[P(=O)(OMe)_2](TMP) \quad (21)$$

but does not react with $P(OPh)_3$ [35], another indication of the steric difficulty of activating bonds to aromatic carbon atoms.

Rh(TMP) removes an allylic H from methyl methacrylate according to (see Section 3.5.2)

$$2Rh(TMP)+CH_2{=}C(CO_2Me)CH_3 \rightarrow Rh(H)(TMP) + Rh[CH_2C(CO_2Me){=}CH_2](TMP) \quad (22)$$

but it does not attack the olefinic double bond because of steric hindrance at one of the olefinic C atoms [112].

The CO adduct Rh(TMP)(CO) gains one H from H_2 and $HSnBu_3$ to give a formyl complex:

$$2Rh(TMP)(CO)+H_2 \rightarrow 2Rh[C(=O)H](TMP) \quad (23)$$

$$2Rh(TMP)(CO)+2HSnBu_3 \rightarrow 2Rh[C(=O)H](TMP)+Bu_3Sn-SnBu_3 \quad (24)$$

The products are consistent with significant delocalization of unpaired electron density on to the CO carbon atom [35].

Rh(TPP), which is electrochemically generated from $Rh(TPP)(NHMe_2)_2^+$ in THF, abstracts alkyl groups from a wide variety of organic halides ($RX \equiv CH_2X_2$, CHX_3, CX_4, CH_3I, CH_3CH_2X, n-PrX, n-BuX, ^{i}BuCl, ^{t}BuCl, and n-$C_5H_{11}X$; $X \equiv Cl$, Br, I) according to

$$Rh(TPP)+RX \rightarrow Rh(R)(TPP)+X^{\cdot} \quad (25)$$

but no Rh(X)(TPP) products are observed in these reactions [104,33]. No reaction of Rh(TPP) is observed with the aromatic halides C_6H_5X ($X \equiv Cl$, Br, I) [33], consistent with the apparent difficulty of activating bonds to aromatic carbon atoms in other studies (see above).

When Rh(TPP) is electrochemically generated in the presence of $RC \equiv CH$ ($R \equiv n$-C_3H_7, n-C_4H_9) in THF, abstraction of $R^{\cdot}$ is believed to occur intramolecularly from coordinated alkyne (98):

$$Rh(TPP)(RC \equiv CH) \rightarrow Rh(R)(TPP)+\text{“}^{\cdot}C \equiv CH\text{”} \quad (26)$$

Dimeric porphyrin compounds react to form some of the same products as those observed for the mononuclear complexes. Dissociated monomer radicals in equilibrium with dimer are generally assumed to be implicated in the mechanisms. For example, both $[Rh(TXP)]_2$ and $[Rh(OEP)]_2$ react with CH_4 [39] and $CH_3C_6H_5$ [39,113,114] to give Rh(H)(por) and Rh(R)(por), but these reactions are kinetically and thermodynamically less favorable than reactions with the mononuclear complexes, and $[Rh(OEP)]_2$ (bond energy 16.5 kcal mol^{-1}) reacts much less readily than $[Rh(TXP)]_2$ (bond energy 12 kcal mol^{-1}) [39].

The following reactions of $[Rh(OEP)]_2$ are believed to require the participation of dissociated Rh(OEP): with H_2/CO to give Rh[C(=O)H](OEP) [115,116]; with $P(OMe)_3$ to give $Rh(CH_3)(OEP)$ and $Rh[P(=O)(OMe)_2](OEP)$ [117]; with CO and H_2O to give Rh[C(=O)H](OEP) and CO_2 [118]; with CNBu and H_2O to give Rh[C(=NBu)H](OEP) and BuNCO [118]; with RC_6H_5 ($R \equiv$ Me, Et, ^{n}Pr, ^{i}Pr) to give Rh[C(R′)(R″)C_6H_5](OEP) and Rh(H)(OEP) (attack occurs at the benzylic hydrogen followed by rearrangement to a more stable product; ^{t}BuC_6H_5 does not react) [114]; with $C_6H_5CH_2Br$ to give RhBr(OEP) and $Rh(CH_2C_6H_5)(OEP)$ [119]; with $HSnBu_3$ to give Rh(H)(OEP) and $Rh(SnBu_3)(OEP)$ [119]; with $C_6H_5CH=CH_2$ and Rh(H)(OEP) to give $Rh(CH_2CH_2C_6H_5)(OEP)$ via the radical intermediate $Rh(CH_2C^{\cdot}HC_6H_5)(OEP)$ [119]; with CO and Rh(H)(OEP) to give Rh[C(=O)H](OEP) via the intermediate Rh(OEP)(CO) [119]; with HC≡CR

(R≡H, Ph) to give (OEP)Rh−CH=C(R)−Rh(OEP) [120]; with $CH_2=C(CO_2Me)CH_3$ to give Rh(H)(OEP) and $Rh[CH_2C(CO_2Me)=CH_2](OEP)$ [112]; with H_2/CNR (R≡2,6-$Me_2C_6H_3$) to give formimidoyl Rh[C(=NR)H](OEP)(CNR) [45]; with CNR (R≡"Bu, CH_3) to give Rh(R)(OEP) and Rh(CN)(OEP)(CNR) [45]; with H_2O and excess CNR in C_6H_6 to give Rh[C(=O)NHR](OEP) and Rh[C(=NR)H](OEP)(CNR) [45]; with CO and RNH_2 (R≡2,6-$Me_2C_6H_3$), "Bu) to give Rh[C(=O)NHR](OEP) and H_2 [45].

3.5.1.2. Non-porphyrin complexes. The complexes *trans*-$RhCl_2(P^tBu_2R)_2$ (R≡Me, Et, "Pr) are prepared in ethanol at room temperature, but when these complexes are refluxed in ethanol [55] or methyl ethyl ketone [54] in the presence of excess phosphine, H abstraction from solvent gives the hydrides $Rh(H)Cl_2(P^tBu_2R)_2$.

An analogous product forms when the complex $RhCl_2(P^iPr_3)_2$ reacts slowly (24 h) with H_2 in C_6H_6 [63,121]:

$$2RhCl_2(P^iPr_3)_2 + H_2 \rightarrow 2RhHCl_2(P^iPr_3)_2 \quad (27)$$

In the presence of the base $Na[N(SiMe_3)_2]$, H_2 reacts with $RhCl_2(P^iPr_3)_2$ with elimination of HCl to give the dihydride $RhH_2Cl(P^iPr_3)_2$ [63].

Exposure of $RhCl_2(Pcy_3)_2$ to H_2 similarly gives $RhHCl_2(Pcy_3)_2$ [121].

Reaction of Rh(ttbsalen) (in equilibrium with dimer) (ttbsalen≡tetra-^{t}butyl-substituted salen (**IV**)) with H_2 in benzene produces Rh(H)(ttbsalen) in a reaction entirely analogous to that of the porphyrins (Eq. (19)) [79a,b]. Unlike the porphyrins, however, the more difficult reaction with CH_4 (0.9 atm, 298 K, toluene) (Eq. (17)) does not occur. The difference is attributed to the reorganization energy necessary to move the unpaired electron from the d_{yz} to the d_{z^2} orbital in the ttbsalen complex [79a].

An Rh(II) compound such as $RhCl(OH)(PPh_3)_2$ is proposed to be an intermediate in the $RhCl(PPh_3)_3$-catalyzed decomposition of cyclohexenyl hydroperoxide. The Rh(II) compound is believed to propagate a radical chain by abstracting $^{\cdot}OH$ from ROOH [122]:

$$RhCl(OH)(PPh_3)_2 + ROOH \rightarrow RhCl(OH)_2(PPh_3)_2 + RO^{\cdot} \quad (28)$$

$RhBr_2(CO)(PMe_2Ph)_2$, a proposed intermediate in the radical chain reaction of $CBrCl_3$ with $RhBr_2(CH_2CH=CHR)(CO)(PMe_2Ph)_2$ (R≡H, Me) to give $Cl_3CCH(R)CH=CH_2$ and $RhBr_3(CO)(PMe_2Ph)_2$, generates $^{\cdot}CCl_3$ in a chain propagation step [123]:

$$RhBr_2(CO)(PMe_2Ph)_2 + CBrCl_3 \rightarrow RhBr_3(CO)(PMe_2Ph)_2 + {}^{\cdot}CCl_3 \quad (29)$$

$Rh(dmgH)_2(PPh_3)$, a transient formed in the flash photolysis of $Rh(^iPr)(dmgH)_2(PPh_3)$, reacts with a variety of alkyl halides (RX≡$CHBr_3$, CCl_4, $C_6H_5CH_2Br$, CH_2Br_2, ^iPrBr, and $CHCl_3$, arranged according to decreasing reactivity) [106]:

$$Rh(dmgH)_2(PPh_3) + RX \rightarrow Rh(X)(dmgH)_2(PPh_3) + R^{\cdot} \quad (30)$$

The same transient, generated photolytically from $Rh(^iPr)(dmgH)_2(PPh_3)$ or from

the dimer $[Rh(dmgH)_2(PPh_3)]_2$, acquires one Cl from $FeCl_3$ [107]:

$$Rh(dmgH)(PPh_3)+FeCl_3 \rightarrow RhCl(dmgH)_2(PPh_3)+FeCl_2 \quad (31)$$

$Rh(NH_3)_4^{2+}$ and I_2^-, formed photolytically from $Rh(NH_3)_5(H_2O)^{3+}$ and I^- in aqueous solution, react to form stable products [101]:

$$Rh(NH_3)_4^{2+}+I_2^-+H_2O \rightarrow \textit{trans}\text{-}RhI(NH_3)_4(H_2O)^{2+}+I^- \quad (32)$$

The oxidative addition of "hindered" iodides RI ($R \equiv {}^iPr$, neopentyl, 2,2-dimethylbutyl) to Rh(I)(PPDOBF$_2$) (**XVII**) to give *trans*-Rh(R)(I)(PPDOBF$_2$) is believed to occur by formation of the Rh(II) iodide which combines with R$^\cdot$ within solvent cages [124]:

$$Rh(I)(PPDOBF_2)+R^\cdot \rightarrow Rh(R)(I)(PPDOBF_2) \quad (33)$$

$Rh(tfa)_2(ROH)_2$ ($R \equiv Et$, ^iPr), a transient detected during the photolytic decomposition of *trans*-$Rh(tfa)_3$, is believed to undergo an intramolecular radical abstraction reaction [125]:

$$Rh(tfa)_2(ROH)_2 \rightarrow Rh(H)(tfa)_2(ROH)+RO^\cdot \quad (34)$$

3.5.2. Other oxidation reactions

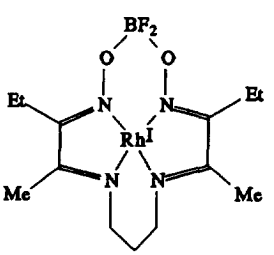
3.5.2.1. Chemical oxidants. Reactions of rhodium(II) porphyrins with olefins produce alkyl-bridged binuclear Rh(III) compounds. Rh(TMP) reacts with C_2H_4 [35,36] and $CH_2=CHCO_2H$ [112] to form similar products ($R \equiv H$, CO_2H):

$$2Rh(TMP)+CH_2=CHR \rightarrow (TMP)Rh-CH_2CH(R)-Rh(TMP) \quad (35)$$

For $CH_2=CHCO_2R$ ($R \equiv Me$, Et), steric interaction of the $-CO_2R$ group with the bulky TMP ligands is significant enough to give the μ-C_4 product $(TMP)Rh-CH_2CH(CO_2R)-CH(CO_2R)CH_2-Rh(TMP)$ [112].

The adduct Rh(TMP)(CO) shows similar reactivity with styrene [34]:

$$2Rh(TMP)(CO)+CH_2=CHC_6H_5 \rightarrow$$
$$(TMP)Rh-C(=O)CH_2CH(C_6H_5)C(=O)-Rh(TMP) \quad (36)$$



XVII

Dimeric $[Rh(OEP)]_2$ also reacts with olefins, presumably via dissociated monomer Rh(OEP), to give (OEP)Rh−$CH_2CH(R)$−Rh(OEP) (R ≡ Me [126], C_6H_5 [119], CO_2R' (R′ ≡ H, Me, Et) [112]).

Dissociated Rh(OEP) is implicated in other oxidation reactions of $[Rh(OEP)]_2$. Reaction with CO gives the metallamonoketone (OEP)Rh−C(=O)−Rh(OEP) as primary product [34,42,44–46]. Reaction with NO gives Rh(III)(OEP)(NO^-) [127]. Reaction with O_2 at −80 °C in toluene gives Rh(III)(OEP)(O_2^-), which is converted to (OEP)Rh−O−O−Rh(OEP) upon warming to 20 °C [30,127].

$Rh(mnt)_2^{2-}$ is oxidized by CH_3I in THF to an Rh(III) polymeric species $[Rh(mnt)_2]_n^{n-}$, although the other products were not identified [128].

Photolytically produced $Rh(NH_3)_4^{2+}$ reacts rapidly with O_2 to give the reactive superoxo species Rh(III)(O_2^-)$(NH_3)_4(H_2O)^{2+}$ [100,129].

In a pulse radiolysis study the reaction of $Rh(bipy)_3^{2+}$ with O_2 to give $Rh(bipy)_3^{3+}$ and O_2^- was observed [110].

$Rh(bipy)_3^{2+}$, produced by photolysis, is believed to reduce H_2O in a reaction catalyzed by Pt [103]:

$$2Rh(bipy)_3^{2+} + 2H_2O \rightarrow 2Rh(bipy)_3^{3+} + H_2 + 2OH^- \quad (37)$$

Electrochemically generated $Rh(sep)^{2+}$ is believed to reduce H_2O similarly [71].

The photolytic transient Rh(pc) is rapidly reoxidized by a variety of oxidants in CH_3CN solution [130]:

$$Rh(pc) + Ox + H^+ + 2CH_3CN \rightarrow Rh(pc)(CH_3CN)_2^+ + HOx \quad (38)$$

3.5.2.2. Electrochemical oxidation. Several one-electron oxidations of Rh(II) species have been observed in cyclic voltammetry studies. These include oxidation of $Rh(TPP)R^-$ to Rh(TPP)R (R ≡ ^{n}Pr, ^{n}Bu, n-C_5H_{11}, n-C_6H_{13}) [98]; of $Rh(np_3)(C{\equiv}CPh)^+$ to $Rh(np_3)(C{\equiv}CPh)^{2+}$ [68]; of Rh(triphos)($E_2C{=}O$) to Rh(triphos)($E_2C{=}O$)$^+$ (E ≡ S, Se) [70]; of $RhH(CO)(PPh_3)_3^+$ in CH_3CN to $RhH(CO)(PPh_3)_3(CH_3CN)^{2+}$ [109]; of $Rh(\eta^5\text{-}C_5H_5)_2$ to $Rh(\eta^5\text{-}C_5H_5)_2^+$ [92]; of $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}L)$ to $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}L)^+$ (L ≡ C_5H_5, C_5Me_5, C_9H_7) at −35 °C [89]; of $(\eta^5\text{-}C_5H_5)Rh[SC_2(CF_3)_2]^-$ to $(\eta^5\text{-}C_5H_5)Rh[SC_2(CF_3)_2]$ [82]; of $Rh(9S3)_2^{2+}$ to $Rh(9S3)_2^{3+}$ [75,76]; and of $Rh(py)_4Cl_2$ to $Rh(py)_4Cl_2^+$ [102].

3.5.3. Reduction reactions

Several chemical and electrochemical examples of Rh(II) reduction reactions have been reported.

The 19-electron Rh(II) complex $Rh(\eta^5\text{-}C_9H_7)(CH_3)[Ph_2PCH_2CH(CH_3)PPh_2]$, generated electrochemically, decomposes rapidly to an Rh(I) product [87]:

$$Rh(\eta^5\text{-}C_9H_7)(CH_3)[Ph_2PCH_2CH(CH_3)PPh_2] \rightarrow$$
$$Rh(\eta^5\text{-}C_9H_7)[Ph_2PCH_2CH(CH_3)PPh_2] + {}^{\cdot}CH_3 \quad (39)$$

Some reduction of $RhCl_3(NO)(PPh_3)_2$ to $RhCl_2(NO)(PPh_3)_2$ accompanies recrystallization from $CHCl_3$/EtOH [84].

Reaction of $Rh(2,4,6\text{-}^{i}Pr_3C_6H_2)_2(tht)_2$ with $^{t}BuNC$ gives an Rh(I) iminoacyl complex and free $2,4,6\text{-}^{i}Pr_3C_6H_3$ (following abstraction of H$^{\cdot}$ from solvent) (Eq. (2)) [72].

Dimerization of $Rh(\eta^5\text{-}C_5H_5)_2$ and $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)$ results in formal reduction to Rh(I) in the ligand-coupled dimers **XI** (Section 2.2) [89,90].

The sandwich complex $Rh(C_6Me_6)_2^{2+}$ can be reduced to $Rh(C_6Me_6)_2^{+}$ by Zn/HCl or $CrCl_2$ [74].

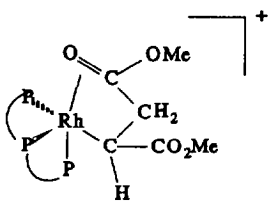
Several one-electron reductions of Rh(II) complexes have been observed in electrochemical studies. These include reduction of $Rh(TMPP)_2(CNR)_2^{2+}$ to $Rh(TMPP)_2(CNR)_2^{+}$ (R ≡ ^{t}Bu, ^{i}Pr) [67]; of $Rh(np_3)(C{\equiv}CPh)^{+}$ to $Rh(np_3)(C{\equiv}CPh)$ [68]; of $Rh(xp_3)(CN)^{+}$ to $Rh(xp_3)(CN)$ (x ≡ N, P) [69]; of Rh(triphos)[η^1:η^2-$CH(CO_2Me)CH_2C(=O)OMe]^{+}$ (**XVIII**) to RhH(triphos)[η^2-$CH(CO_2Me)$=$CHCO_2Me$] [131]; of $RhH(CO)(PPh_3)_3^{+}$ to $RhH(CO)(PPh_3)_3$ [109]; of $Rh(C_6Cl_5)_2(COD)$ to $Rh(C_6Cl_5)_2(COD)^{-}$ [73]; of $Rh(C_6Cl_5)_2[P(OPh)_3]_2$ to $Rh(C_6Cl_5)_2[P(OPh)_3]_2^{-}$ [73]; of $Rh(2,4,6\text{-}^{i}Pr_3C_6H_2)_2(tht)_2$ to $Rh(2,4,6\text{-}^{i}Pr_3C_6H_2)_2(tht)_2^{-}$ [72]; of $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2^{+}$ to $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$ [88]; of $Rh(\eta^5\text{-}C_5H_5)_2$ to $Rh(\eta^5\text{-}C_5H_5)_2^{-}$ [92]; of $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-L})$ to $Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-L})^{-}$ (L ≡ C_5H_5, C_5Me_5, C_9H_7) [89]; of $Rh(\eta^6{:}\eta^1\text{-}Ph_2PCH_2CH_2OC_6H_5)(\eta^1\text{-}Ph_2PCH_2CH_2OC_6H_5)^{2+}$ (**XIX**) to $Rh(\eta^6{:}\eta^1\text{-}Ph_2PCH_2CH_2OC_6H_5)(\eta^1\text{-}Ph_2PCH_2CH_2OC_6H_5)^{+}$ [132]; of $Rh(9S3)_2^{2+}$ to $Rh(9S3)_2^{+}$ [77]; of $Rh(N{-}N)_2Cl_2$ to $Rh(N{-}N)_2Cl + Cl^{-}$ (N—N ≡ bipy, phen) [96,97]; and of $Rh(N{-}N)_3^{2+}$ in CH_3CN to $Rh(N{-}N)_2(CH_3CN)^{+} + N{-}N$ (N—N ≡ bipy, phen) [96,97].

3.6. Catalysis

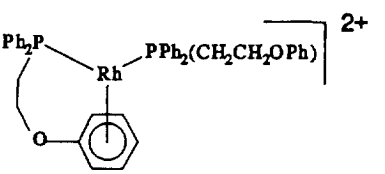
Rhodium compounds have long been used as catalysts for a variety of reactions, functioning most often by mechanisms that interconvert Rh(I) and Rh(III) in oxidative addition and reductive elimination steps. Rhodium (II) compounds must necessarily employ different oxidation or reduction mechanisms, but conversions to Rh(I) or Rh(III) species are normally facile processes (Section 3.5). Catalysis by rhodium (II) compounds is relatively unexplored, but a few cases have been documented.

Both $RhCl_2(P^{o}tol_3)_2$ and $RhCl_2(Pcy_3)_2$ have been found to catalyze hydrosilation of 1-octene according to ($X_3 = Et_3$, Me_2Ph, $(OEt)_3$, $Me(OEt)_2$),

$$^{n}C_6H_{13}CH{=}CH_2 + HSiX_3 \rightarrow {}^{n}C_6H_{13}CH_2CH_2SiX_3 \qquad (40)$$



XVIII



XIX

Table 1
Mononuclear Rh(II) compounds

Formula	Stability[a]	Preparation	Comments	Ref(s).
Porphyrin-containing compounds				
Rh(TTiPP)	A	Photolysis of Rh(TTiPP)(R)		[34]
Rh(TTEPP)	A	Photolyis of Rh(TTEPP)(R)		[35,36]
Rh(TMP)	A	Photolysis of Rh(TMP)(CH_3)		[37–39]
Rh(TPP)py·$2H_2O$	A	Photolysis of (μ-TPP)$Rh_2(CO)_4$ in presence of py		[136]
·Rh(por—$O(CH_2)_6O$—por)Rh· (por≡ *meso*-tris(mesityl)phenylporphyrinato)	A	Photolysis of MeRh(por—$O(CH_2)_6O$—por)RhMe	Biporphyrin sterics prevents Rh—Rh bonding	[111]
Rh(TTiPP)(CO)	A	0.1–1.0 atm CO in toluene	No dimerization	[34]
Rh(TTiPP)(C_2H_4)	B	0.3 atm C_2H_4 in C_6H_6	Stabilized at 90 K	[35,36]
Rh(TMP)(CO)	B	0.1–1.0 atm CO	Minor product relative to diketone dimer	[34,41,42]
Rh(TMP)L (L≡NEt_3, $NHEt_2$, py, 2,6-Me_2Py, PEt_3, PPh_3, $AsPh_3$, CNR)	B	Rh(TMP)+L in toluene, 90 K	Stabilized at 90 K or below; EPR at 90 K	[35,45]
Rh(TXP)	B		Dimer bond $E=12$ kcal mol^{-1}	[39]
Rh(TPP)	B	Photolysis of dimer, Rh(TPP)Cl or (μ-TPP)$Rh_2(CO)_4$; electrochemical reduction of Rh(TPP)$(NHMe_2)_2^+$		[30–33,40]
Rh(TPP)$(NHMe_2)_2$	B	Electrochemical reduction of +1 Rh(III) analogue at −78°C	Unstable to dimerization at room temperature	[104,137]
Rh(TPP)(RC≡CH) (R≡n-C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13})	B	Electrochemical reduction of Rh(TPP)$(NHMe_2)_2^+$ in presence of RC≡CH		[98]
Rh(TPP)R^- (R≡n-C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13})	B	Electrochemical reduction of Rh(TPP)R		[98]
Rh(TTEPP)(C_2H_4)	D	0.25 atm C_2H_4 in C_6H_6	Unstable to μ-$(CH_2)_4$ dimerization	[35,36]
Rh(TMP)(C_2H_4)	D		Unstable to μ-$(CH_2)_2$ dimerization	[35,36]
Rh(TMP)(CH_2=$CHCO_2X$) (X≡H, Me, Et)	D		Unstable to μ-C_2 (X≡H) or μ-C_4 (X≡Me, Et) dimerization	[112]

Rh(TXP)(CO)	D	0.1 atm CO	Unstable to μ-diketone dimer	[34,42,43]
Rh(OEP)	D		Dimer bond $E=16.5$ kcal mol^{-1}	[28,29]
Rh(OEP)[P(OMe)$_3$]	D		Unstable to methyl abstraction and metal phosphonate	[117]
Rh(OETAP)py	D	[Rh(OETAP)]$_2$ + py	Rapidly adds a second py to give Rh^{III}(OETAP$^{\cdot 3-}$)py$_2$	[80]
Phosphine complexes				
RhCl$_2$(P^{o}tol$_3$)$_2$	A	RhCl$_3$ + PR$_3$ in EtOH	Trans isomer; two forms	[50,51,133]
RhCl$_2$(PPh^{o}tol$_2$)$_2$	A	RhCl$_3$ + PR$_3$	μ_{eff} low	[51]
RhCl$_2$(PR^{t}Bu$_2$)$_2$ (R ≡ Me, Et, ^{n}Pr, CH$_2$(CH$_2$)$_n$CO$_2$Et (n=1,2), CH$_2$(2-MeO-5-MeC$_6$H$_3$)	A	RhCl$_3$ + PR$_3$ in EtOH	μ_{eff} low in solid state (R ≡ Me, Et, ^{n}Pr); normal in CH$_2$Cl$_2$	[54–57]
Rh[η^2-P^{t}Bu$_2$(^{o}C$_6$H$_4$O−)]$_2$	A	RhCl$_3$ + PR$_3$	Trans isomer	[58]
RhBr$_2$[P(CH$_2$SiMe$_3$)$_3$]$_2$	A	RhCl$_3$ + LiBr + P(CH$_2$SiMe$_3$)$_3$ in EtOH		[59]
RhX$_2$(Pcy$_3$)$_2$ (X$_2$ ≡ Cl$_2$, Br$_2$, ClBr, ClI)	A	RhX$_3$ + PR$_3$ in ^{i}PrOH (X ≡ Cl, Br) or RhX(Pcy$_3$)$_2$ + X$_2$′		[60,61,121,133]
RhCl$_2$(Pcy$_3$)$_2$(CO)	A	RhCl$_2$(Pcy$_3$)$_2$ + CO in solid state	Unstable to disproportionation	[99]
RhCl$_2$(P^{i}Pr$_3$)$_2$	A	[Rh(C$_8$H$_{14}$)Cl]$_2$ + PR$_3$ + N$_2$ + *N*-chlorosuccinimide or [RhCl(P^{i}Pr$_3$)]$_n$ + CCl$_4$	X-Ray structure	[62,63,121]
"RhCl$_2$(PPh$_3$)$_2$"	A	[Rh(COD)Cl]$_2$ + PPh$_3$	X-Ray structure, but re-evaluated as *trans*-RhCl(CO)(PPh$_3$)$_2$ [158]	[52,53,138]
RhCl$_3$(NO)(PPh$_3$)$_2$	A	RhCl$_3$ + NO + PPh$_3$	Mixed with Rh(NO)Cl$_2$(PPh$_3$)$_2$; ESR rules out Rh^{IV}/NO$^-$	[84]
RhCl(*s*-bqdi)(PPh$_3$)$_2$	A	RhCl(PPh$_3$)$_2$ + *o*-phenylenediamine + O$_2$	Square pyramidal with apical PPh$_3$	[86]
RhCl(*s*-disn)(PPh$_3$)$_2$	A	RhCl(PPh$_3$)$_2$ + diaminomaleonitrile + O$_2$	Square pyramidal with apical PPh$_3$	[86]
[Rh(η^3-TMPP)$_2$](BF$_4$)$_2$	A	Rh$_2$(CH$_3$CN)$_{10}^{4+}$ + TMPP in MeOH	X-Ray structure; six-coordinated Rh with elongated axial O atoms	[64–66]
[Rh(η^1-TMPP)$_2$(CNR)$_2$](BX$_4$)$_2$ (R ≡ ^{t}Bu, ^{i}Pr; (X ≡ F, Ph)	A	Rh(TMPP)$^{2+}$ + CNR	X-Ray structure (R ≡ ^{t}Bu, X ≡ Ph); trans planar	[67]
RhCl$_2$(dppe)	A	RhCl$_2$(2-Me-allyl) + H$_2$ + dppe		[71]

Table 1 (*continued*)

Formula	Stability[a]	Preparation	Comments	Ref(s).
$RhCl_2(PDPBP)$	A	$RhCl_3$ + PDPBP	Bound to polystyrene backbone in solid state; three-coordinate Rh	[134]
$[Rh(np_3)(-C{\equiv}CPh)]BPh_4$	A	Oxidation of neutral Rh(I) analogue or reduction of +2 Rh(III) analogue; or via protonation of neutral Rh(I) analogue and vinylidene intermediate	Square pyramidal with basal N and acetylide	[68]
$Rh(pp_3)(-C{\equiv}CPh)^+$	A	Oxidation of neutral Rh(I) analogue with H^+		[68]
Rh(triphos)($S_2C{=}O$)	A	Electrochemical or chemical reduction of +1 Rh(III) analogue	Square pyramidal with basal S_2CO^{2-}	[70]
Rh(triphos)($Se_2C{=}O$)	A	Electrochemical reduction of +1 Rh(III) analogue	Square pyramidal with basal Se_2CO^{2-}	[70]
$RhH(CO)(PPh_3)_3^+$	B	Electrochemical oxidation of neutral Rh(I) analogue	Stabilized at −30°C	[109,139]
$Rh(NBD)(PDABP)_2^{2+}$ (dialkyl=Ph_2, MePh, PhMenthyl)	B	Rh(NBD)(acac) + PDABP	Bound to polysterene backbone; *cis*-phosphines; coexists with Rh(I) analogue	[135]
$Rh(np_3)(CN)^+$	B	Electrochemical oxidation of neutral Rh(I) analogue	Square pyramidal with basal CN	[69]
$Rh(pp_3)(CN)^+$	B	Electrochemical oxidation of neutral Rh(I) analogue	Square pyramidal with basal CN	[69]
Rh(triphos)($S_2C{=}NPh$)	B	Rh(triphos)($S_2C{=}O$)$^+$ + SCNPh followed by reduction of Rh(triphos)($S_2C{=}NPh$)$^+$	Square pyramidal with basal S_2CNPh^{2-}	[70]
Rh(triphos)(3,5-DBCat)	B	Electrochemical reduction of +1 Rh(III) analogue	Square pyramidal with basal $DBcat^{2-}$	[140]
Rh(triphos)[$\eta^1{:}\eta^2$-$CH(CO_2Me)CH_2C(=O)OMe$]$^+$	B	Oxidation of Rh(triphos)H[η^2-$CH(CO_2Me){=}CH(CO_2Me)$]	η^2-C=O from β-ester group	[131]
Rh($\eta^6{:}\eta^1$-$Ph_2PCH_2CH_2OC_6H_5$)(η^1-$Ph_2PCH_2CH_2OPh$)$^{2+}$	B	Electrochemical oxidation of +1 Rh(I) analogue		[132]
$RhCl(OH)(PPh_3)_n$ (n=2,)	D		Intermediate in $RhCl(PPh_3)_3$ catalysis of ROOH decomposition	[122]

$RhBr_2(CO)(PMe_2Ph)_2$	D	Abstraction of $^{\cdot}R$ from $Rh(R)Br_2(CO)(PMe_2Ph)_2$ by $^{\cdot}CCl_3$	Rapidly abstracts $^{\cdot}Br$ from $CBrCl_3$ to give $RhBr_3(CO)(PMe_2Ph)_2$	[123]
$Rh(TMPP)_2(CO)_n^{2+}$ $(n=1, 2)$	D		Unstable to disproportionation	[65,66]
Organometallics				
$Rh(C_6Cl_5)_2(COD)$	A	$[Rh(COD)Cl]_2+LiC_6Cl_5$ and oxidation of $Rh(C_6Cl_5)_2(COD)^-$	Labile COD	[73]
$Rh(C_6Cl_5)_2[P(OPh)_3]_2$	A	Oxidation of -1 Rh(I) analogue	X-Ray structure: trans	[73]
$Rh(C_6Cl_5)_2L_2$ ($L_2 \equiv [P(OMe)_3]_2$, $(PPh_3)_2$, py_2, dppe, dppm)	A	$Rh(C_6Cl_5)_2(COD)+L_2$		[73]
$Rh(2,4,6\text{-}^iPr_3C_6H_2)_2(tht)_2$	A	$RhCl_3(tht)_3+LiR$	X-Ray structure: trans	[72]
$[Rh(C_6Me_6)_2](AlX_4)_2$ ($X \equiv Cl$, Br)	A	$RhCl_3+AlBr_3+Al+C_6Me_6$	Anion replaceable by $PtCl_6^{2-}$ or PF_6^{2-}	[74]
$Rh(2,4,6\text{-}^iPr_3C_6H_2)_2(tht)_2(CO)_n$ $(n=1, 2)$	B	$RhR_2(tht)_2$ + excess CO in hexane	Mixture of adducts	[72]
$Rh(\eta^5\text{-}C_5H_5)_2$	B	$Rh(\eta^5\text{-}C_5H_5)_2^+$ + Na or electrochemical reduction	Stabilized at 77 K; μ-(η^4-C_5H_5-η^4-C_5H_5) $[Rh(I)(\eta^5\text{-}C_5H_5)]_2$ dimer at 298 K	[90–92]
$Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}L)$ ($L \equiv C_5H_5$, C_5Me_5, C_9H_7)	B	Electrochemical reduction of +1 Rh(III) analogue below -35 °C, or chemical reduction with Na in THF	$L \equiv C_5H_5$: unstable to (η^5-C_5H_5)Rh(I)[μ-(η^4-C_5Me_5-η^4-C_5H_5)]Rh(I)(η^5-C_5Me_5) dimer; $L \equiv C_5Me_5$: unstable to $Rh(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5Me_5H)$; $L \equiv C_9H_7$: "stable" radical	[89,93]
$Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2^+$	B	Electrochemical oxidation of neutral Rh(I) analogue		[88]
$Rh(\eta^5\text{-}C_5H_5)[S_2C_2(CF_3)_2]^-$	B	Electrochemical reduction of neutral Rh(III) analogue		[82,83]
$Rh(\eta^5\text{-}C_9H_7)(CH_3)[Ph_2PCH(CH_3)CH_2PPh_2]$	B	Electrochemical reduction of +1 Rh(III) analogue	Unstable to loss of $^{\cdot}CH_3$	[87]
Sulfur donor complexes				
$(Bu_4N)_2[Rh(mnt)_2]$	A	$Rh_2(O_2CCH_3)_4+Na_2mnt$ in MeOH	X-Ray powder: square planar	[94,128,141]
$Rh(cysteine)_2$	A	$Rh_2(O_2CCH_3)_4$ + cysteine in H_2O	η^2 via NH_2 and S^-	[81]

Table 1 (*continued*)

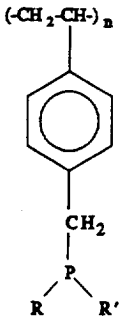
Formula	Stability[a]	Preparation	Comments	Ref(s).
$Rh(cysteine\ methyl\ ester)_2$	A	$Rh_2(O_2CCH_3)_4$ + cysteine methyl ester in H_2O		[81]
$Rh(penicillamine)_2$	A	$Rh_2(O_2CCH_3)_4$ + penicillamine in H_2O		[81]
$Rh(S_2CNR_2)_2$ (R ≡ Me, Et)	A	$RhCl_2(NO)(PPh_3)_2 + Na(SCNR_2)$ refluxed in C_6H_6	Planar	[95]
$Rh(S_2CNR_2)_2(PPh_3)$ (R ≡ Me, Et)	A	$RhCl_2(NO)(PPh_3)_2 + Na(S_2CNR_2)$ in C_6H_6	Square pyramidal with axial PPh_3	[95]
$Rh(9S3)_2^{2+}$	B	Electrochemical reduction of +3 ion		[75–77]
$Rh(12S3)_2^{2+}$	B	Electrochemical reduction of +3 ion	Less stable than 9S3 analogue	[76]
N, O and halide donor complexes				
Rh(salen)	A	$[Rh(CO)_2Cl]_2 + H_2salen + NEt_3$ in MeOH	Partially dissociated from dimer in solid state	[79]
Rh(ttbsalen)	A	$Rh_2(C_2H_3O_2)_4 + H_2ttbsalen + NaOEt$ in EtOH	Partially dissociated from dimer in benzene and in solid state	[79a]
Rh(ttbsaloph)	A	Photolysis of Rh(ttbsaloph)(R)(R ≡ Et, ^{n}Bu)		[79b]
$Rh(ttbsalen)(PPh_3)$	A	$[Rh(ttbsalen)]_2 + PPh_3$ in benzene		[79a]
$Rh(C_{14}H_8O_6S)\cdot 4H_2O$	A	$RhCl_3$ + 5,5′-thiodisalicylic acid		[142]
$[Rh(bipy)_2](NO_3)_2$	A	Disproportionation of $Rh(bipy)_2NO_3\cdot 3H_2O$ to Rh(0) and Rh(II)		[143]
$Rh(DMA)_{4-x}Cl_x^{(x-2)-}$	B	$[Rh(C_8H_{14})_2Cl]_2 + O_2 + LiCl$ in DMA	Unknown mixture	[144,145]
$Rh(phen)_3^{2+}$	B	Electrochemical reduction of $Rh(phen)_3^{3+}$	Loses one phen readily	[97]
$Rh(py)_4Cl_2$	B	Electrochemical reduction of $Rh(py)_4Cl_2^+$		[102]
$RhCl_3(NO)\cdot nEtOH$	B	$RhCl_3\cdot 3H_2O + NO$ in EtOH		[84]
$Rh(DMA)_yCl_x(O_2)^{(x-1)-}$	B	$[Rh(C_8H_{14})_2Cl]_2 + O_2 + LiCl$ in DMA	Unknown mixture	[145,146]
$Rh(bipy)_2(MeCN)^{2+}$	B	Photochemical reaction of $Rh(bipy)_3^{3+}$ with $Ru(bipy)_3^{2+}$ in MeCN; or displacement of bipy from		[96,147]

$Rh(bipy)_2Cl^+$	B	Loss of Cl^- from electrochemically generated $Rh(bipy)_2Cl_2$ or displacement by Cl^- of bipy from electrochemically generated $Rh(bipy)_3^{2+}$		[96]
$Rh(phen)_2(MeCN)^{2+}$	B	Displacement of phen from electrochemically generated $Rh(phen)_3^{2+}$ in MeCN		[97]
$Rh(phen)_2Cl_2$	B	Electrochemical reduction of $Rh(phen)_2Cl_2^+$		[97]
$Rh(phen)_2Cl^+$	B	Loss of Cl^- from electrochemically generated $Rh(bipy)_2Cl_2$ or displacement by Cl^- of phen from electrochemically generated $Rh(phen)_3^{2+}$		[97]
$Rh(pc)Cl(L)^-$ (L≡py, DMSO)	B	Electrochemical reduction of Rh(pc)Cl(L)	Loses Cl^- and L rapidly prior to dimerization	[85]
$Rh(dmgH)_2(PPh_3)$	C	Flash photolysis of dimer or $Rh(^iPr)(dmgH)_2(PPh_3)$	Unstable to dimerization	[106,107]
$Rh(NH_3)_4^{2+}$	C	CTTM[b] photolysis of $Rh(NH_3)_5I^{2+}$ or pulse radiolysis of $Rh(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5(H_2O)^{3+}$ or $Rh(NH_3)_4Br_2^+$		[100,101]
$Rh(NH_3)_5(H_2O)^{2+}$	C	Photoassisted reaction of I^- with $Rh(NH_3)_5(H_2O)^{3+}$	Loses one NH_3	[101]
$Rh(NH_3)_5^{2+}$	C	CTTM photolysis of $Rh(NH_3)_5N_3^{2+}$		[148]
$Rh(sep)^{2+}$	C	Radiolysis or electrochemical reduction of $Rh(sep)^{3+}$	Powerful reductant	[78]
$Rh(bipy)_3^{2+}$	C	Photoassisted reaction of $Rh(bipy)_3^{3+}$ with $Ru(bipy)_3^{2+}$; radiolysis or electrochemical reduction of $Rh(bipy)_3^{3+}$	Loses one bipy readily	[96,103,110,147]
$Rh(O_2CR)_2$ (R≡CH_3, CF_3)	C	γ Irradiation of $Rh_2(O_2CR)_4$ at 77 K	Stabilized at 77 K	[149]
$Rh(O_2CR)_2(CD_3OD)$ (R≡H, CH(OH)Ph)	C	γ Irradiation of $Rh_2(O_2CR)_4(CD_3OD)_2$ or $Rh_2(O_2CR)_2(bipy)_2Cl_2$		[150]
$Rh(O_2CR)(N-N)(CD_3OD)_xCl_{1-x}^{x+}$ (R≡H, CH(OH)Ph) (N−N≡bipy, phen)	C	Minor product in irradiation of $Rh_2(O_2CR)_2(N-N)_2Cl_2$		[150]
$Rh(tfa)_2(ROH)_2$ (R≡Et, ^{i}Pr)	C	Loss of Htfa from presumed intermediate $Rh(tfa)_2(Htfa)$ photolytically generated from $Rh(tfa)_3$ in ROH	Oxidizes to $Rh(tfa)_2(H)(ROH)$	[116,125]

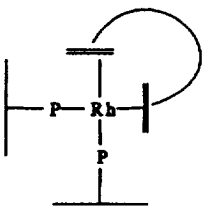
Table 1 (*continued*)

Formula	Stability[a]	Preparation	Comments	Ref(s).
Rh(pc)	C	Photolysis of Rh(pc)X(CH_3OH) (X≡Cl, Br, I) or loss of Cl^- and L from electrochemically generated Rh(pc)Cl(L) (L≡py, DMSO)	Unstable to dimerization or oxidation	[85,130]
$Rh(NH_3)_5Cl^+$	D	Pulse radiolysis of $Rh(NH_3)_5Cl^{2+}$	Loses Cl^- and NH_3 rapidly	[100]
$Rh(NH_3)_4Br_2$	D	Pulse radiolysis of $Rh(NH_3)_4Br_2$	Loses $2Br^-$ rapidly	[100]
$Rh(py)_3Cl_2$	D	Loss of py from $Rh(py)_4Cl_2$	Unstable to Cl^- loss	[102]
$Rh(py)_4Cl^+$	D	Loss of Cl^- from $Rh(py)_4Cl_2$	Unstable to py loss	[102]
$Rh(tfa)_2(Htfa)$	D	Flash photolysis of $Rh(tfa)_3$ in ROH followed by H abstraction from ROH	Unstable to Htfa loss	[125]
$Rh(DMA)_yCl_x(O_2H)^{(x-1)-}$	D	Abstraction by $Rh(DMA)_yCl_x(O_2)^{(x-1)-}$ of H from RH	Intermediate in oxidation of RH to RO_2H	[145]
$Rh(bipy)_2^{2+}$	D	Loss of bipy from $Rh(bipy)_3^{2+}$	Intermediate in disproportionation	[103,110]
$Rh(py)_3Cl^+$	D	Loss of py from $Rh(py)_4Cl^+$	Unstable to dimerization	[102]
$RhI(PPDOBF_2)$	D	$Rh(I)(PPDOBF_2)+RI$ (R≡neopentyl, 2,2-dimethylbutyl, ^iPr)	Captured very rapidly by R· to give trans-RhI(R)(PPDOBF2)	[124]
Rh^{2+} in diamagnetic host lattices				
$RhCl_2(CN)_4$	A	Irradiation of $Rh(CN)_6^{3-}$ in KCl		[151]
$Rh(CN)_6^{4-}$	A	Irradiation of $K_3Rh(CN)_6$ in KCl		[152,153]
$RhCl_6^{4-}$	A	Irradiation of $RhCl_6^{3-}$ in NaCl or of $Na_3[RhCl_6]\cdot 12H_2O$ or reduction of $RhCl_3$ in AgCl		[154]
$RhBr_6^{4-}$	A	Irradiation of $RhBr_3$ in AgBr		[155]
RhO_6^{n-}	A	Rh^{2+} doped into $ZnWO_4$ or MgO		[156–159]
RhH_6^{n-}	A	Rh^{2+} doped into LiH or LiD		[160]
Rh^{2+} on silica gel	A	$RhCl_3\cdot 3H_2O$ added to silica gel, heated		[161]

[a] A, isolable compound or persistent species in solution; B, transient with sufficient longevity in solution to observe spectra or reactivity (chemical or electrochemical); C, highly reactive photolysis or radiolysis transient with observable rate of decay; D, postulated intermediate. [b]Charge transfer to metal.



XX



XXI

and of 1-hexyne according to ($X_3 = Et_3$, Me_2Ph) [133]

$$^nBuC{\equiv}CH + HSiX_3 \rightarrow \textit{cis}\text{- and } \textit{trans}\text{-}^nBuCH{=}CHSiX_3 \quad (41)$$

$RhCl_2(Pcy_3)_2$ is found to be somewhat more active than $RhCl_2(P^otol_3)_2$, and both were judged to be as active as Rh(I) species. In the presence of $AlEt_3$ both compounds are active hydrogenation catalysts [133].

$RhCl_2$(dppe) is found to catalyze olefin hydrogenation with activity comparable with that of other rhodium hydrogenation catalysts [71]. $RhCl_2$(dppe) might be expected to activate H_2 in a manner similar to that of mononuclear Rh(II) porphyrins (Eq. (19)) or to that of $RhCl_2(P^iPr_3)_2$ (Eq. (27)).

A heterogeneous Rh(II) hydrogenation catalyst, $RhCl_2$(PDBP), is made by reacting $RhCl_3$ with polymeric diphenylbenzylphosphine (**XX**) ($R \equiv R' \equiv C_6H_5$), a phosphinated polystyrene. This substance, believed to contain three-coordinate Rh(II)Cl_2P, catalyzes the hydrogenation of many olefins in moderately coordinating solvents (alcohols, DMF, acetone), but shows little activity for alkyne hydrogenation [134].

A similar phosphinated resin (**XX** with $R \equiv C_6H_5$, $R' \equiv C_6H_5$, CH_3, menthyl, and some cross-linking of polystyrene chains by divinyl benzene) is used to synthesize a heterogeneous catalyst initially containing Rh(I) with two coordinated phosphines and a norbornadiene (**XXI**). This system catalyzes hydrogenation of olefins and ketones by a mechanism that is believed to involve the participation of Rh(II) species, detected in the catalyst both during and after the reaction [135].

Similarly, the decomposition of cyclohexenyl hydroperoxide is a radical chain process catalyzed homogeneously by $RhCl(PPh_3)_3$, but formation of an Rh(II) species such as $RhCl(OH)(PPh_3)_2$ is very likely essential for chain propagation (e.g. Eq. (28)) [122].

4. Summary

Numerous mononuclear Rh(II) species with widely varying compositions and stabilities have been reported in the literature (Table 1). Many of the factors that

promote stability and/or hinder reactivity of the known mononuclear Rh(II) compounds have been identified. Ligands that are sufficiently bulky can protect the metal from external attack by all but the smallest reagent molecules. In some situations, bulky ligands can inhibit disproportionation by disallowing the coordination number increase favored by Rh(III). Polydentate ligands can protect a portion of the periphery of the complex from external attack and can impose coordination numbers or geometrical constraints that destabilize potential Rh(I) (favoring four coordination) or Rh(III) (favoring six coordination) reaction products. Electronic structures of ligands that promote delocalization of the unpaired electron from the rhodium on to the ligand can also promote stability against dimerization, disproportionation and oxidation–reduction. Electronic properties of ligand donor atoms (e.g. σ–π donor–acceptor tendencies, hardness, softness) often have a strong influence on reactivity. In general, several of these factors often operate simultaneously to affect the stability of complexes.

The reactions presented for the known mononuclear Rh(II) compounds have been grouped according to six major reaction types: adduct formation, ligand dissociation and substitution, dimerization, disproportionation, oxidation and reduction. For the most part, rationales for observed reactivity can be related to the structural and electronic ligand properties that influence stability. Highest reactivity is observed for the Rh(II) species with the fewest stabilizing features, especially for complexes containing only N, O and halide donor ligands.

Porphyrin complexes of Rh(II) enjoy the high substitutional stability of the rigid porphyrin ring system that bars both dissociation of porphyrin and equatorial attack at rhodium. However, the planar porphyrin template promotes adduct formation, dimerization and attack by reagents at the axial sites unless these processes are inhibited by bulky meso substituents. Sufficiently bulky substituents stabilize mononuclear Rh(II) porphyrin complexes but still allow attack by small molecules (e.g. CO, H_2, CH_4). The reluctance of mononuclear Rh(II) porphyrins to activate aromatic C–H bonds is a consequence of a steric barrier to assembling the appropriate four-center transition state. The conjugated electronic structure of the porphyrin ring system contributes some stability to the mononuclear complexes by delocalizing unpaired electron spin density, but interaction of strong σ donor ligands in the axial positions can induce complete electron transfer via ligand molecular orbitals that results in oxidation and/or disproportionation.

Mononuclear Rh(II) phosphine complexes are stabilized by the presence of bulky R groups in the PR_3 ligands that inhibit access of reagent molecules to the metal center. Polydentate phosphine ligands can also promote stability by steric protection of the metal. The π-accepting (soft) nature of the P donor atoms helps to delocalize unpaired electron density. Intermolecular magnetic Rh–Rh interaction is observed as the steric protection of the ligands decreases, but well-defined dimers are not well-known as they are for porphyrin complexes. The phosphine complexes are relatively more susceptible than porphyrin complexes to disproportionation or to simple oxidation or reduction as stability decreases. Stable Rh(II) complexes $RhX_2(PR_3)_2$ are known to react with H_2 to give Rh(III) hydrides, and although these reactions

are formally analogous to those of the porphyrin complexes, the mechanisms have not yet been established for the phosphine complexes.

Rh(II) complexes with sulfur donor ligands are stabilized by steric bulk, but considerable stability derives from the π acceptor (soft) nature of S that serves to delocalize unpaired electron density and to destabilize Rh(III) relative to the lower oxidation states. Many of the sulfur donor ligands in stable Rh(II) complexes also have conjugated electronic structures which enhance delocalization of Rh electron density. No predominant pattern of reactivity is evident for these complexes, but the redox behavior of many has been elucidated by cyclic voltammetry.

Organometallic Rh(II) complexes are stabilized by the electron-delocalizing influence of the organic fragments in almost every case. In some cases dimerization occurs by coupling carbon atoms that contain a significant amount of the unpaired spin density. Redox parameters have been observed by cyclic voltammetry for most of the known mononuclear Rh(II) examples.

Some of the reactive properties of mononuclear Rh(II) complexes have potential synthetic and catalytic applications. The selective activation of bonds to aliphatic carbon by some of the four-coordinate 15-electron Rh(II) compounds is a promising example. Reactions of Rh(II) porphyrins with CO and H_2 to form dimetal monoketones, dimetal diketones and metalloformyl complexes provide other intriguing examples. Further work in developing the chemistry of mononuclear Rh(II) is surely warranted.

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