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Electrochemistry of $(R_3P)_2Ru(CO)_2Cl_2$ and $(R_3P)_3Ru(CO)Cl_2$ complexes

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Abstract

The redox behavior of a series of sixteen ruthenium(II) complexes of the types $(R_3P)_2Ru(CO)_2Cl_2$ ($R_3P = Bzl_3P$, Me_3P, Ph_2MeP and $PhMe_2P$) and $(R_3P)_3Ru(CO)Cl_2$ ($R_3P = Me_3P$, Ph_2MeP and $PhMe_2P$) has been studied by cyclic and differential pulse voltammetry at a stationary platinum electrode in dichloromethane. The redox potentials for the Ru^{II}/Ru^{III} processes are a function of complex geometry, stoichiometry and the nature of the phosphine. This process is electrochemically reversible and is followed by a chemical step, the rate of which is a function of the complex geometry and the nature of the phosphine. The chemical step is fast for the *cis*-$(R_3P)_3Ru(CO)Cl_2$ and *cct*-$(R_3P)_2Ru(CO)_2Cl_2$ complexes whereas for the corresponding *trans* and *ttt* complexes it is slow. For some of the latter complexes, the rate constants for the chemical step have been determined. A few of the complexes also underwent irreversible Ru^{II}/Ru^{I} and Ru^{III}/Ru^{IV} processes in the accessible potential range. There is no correlation between the redox behavior of these complexes and their activity as homogeneous hydrogenation catalysts.

Introduction

In a recent report [1] concerning the catalytic activity of a series of $(R_3P)_3Ru(CO)Cl_2$ and $(R_3P)_2Ru(CO)_2Cl_2$ complexes it was noted that 1-hexene isomerization was more rapid than 1-hexene hydrogenation for all complexes studied. This implies that the catalytic cycle involves a monohydride intermediate. The rate determining step in such catalytic cycles could be oxidative addition of hydrogen to the coordinatively unsaturated $(R_3P)_2Ru(CO)Cl_2$ species [2]. In such a case one might expect [3] the ease of oxidative addition to parallel the oxidation potential of the complex. In this light James [4] has shown that carbonyl ligands

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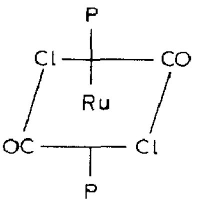
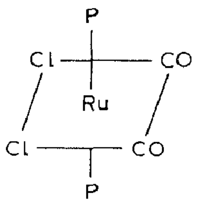
hinder oxidative addition by removing electron density from the metal center by way of π-back bonding and catalytic activity decreases in the order $Ru^{II} > Ru^{II}CO > Ru^{II}(CO)_2$. The experimental results of the catalysis study [1] suggest, however, that entry into the catalytic cycle by ligand dissociation is more important than the rate of the oxidative addition step in determining the catalytic activity of these systems. In order to determine whether there is a relationship between the catalytic activity and the ease of oxidation, the electrochemical behavior of these complexes was investigated. With exception of $(PhMe_2P)_3Ru(CO)Cl_2$ the electrochemistry of these complexes has not been previously reported. For this complex a reversible one-electron oxidation was observed [5] under conditions similar to those employed herein.

Results

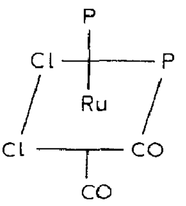
The notation for the geometry of the complexes is shown below.



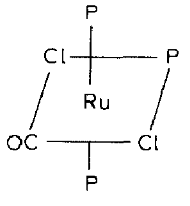
ttt



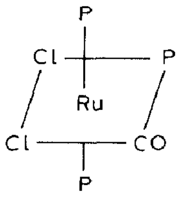
cct



ccc



trans



cis

The usual diagnostic criteria utilized in cyclic voltammetry [6] point out that the mechanism of the oxidation of the ruthenium(II) species occurs by reaction 1 (EC mechanism) where k_f is a first order or pseudo first order rate constant. That the

$$\begin{array}{c}[(R_3P)_{2,3}Ru(CO)_{2,1}Cl_2] \rightleftarrows [(R_3P)_{2,3}Ru(CO)_{2,1}Cl_2]^{+} + e^{-} \\ \downarrow k_f \\ \text{product}\end{array} \qquad (1)$$

Ru^{II}/Ru^{III} process is monoelectronic is corroborated by comparing the half peak widths ($W_{1/2}$) [7] obtained by differential pulse voltammetry of the complexes with the corresponding value for the ferrocene oxidation (Fig. 1). In addition, controlled potential coulometry gave $n = 1$ for this process.

For these *cis* and *cct* complexes, the follow up chemical step is fast, as no cathodic wave can be seen on the return sweep, even at high scan rates as exemplified by a typical voltammogram shown in Fig. 2. For the *trans* and *ttt* complexes, the chemical step is slower, and a return cathodic wave is always present in the cyclic voltammogram (Figs. 3, 4). However, with slow scan rates the ratios of

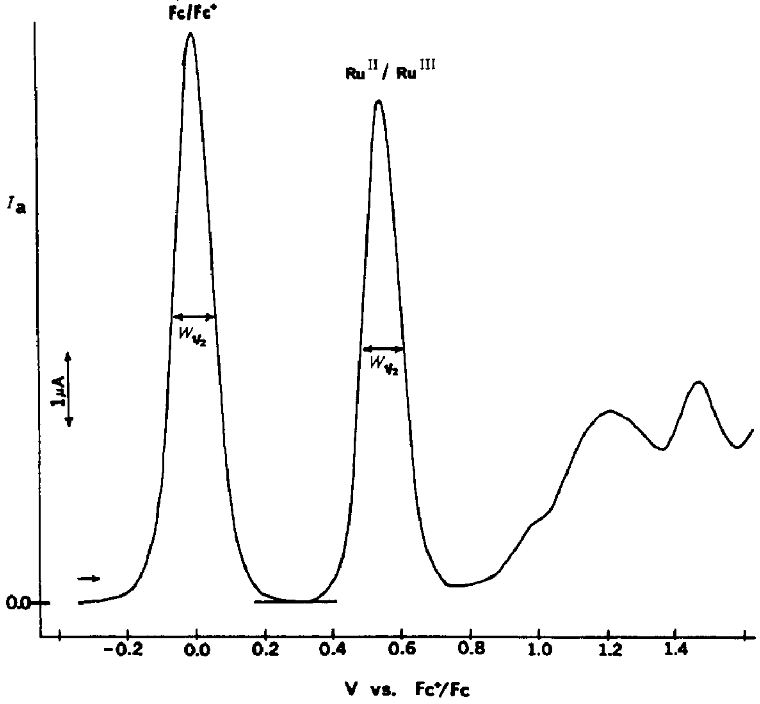


Fig. 1. Differential pulse voltammograms for the oxidations of 1×10^{-3} *M* solutions of ferrocene and *trans*-$(PhMe_2P)_3Ru(CO)Cl_2$ in CH_2Cl_2 (0.1 *M* TBAP) at 25±0.1°C. (Scan rate 5 mV s^{-1}; duration between pulses 0.5 s; pulse amplitude 50 mV).

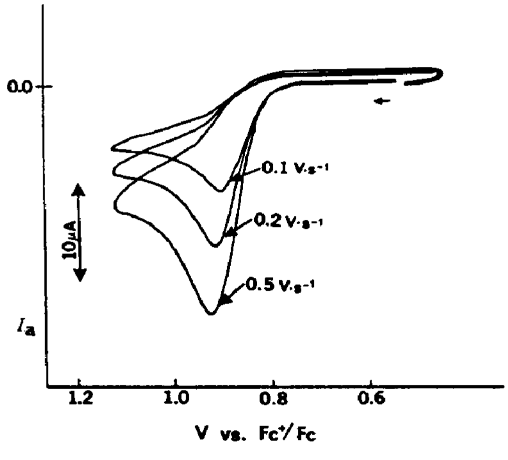


Fig. 2. Cyclic voltammograms for the oxidation of a 1×10^{-3} *M* solution of *cis*-$(PhMe_2P)_3Ru(CO)Cl_2$ in CH_2Cl_2 (0.1 *M* TBAP) at 25±0.1°C.

the cathodic to anodic peak currents are less than one. Thus, the rate constant (k_f) for the follow up chemical step may be calculated from the cyclic voltammetry experiments by the method developed by Nicholson and Shain [6*]. This method is

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* Reference number with asterisk indicates a note in the list of references.

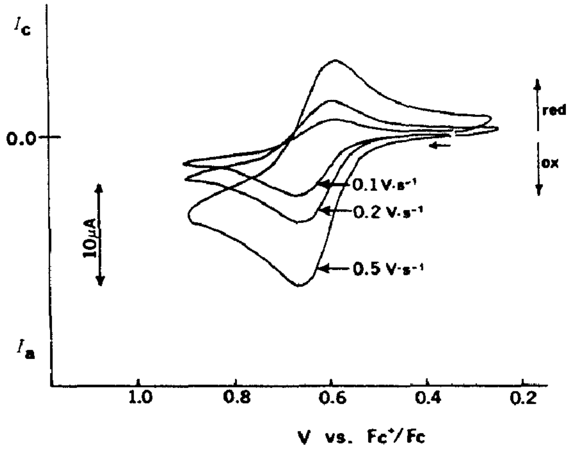

Fig. 3. Cyclic voltammograms for the oxidation of a 1×10^{-3} *M* solution of *trans*-$(Ph_2MeP)_3Ru(CO)Cl_2$ in CH_2Cl_2 (0.1 *M* TBAP) at 25 ± 0.1° C.

based upon measuring the ratio of the peak currents which is a function of the product $k_f \cdot \tau$ (where τ is the time between $E_{1/2}$ and the switching potential). The peak current ratios were determined from single cycle voltammograms by the semiemperical procedure described by Nicholson [8]. The rate constants in Table 1 are the average of at least six values determined at different scan rates (150 to 500 mV s^{-1}).

In some cases a second oxidation, $Ru^{III} \rightarrow Ru^{IV}$ was observed. We assume that this is also a one electron process based upon the values of the peak potentials

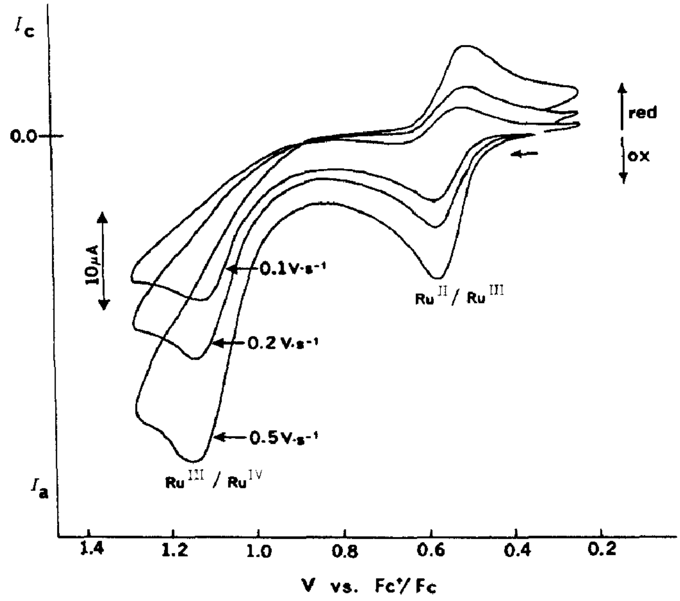

Fig. 4. Cyclic voltammograms for the oxidations of a 1×10^{-3} *M* solution of *trans*-$(PhMe_2P)_3Ru(CO)Cl_2$ in CH_2Cl_2 (0.1 *M* TBAP) at 25 ± 0.1° C.

Table 1

Electrochemical properties of some Ru^{II} complexes

Complex	$E_{1/2}$ ($E_{pa}-E_{pc}$) or E_p [a]				k_f (s^{-1}) [d]
	Isomer	Ru^{II}/Ru^{I}	Ru^{II}/Ru^{III}	Ru^{III}/Ru^{IV}	
$(Ph_2MeP)_3Ru(CO)Cl_2$	*trans*	–	0.61 (68 mV)	–	0.24 ± 0.02
	cis	–	0.98 [b]	–	
$(PhMe_2P)_3Ru(CO)Cl_2$	*trans*	–	0.55 (60 mV)	1.13 [b]	(4.2 ± 0.6)
	cis	–	0.93 [b]	1.32 [b]	$\times 10^{-2}$
$(Me_3P)_3Ru(CO)Cl_2$	*trans*	–	0.51 (59 mV)	–	
	cis	–	0.88 [b]	–	
$(Ph_2MeP)_2Ru(CO)_2Cl_2$	*ttt*	–	1.00 (71 mV)	–	0.21 ± 0.06
	cct	−2.43 [b]	1.46 [b]	–	
	ccc	−2.16 [b]	1.45 [b]	–	
$(PhMe_2P)_2Ru(CO)_2Cl_2$	*ttt*	–	0.96 (67 mV)	1.29 [b]	(5.9 ± 0.9)
	cct	–	1.40 [b]	–	$\times 10^{-2}$
	ccc	−2.42 [b]	[c]	–	
$(Me_3P)_2Ru(CO)_2Cl_2$	*ttt*	–	0.95 (101 mV)	–	$\sim 5 \times 10^{-3}$
	cct	–	0.97 [b]	–	
$(Bzl_3P)_2Ru(CO)_2Cl_2$	*ttt*	−2.38 [b]	1.00 (79 mV)	–	
	cct	–	[c]	–	

[a] Measured in CH_2Cl_2 solution at a Pt working electrode, Ag/AgCl reference electrode, 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte. All potentials are vs. Fc/Fc^+. Scan rate 100 mV s^{-1}. [b] The potential cited is the peak potential. [c] Very near the limited for the solvent/electrolyte/electrode system. [d] See text for details.

which are similar to those observed for the Ru^{III}/Ru^{IV} process in other systems [9]. However, the relative peak heights for the Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} processes in addition to the shape of the wave for the latter suggest that the latter process may be a multi-electron transfer.

Discussion

The data in Table 1 show that both the geometry of the Ru^{II} complexes and the nature of the phosphine ligand affect the redox potentials. In most cases the *trans* (or *ttt*) isomer is easier to oxidize by about 400 millivolts than the corresponding *cis* (or *cct*) isomer. The exception is the isomeric pair of $(Me_3P)_2Ru(CO)_2Cl_2$ complexes which show very similar oxidation potentials. The dependence of the oxidation potential on the geometric structure is probably due to the greater π-acceptor ability of CO *trans* to Cl in the *cis* and *cct* isomers than when it is *trans* to R_3P as in the *trans* or to CO as in the *ttt* isomers. This is in agreement with the values of the CO stretching energies and force constants for the $(R_3P)_2Ru(CO)_2Cl_2$ complexes [2].

The irreversible $Ru^{II} \rightarrow Ru^{I}$ reduction that is seen for four of the complexes comes very near the solvent limit for this system. One might infer that since the other complexes are generally more easily oxidized, they would also be more difficult to reduce. This would place their Ru^{II}/Ru^{I} couples at negative potentials outside the range for this system. Reversible reductions to Ru^{I} have previously been reported for $[RuCl(DPP)_2]^+$ [10] and $[RuNO(DPP)_2]^+$ [11] where DPP = bis(diphenylphosphino)propane.

For all of the $(R_3P)_3Ru(CO)Cl_2$ complexes, substitution of a methyl group for a phenyl group on the phosphine results in an increase in the ease of oxidation by about 50 millivolts. A similar relationship is seen between the $(Ph_2MeP)_2Ru(CO)_2Cl_2$ and $(PhMe_2P)_2Ru(CO)_2Cl_2$ complexes, with $(Me_3P)_2Ru(CO)_2Cl_2$ being the exception. This trend is easily rationalized in terms of an increase in the electron density at ruthenium provided by the more basic phosphine ($Me_3P > PhMe_2P > Ph_2MeP$). For $MeCp(CO)_2Mn(R_3P)$ complexes [12] substitution of a methyl group for a phenyl group results in an increase in the ease of oxidation by about 37 millivolts.

A comparison of the data for the $(R_3P)_3Ru(CO)Cl_2$ and $(R_3P)_2Ru(CO)_2Cl_2$ complexes shows that substitution of a phosphine for a carbonyl group increases the ease of complex oxidation by about 400 millivolts. This is most likely the result of an increase in electron density caused by the replacement of a π acceptor ligand (CO) with a good σ donor ligand (R_3P) [12]. A decrease in catalytic activity for some ruthenium systems with an increasing number of carbonyl ligands has been attributed [4] to this same effect and related to the increased difficulty of oxidative addition of H_2. We have observed that for $(DBP)_nM(CO)_{6-n}$, [M = Cr, Mo, W, DBP = 1-phenyldibenzophosphole] complexes that replacing a CO with the phosphole increases the ease of oxidation by about 350 millivolts [13].

The kinetic data (Table 1) show that for the *trans* and *ttt* complexes substitution of a methyl group for a phenyl group on the phosphine results in approximately an order of magnitude increase in the kinetic stability of the oxidized species. Also, the oxidized *trans*-$(R_3P)_3Ru(CO)Cl_2$ and *ttt*-$(R_3P)_2Ru(CO)_2Cl_2$ species with the same phosphine have roughly the same kinetic stabilities.

Several observations can be made in regard to the ease of oxidation of the Ru^{II} complexes and their effectiveness as homogeneous catalysts. The *ttt* isomers are much easier to oxidize than the *cct* isomers and are also much better catalysts [1]. Both these results may be related to the relatively weak M–C bond in the *ttt* isomer [2]. The latter observation is consistent with the easier dissociation of CO from the *ttt* isomer than from the *cct* isomer [2] and the former the result of reduced M–CO π-backbonding in the *ttt* isomer. No such correlation is seen for the $(R_3P)_3Ru(CO)Cl_2$ complexes, and none is expected since only the *cis* isomer is present under catalytic conditions [1] due to the rapid *trans* to *cis* isomerization [2].

Although oxidation occurs much more easily for the $(R_3P)_3Ru(CO)Cl_2$ than for the $(R_3P)_2Ru(CO)_2Cl_2$ complexes, this is not reflected in increased rates of catalysis for the $(R_3P)_3Ru(CO)Cl_2$ complexes. For example, *cct*-$(Ph_2MeP)_2Ru(CO)_2Cl_2$ is as good a catalyst as *cis*-$(Ph_2MeP)_3Ru(CO)Cl_2$ [1], even though the former is more difficult to oxidize (1.46 vs. 0.98 V).

Finally, although the basicity of the phosphine has only a relatively small effect on the oxidation potentials, the rates of catalysis change markedly with changes in the phosphine [1]. The ease of electrochemical oxidation is probably due only to the donor ability of the ligands (a global electronic effect) [12]. On the other hand, the large difference in catalytic rates for the different $(R_3P)_2Ru(CO)_2Cl_2$ complexes is attributable largely to steric effects.

It was thought [1] that perhaps the oxidation of the complexes during the catalytic cycle could be responsible for the accelerated rates of geometric isomerization [2] observed under catalytic conditions. Sullivan and Meyer [14] have reported that *trans*-$RuCl_2(dppe)_2$ (dppe = diphenylphosphinoethane) isomerizes to the *cis*-isomer upon a one electron oxidation. Similarly, a facial to meridional rearrangement of $RuCl_2(x\text{-}MePhCN)_3MeOH$ (x = *ortho*, *meta*) occurred as a result of one-electron oxidation [9]. Also, oxidation is known to accelerate the rate of geometric isomerization of *fac*-$(R_3P)_3M(CO)_3$ (M = Cr, Mo, W) [13,15] to the *mer* isomers. However, no electrochemically induced isomerization was noted for any of the complexes listed in Table 1. The electrochemical oxidation is an outer-sphere electron transfer whereas oxidative addition is most likely an inner-sphere electron transfer. Still, it is tempting to suggest that oxidative addition of H_2 is probably not the cause of the fast geometric isomerization during catalysis.

Experimental

All cyclic voltammograms were recorded at $25 \pm 0.1°C$ in freshly distilled dichloromethane containing 0.1 *M* tetrabutylammonium perchlorate (TBAP) using an EG&G PAR electrochemical system consisting of a Model RE 0073 recorder, a Model 173 potentiostat and a Model 175 universal programmer. The differential pulse voltammetry experiments were performed with an EG&G PAR 174A polarographic analyzer. A three electrode system with IR compensation was used throughout. The working and auxiliary electrodes were a stationary platinum disk and wire, respectively. The reference electrode was Ag/AgCl (saturated LiCl in ethanol). The test solution was separated from the reference electrode by a salt bridge containing a Vycor plug and filled with the solvent/supporting electrolyte. Temperature regulation was achieved with a Brinkman Lauda K-2/R temperature controller with the electrochemical cell immersed in the constant temperature bath. As recommended by IUPAC [16] for electrochemistry in non-aqueous solvents, the ferricinium (Fc^+)/ferrocene (Fc) couple was employed as the reference, and all potentials reported herein are given vs. this couple. As suggested by Gagné et al. [17], whenever possible, ferrocene was used as an internal standard to compensate for the junction potential variability among experiments. TBAP (Fluka, purum) was recrystallized from ethanol/water and dried under vacuum at 100°C overnight. Dichloromethane was distilled over P_2O_5 and stored over Linde 4Å molecular sieves. All test solutions were degasssed with prepurified nitrogen before measurements were taken and were kept under a nitrogen blanket during the experiments.

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