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Complexes of the Platinum Metals. 7.[1] Homogeneous Ruthenium and Osmium Catalysts for the Dehydrogenation of Primary and Secondary Alcohols

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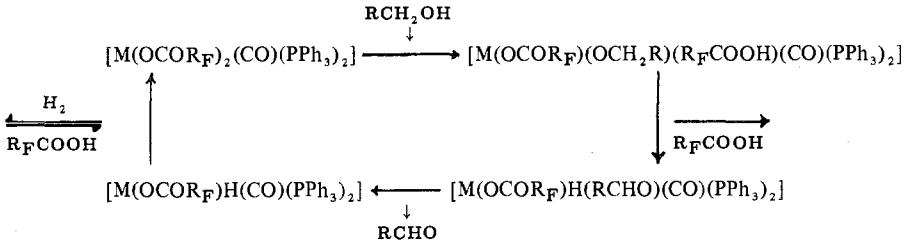
Ruthenium and osmium complexes $[M(OCOR_F)_2(CO)(PPh_3)_2]$ (R_F = CF_3, C_2F_5, or C_6F_5) are catalysts for the dehydrogenation of primary and secondary alcohols to aldehydes and ketones, respectively. The catalysis is promoted by the addition of small amounts of free acid (R_FCOOH) and is inhibited by the accumulation of aldehyde or ketone and by the addition of large amounts of acid. In the presence of acid, R_FCOOH, the hydride complexes $[MH(OCOR_F)(CO)(PPh_3)_2]$ also function as catalysts. The mechanism proposed for the catalytic process involves solvolysis of the catalysts $[M(OCOR_F)_2(CO)(PPh_3)_2]$ to form alkoxides $[M(OAlk)(OCOR_F)(CO)(PPh_3)_2]$ which subsequently undergo a β elimination to generate aldehyde (or ketone) and form the hydrides $[MH(OCOR_F)(CO)(PPh_3)_2]$. Acid attack on the hydrides liberates dihydrogen and regenerates the catalysts. Dehydrogenation has been observed to occur with an extensive range of primary, secondary, and cyclic alcohols. Kinetic data have been recorded; the initial rate of dihydrogen elimination increases with increasing boiling point of the alcohol and for the primary alcohols ranges from 7.50×10^{-3} mol s^{-1} (mol of catalyst)$^{-1}$ (ethanol) to 2.27 mol s^{-1} (mol of catalyst)$^{-1}$ (benzyl alcohol) for the catalyst $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ under optimum conditions. Catalyst efficiency decreases in the sense Ru > Os and $CF_3 \sim C_2F_5 > C_6F_5$ for a given alcohol under standard conditions.

The reactions of alcohols with platinum metal species in the presence of base have been extensively employed as a route for the formation of hydride complexes.[2] These syntheses are accompanied by liberation of aldehyde or ketone and have been shown to involve the elimination of hydride ions from the α-CH_2 group of a coordinated alkoxide anion (the β-elimination process).[3] We now describe a homogeneous catalytic reaction for the dehydrogenation of primary and secondary alcohols based on this process and employing the ruthenium and osmium perfluorocarboxylates $[M(OCOR_F)_2(CO)(PPh_3)_2]$[4] as catalysts. Although the stoichiometric dehydrogenation of alcohols by group 8 metal species is a commonplace phenomenon, extensively employed in the synthesis of metal hydride complexes, homogeneous systems capable of catalyzing this reaction are rare. The only system directly comparable with that discussed in this paper is the one reported by Charman involving use of rhodium trichloride,[5] preferably in the presence of stannous chloride.[6] Charman's catalyst is less efficient than the present one and its nature and mode of operation are less clearly defined. However, other workers have described numerous transition metal species capable of catalyzing hydrogen transfer from primary or secondary alcohols to a variety of substrates including aldehydes or ketones,[7-13] olefins,[14-17] acetylenes[18,19] and carbon tetrachloride.[20] Evidence supporting the α-hydrogen-transfer (β-elimination) mechanisms proposed for these reactions has been obtained from H–D exchange and from racemization reactions involving optically active alcohols.[21] More extensive surveys of transition metal catalyzed hydrogen-transfer reactions are given in recent reviews.[22,23] A preliminary report on this work has been published.[24]

Experimental Section

Alcohols were dried and distilled using standard techniques; catalysts were prepared as previously described.[4] Reactions were performed at the boiling point of the alcohol using a reflux apparatus attached to a gas buret. The refluxing alcohol was allowed to reach equilibrium; then a measured quantity of catalyst was introduced, the system was closed, and the volume of evolved gas was measured at atmospheric pressure. An efficient double-walled condenser was employed to remove volatile organic products from the vapor phase; therefore

Scheme I



measured volumes correspond directly to volume of dihydrogen evolved. Gaseous products were analyzed by infrared and mass spectrometry; aldehydes and ketones were identified as 2,4-dinitrophenylhydrazine derivatives and by gas chromatography. Free acid, when employed, was either mixed with the alcohol prior to commencement of the catalysis or introduced with the catalyst. A typical procedure is given below.

1-Propanol (10 ml, 0.134 mol) was heated under reflux in a 50-ml two-necked, round-bottomed flask fitted with an injection port and a condenser with attached gas buret. After the system had reached equilibrium and had been adjusted to atmospheric pressure, a solution of the catalyst $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ (0.0391 g, 4.45×10^{-5} mol) and trifluoroacetic acid (0.0630 g, 5.53×10^{-4} mol) in 1-propanol (1.0 ml) was injected. Total volume of gas evolved, measured at NTP, was plotted against lapsed time. After 1 h the evolved gas was sampled and analyzed; the reaction solution was distilled and fractions collected over the range 40–95 °C were used for GC and preparation of 2,4-dinitrophenylhydrazine derivatives. Other alcohols examined in a similar fashion were methanol, ethanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, benzyl alcohol, 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, *tert*-butyl alcohol, allyl alcohol, and propargyl alcohol. For reasons of cost and efficiency detailed studies were performed using the ruthenium catalysts rather than their less labile osmium analogues.

Results

The catalysts $[M(OCOR_F)_2(CO)(PPh_3)_2]$, which are members of a general class of platinum group metal perfluorocarboxylates recently synthesized in our laboratory,[4] are readily attacked by primary and secondary alcohols to liberate aldehydes and ketones respectively with concomitant formation of the hydride species $[MH(OCOR_F)(CO)(PPh_3)_2]$. Acid ($R_FCOOH$) attack on these hydridic intermediates regenerates the parent complexes $[M(OCOR_F)_2(CO)(PPh_3)_2]$ and liberates dihydrogen, thereby completing a catalytic cycle (Scheme I). As implied by the proposed cycle, the hydrides $[MH(OCOR_F)(CO)(PPh_3)_2]$ also function as catalysts in the presence of ca. 12 mol of added acid per mole of complex.

Two other series of complexes, both containing carboxylate anions trans to triphenylphosphine ligands, are attacked by boiling alcohols but do not give rise to catalytic cycles. The platinum complex $[Pt(OCOCF_3)_2(PPh_3)_2]$, which has been shown by NMR [^1J(Pt–P) = 3935 Hz] to have cis rather than trans stereochemistry,[4] undergoes alcoholysis to yield the hydride *trans*-$[PtH(OCOCF_3)(PPh_3)_2]$.[25] However, the platinum(II) hydride is reluctant to react with free acid and the system is therefore not catalytic. The rhodium complexes $[Rh(OCOR_F)(PPh_3)_3]$ react readily in alcoholic solution to yield the carbonyls *trans*-$[Rh(OCOR_F)(CO)(PPh_3)_2]$[26] which show no activity as dehydrogenation catalysts in our systems. All other perfluorocarboxylato complexes prepared in connection with this work[4] lack labile perfluorocarboxylate groups and do not display any tendency to undergo alcoholysis.

The catalytic species $[M(OCOR_F)_2(CO)(PPh_3)_2]$ and $[MH(OCOR_F)(CO)(PPh_3)_2]$ react with carbon monoxide to form catalytically inactive dicarbonyls $[M(OCOR_F)_2(CO)_2(PPh_3)_2]$ and $[MH(OCOR_F)(CO)_2(PPh_3)_2]$, respectively. However, they are not susceptible to carbonylation by alcohols, aldehydes, or ketones under the conditions of the dehydrogenation catalysis and are therefore not rendered inoperative.

Table I. Initial Rates of Dihydrogen Evolution

Alcohol	Rate, mol s^{-1} (mol of catalyst)$^{-1}$ [a]	Alcohol	Rate, mol s^{-1} (mol of catalyst)$^{-1}$ [a]
Ethanol	0.0075	1-Hexanol	0.410
1-Propanol	0.0227	1-Heptanol	0.820
1-Butanol	0.068	Benzyl alcohol	2.270
1-Pentanol	0.170		
2-Propanol	0.0033	2-Pentanol	0.026
2-Butanol	0.0097	2-Hexanol	0.065
Cyclopentanol	0.051	Cycloheptanol	0.295
Cyclohexanol	0.147	Cyclooctanol	0.450

[a] Catalyst $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ with optimum concentration of added acid (see text).

The relative efficiencies of the catalysts $[M(OCOR_F)_2(CO)(PPh_3)_2]$ reflect the usual lability trend $Ru^{II} > Os^{II}$ and are also dependent upon the nature of the carboxylate group (R_F) in the sense $CF_3 \sim C_2F_5 > C_6F_5$. Much reduced catalytic activity found for the corresponding acetates $[M(OCOMe)_2(CO)(PPh_3)_2]$ is in accord with our conclusion that the good leaving characteristics of the perfluorocarboxylate anions are an important feature of the catalysts (vide infra).

Seventeen alcohols were examined (see Experimental Section); of these only two, methanol and *tert*-butyl alcohol, failed to dehydrogenate—the former because its boiling point was too low or, possibly, because the methyl C–H bonds in methanol are significantly stronger than the α C-H bonds in other primary and secondary alcohols and the latter because it lacked an α-CH group. The remaining alcohols all evolved dihydrogen and gave the expected aldehyde or ketone. In addition, two functional alcohols, $CH_2{=}CHCH_2OH$ and $CH{\equiv}CCH_2OH$, were tested. The former gave acrolein ($CH_2{=}CHCHO$) plus propene; the latter rapidly destroyed the catalyst. Formation of acrolein, propene, and propionaldehyde from allyl alcohol by ruthenium(II)-catalyzed inter- and intramolecular hydrogen transfer has previously been reported.[27] Plots of total volume of gas evolved against lapsed time are given for different primary and secondary alcohols in Figure 1. Initial rates of catalysis are given in Table I. The reduction in the rate of gas evolution, which is observed with longer reaction times, is attributed to inhibition of the dehydrogenation process by accumulated aldehyde or ketone. Removal of the dehydrogenation products by fractional distillation restores the initial rate of reaction. Addition of small amounts of the appropriate free aldehyde or ketone produces the expected suppression of dihydrogen evolution.

Plots of rate of gas evolution against catalyst concentration (Figure 2) for 1-propanol in the absence of added free acid reveal that the rate of dehydrogenation is directly proportional to catalyst concentration for concentrations less than ca. 9×10^{-4} mol/mol of alcohol. At higher catalyst concentrations the linear relationship is distorted by the precipitation of the rather insoluble catalytic intermediate $[RuH(OCOCF_3)(CO)(PPh_3)_2]$ from solution.

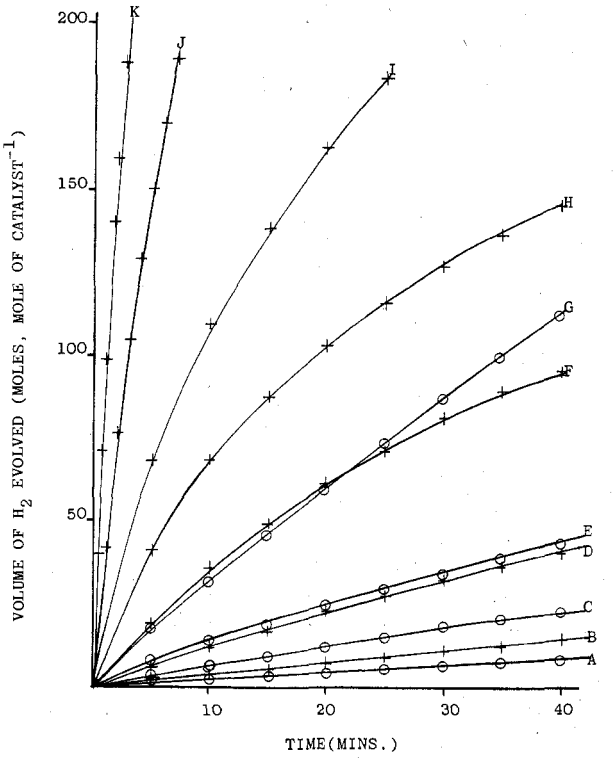


Figure 1. Dehydrogenation of primary and secondary alcohols—volume of hydrogen evolved as a function of time. Alcohols examined are (A) 2-propanol, (B) ethanol, (C) 2-butanol, (D) 1-propanol, (E) 2-pentanol, (F) 1-butanol, (G) 2-hexanol, (H) 1-pentanol, (I) 1-hexanol, (J) 1-heptanol, and (K) benzyl alcohol. Conditions employed were $[Ru(OCOCF_3)_2(CO)PPh_3)_2]$ (4.45×10^{-5} mol) and CF_3COOH (5.53×10^{-4} mol) in boiling alcohol (0.134 mol): +, primary alcohols; ○, secondary alcohols.

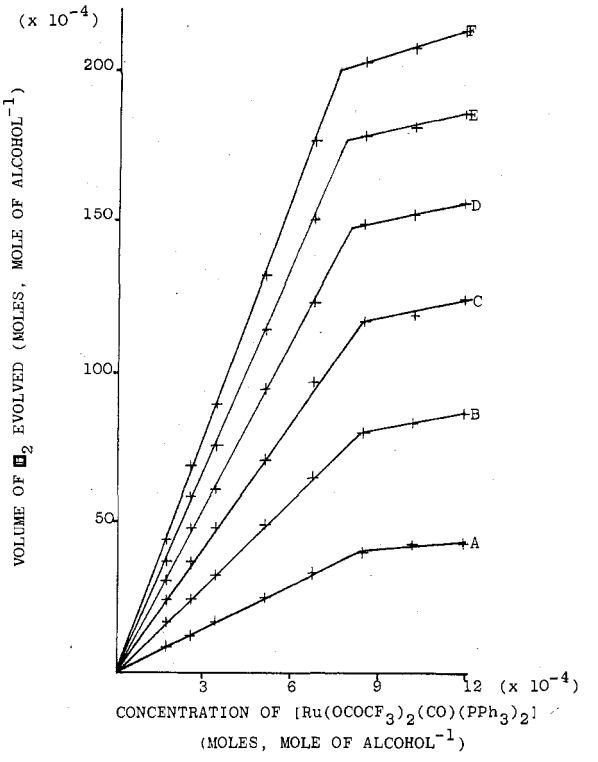


Figure 2. Dehydrogenation of 1-propanol catalyzed by $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ in the absence of added acid—volume of hydrogen evolved as a function of catalyst concentration. Plots are for volume of hydrogen evolved after (A) 10, (B) 20, (C) 30, (D) 40, (E) 50, and (F) 60 min for each concentration of catalyst used. Discontinuity in each plot reflects onset of catalyst precipitation.

The catalysis is promoted by added free acid (CF_3COOH) up to an optimum concentration of ca. 12 mol/mol of catalyst but is progressively inhibited by higher concentrations (Figure 3).

Given the unfavorable thermodynamics of the dehydrogenation process, all reactions were, of necessity, performed at the boiling point of the alcohol concerned in order to achieve effective removal of evolved dihydrogen from the solution. Therefore it was not practicable to collect rate data for a single alcohol over an extended temperature range. However, at constant acid and catalyst concentrations the initial rates of dehydrogenation of primary and secondary alcohols showed the expected increase with the increasing boiling points of the alcohols concerned, the latter being the reaction temperature in each instance.

The catalyst $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ was recovered from solution after 250 catalytic cycles and showed no detectable loss of activity when reintroduced to the catalytic system. The intermediate $[RuH(OCOCF_3)(CO)(PPh_3)_2]$, prepared by the stoichiometric reaction of $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ with ethanol and isolated as air-sensitive yellow crystals, showed the expected catalytic activity when reintroduced to the system in the presence of free acid (12 mol/mol of complex).

Attempts to obtain isolable phenoxide or alkoxide complexes, analogous to the species postulated as intermediates in the catalysis, by reacting the catalysts with phenols or tertiary alcohols were unsuccessful. Recovery of starting material on each occasion presumably indicates that the equilibrium

$$[M(OCOR_F)_2(CO)(PPh_3)_2] \underset{R_FCOOH}{\overset{RCH_2OH}{\rightleftharpoons}} [M(OCH_2R)(OCOR_F)(CO)(PPh_3)_2]$$

lies far to the left.

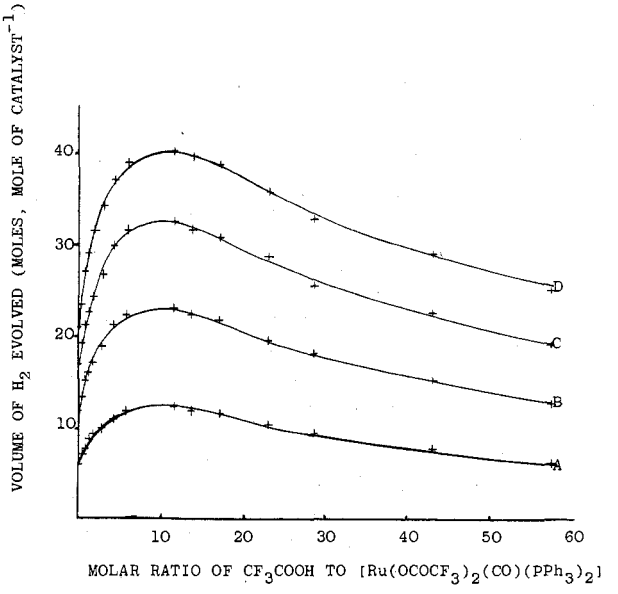
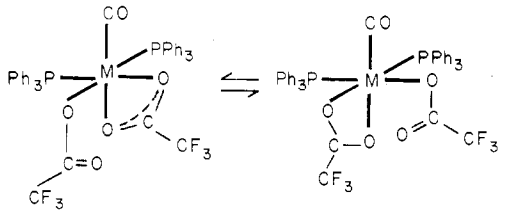


Figure 3. Dehydrogenation of 1-propanol catalyzed by $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$—volume of hydrogen evolved as a function of molar ratio of CF_3COOH to $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$. Plots are for hydrogen evolved after (A) 10, (B) 20, (C) 30, and (D) 40 min for each acid:catalyst concentration ratio employed.

Prior to discussing theories concerning the detailed mechanism of the dehydrogenation process, it is necessary to establish the stereochemistry of the catalysts $[M(OCOR_F)_2(CO)(PPh_3)_2]$ and those intermediates which are accessible to structural or spectroscopic investigation. This information, in addition to providing an insight into the

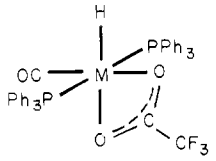
stereochemistry of the catalytic reaction, should afford some explanation for the facile alcoholysis step which is an essential feature of the catalysis system. The stereochemistry of the catalysts $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ has been established by variable-temperature NMR data [^{19}F NMR, doublet coalescing to singlet above 302 K (Ru) or 321 K (Os); ^{31}P NMR, AB pattern coalescing to singlet above 271 K (Ru) or 293 K (Os)]. These clearly indicate that the two perfluorocarboxylate ligands share one face of the coordination octahedron and are in dynamic equilibrium,[4,28] e.g.



Ia Ib

The kinetics and mechanism of this and related dynamic equilibria involving carboxylate ligands are under investigation and will be reported elsewhere.

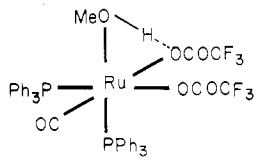
The high-field ^1H NMR spectra of the solvolysis products $[MH(OCOCF_3)(CO)(PPh_3)_2]$ each show a triplet pattern [M = Ru, MH τ 27.2, $^2J(PH)_{cis}$ = ca. 18 Hz] indicative of stereochemistry II with hydride trans to perfluorocarboxylate.



II

This assignment is confirmed by the ^{31}P NMR spectra (^1H decoupled), each of which comprises a singlet.

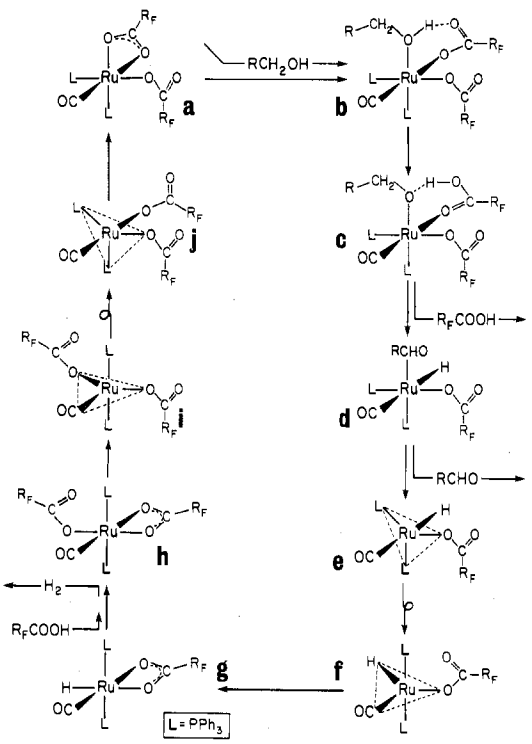
Finally, the methanol solvate $[Ru(OCOCF_3)(CO)(PPh_3)_2(MeOH)]$ has been shown by x-ray diffraction to possess structure III[29] with the methanol occupying a coordination site vacated by the chelate carboxylate ligand of the nonsolvated complex. The structure also shows evidence (see below) of H bonding between the methanol and one of the monodentate carboxylate ligands. Variable-temperature ^{19}F and ^{31}P NMR spectra indicate that in solution this solvated structure persists in equilibrium with the nonsolvated complex,[30] and it appears probable that a similar solvate is involved in the initial stages of the catalytic cycle. The stereochemical assignments indicate that the interconversion of the complexes $[M(OCOR_F)_2(CO)(PPh_3)_2]$ and $[MH(OCOR_F)(CO)(PPh_3)_2]$ in the catalysis cycle is accompanied by stereochemical rearrangement of the residual ligands. We now turn attention to this problem.



III

Given the ease with which chelate perfluorocarboxylate ligands relinquish one coordination site to become monodentate and the tendency for dissociative mechanisms to predominate in substitution reactions of octahedral complexes, it appears probable that the observed stereochemical rearrangements are accomplished either by formation of square-pyramidal five-coordinate intermediates which undergo reverse Berry pseudorotations[31] or by formation of nonrigid seven-coordinate hydrido complexes. Twist mechanisms involving six-coordinate species are considered improbable but have not been systematically excluded. The mechanism discussed below (Scheme II) is a detailed version of that outlined in Scheme I and takes cognizance of the stereochemical information deduced above. The initial step in the dehydrogenation sequence is thought to involve coordination of a molecule of the alcohol to form an adduct (**b**) (see Scheme II for identity of species **a**–**j**) with a structure analogous to that found for the methanol solvate $[Ru(OCOCF_3)_2(MeOH)(CO)(PPh_3)_2]$ (III). Hydrogen bonding (CF_3CO_2---H—OMe), evident in the crystal structure of III,[32] points to a mechanism for facile interligand proton transfer (**b** → **c**). Similar metal-assisted proton transfer between coordinated water and amino acid ligands has recently been reported and is thought to play an important role in some enzyme reactions.[33] The resultant alkoxide complex (**c**) presumably undergoes a rapid β-elimination step with the proton migrating to the coordination site vacated by the departing perfluorocarboxylic acid ligand.[34] Loss of the weakly coordinated aldehyde (or ketone) ligand, followed by a reverse Berry pseudorotation (**e**–**f**) on the resultant five-coordinate square-pyramidal (d^6) intermediate and subsequent rechelation of a carboxylate group, could account for formation of the observed hydride (**g**). The proposed form of the reverse Berry pseudorotation (**e**–**f**) minimizes steric interactions between the bulky triphenylphosphine ligands. The course of the reaction leading to regeneration of the catalysts (**a**) is more difficult to elucidate. It is possible that acid (R_FCOOH) attack on the hydrides $[MH(OCOR_F)(CO)(PPh_3)_2]$ occurs with retention of stereochemistry and leads to formation of dicarboxylato complexes $[M(OCOR_F)_2(CO)(PPh_3)_2]$ with mutual trans triphenylphosphine ligands. Regeneration of the observed isomeric species (**a**) could then occur by a further reverse Berry pseudorotation sequence (**i**–**j**). Alternatively, the conversion of the hydrides $[MH(OCOR_F)(CO)(PPh_3)_2]$ to the dicarboxylates $[M(OCOR_F)_2(CO)(PPh_3)_2]$ by acid, R_FCOOH, may involve a protonation step leading to formation of seven-coodinate ruthenium(IV) or osmium(IV) species $[MH_2(OCOR_F)(CO)(PPh_3)_2]^+$ or $[MH_2(OCOR_F)_2(CO)(PPh_3)_2]$

Scheme II



which undergo reductive elimination of dihydrogen to yield the observed isomer of $[M(OCOR_F)_2(CO)(PPh_3)_2]$ directly. The inhibitory effect of accumulated aldehyde (or ketone) is similar to that previously observed in related alcohol-dehydrogenation[5,6] and hydrogen-transfer[16] processes and is presumably attributable to competition between the alcohol and the carbonyl product in the initial coordination step (**a** → **b**). Synthesis of ketone solvates supports this suggestion. The very low concentrations of dihydrogen present in the boiling alcohol should ensure that the back-reaction—hydrogenation of aldehyde or ketone—does not play a significant role. The observed acid dependence of the catalyst system (Figure 3) can be accommodated if we assume that the acid-promoted catalyst regeneration reaction (**g** → **h**) is superseded by the solvolysis process (**c** → **d**) as the rate-determining step at acid concentrations greater than ca. 12 mol/mol of catalyst. Weakly bound perfluorocarboxylate ligands of exceptional lability appear to be a characteristic and essential feature of the catalytic complexes $[M(OCOR_F)_2(CO)(PPh_3)_2]$. It is therefore useful to consider the origin of this phenomenon. Two plausible explanations, trans effect or trans influence and available sites for alcohol coordination, merit special consideration.

Trans effect and trans influence in octahedral complexes in general and ruthenium(II) species in particular are both thought to decrease in the sequence $PR_3 > CO > Cl$.[35-37] Data for oxygen donors bound to platinum group metals are sparse but it seems probable that the trans effect and trans influence of carboxylate ligands in these systems are not greater than those of chloride. These conclusions are supported by ligand-exchange rates, which indicate that chloride trans to phosphine is more labile than chloride trans to carbonyl or chloride,[37] and by x-ray diffraction data, which reveal that Ru–O and Ru–P linkages trans to triphenylphosphine are consistently longer than those trans to carboxylate in the complexes $[RuH(OCOMe)(PPh_3)_3]$,[38] $[RuH(OCOH)(PPh_3)_3]$,[39] $[Ru_2(OCOC_3H_7)_4Cl]$,[40] and $[Ru_3O(OCOMe)_6(PPh_3)_3]$.[41] Moreover, our previous observation that only complexes containing perfluorocarboxylate anions (see above) or related oxygen donor anions[42] trans to triphenylphosphine suffer alcoholysis appears to be in accord with these results. However, contrary to our expectations, an x-ray diffraction study of the methanol solvate $[Ru(OCOCF_3)_2(MeOH)(CO)(PPh_3)_2]$ reveals relatively long Ru–P bonds (2.339–2.361 Å) trans to trifluoroacetate and methanol and rather short Ru–O bonds trans to carbonyl (2.138 Å) and, in particular, triphenylphosphine (2.104 Å).[43] Although the metal–ligand bond data for related carboxylato and perfluorocarboxylato complexes are obviously not directly comparable, they do suggest that in our catalytic system the perfluorocarboxylate ligands are not subject to particularly strong trans effect or trans influence. We therefore turn to the alternative explanation for the lability of the perfluorocarboxylate ligands, namely, the presence of accessible coordination sites available to the attacking alcohol molecules. Isolation of the methanol adduct $[Ru(OCOCF_3)_2(MeOH)(CO)(PPh_3)_2]$ of structure III implies that the alcoholysis process involves coordination of a molecule of alcohol followed by hydrogen transfer from the alcohol to the carboxylate anion and subsequent elimination of the latter as free acid. It therefore appears probable that the alcohol coordination step is rate determining (at high acid concentrations) and that the presence of a chelate carboxylate capable of surrendering a coordination site to the incoming alcohol is primarily responsible for the occurrence of the facile alcoholysis reaction. Labilization of the perfluorocarboxylate anions due to the trans effect of triphenylphosphine and/or carbonyl ligands may be a contributory factor. However, we conclude that the structural data, while supporting the proposed reaction cycle (Scheme II), do not fully account for the unusual lability and reactivity of the catalysts. Further work designed to elucidate this problem and yield more efficient catalysts is in progress and will be reported elsewhere.

Acknowledgment. We thank Dr. M. B. Hursthouse for performing the x-ray diffraction study, the Science Research Council for an award to A.D., and Johnson Matthey & Co. Ltd. for a generous loan of ruthenium salts.

Registry No. Ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; benzyl alcohol, 100-51-6; 2-propanol, 67-63-0; 2-butanol, 78-83-1; 2-pentanol, 6032-29-7; 2-hexanol, 626-93-7; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; cycloheptanol, 502-41-0; cyclooctanol, 696-71-9; $Ru(OCOCF_3)_2(CO)(PPh_3)_2$, 38596-61-1; $RuH(OCOCF_3)(CO)(PPh_3)_2$, 60451-51-6.

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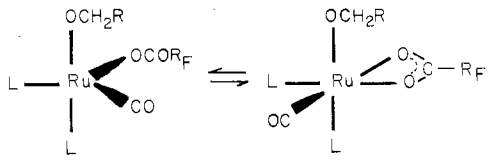
(34) We have assumed in Scheme II that the carboxylate ligand trans to CO will be lost as carboxylic acid since in the crystal structure it is the one participating in hydrogen bonding to the alcohol and has the longest (and weakest?) Ru–O linkage. However, in solution all three oxygen donor ligands are free to rotate and both carboxylate ligands will have the opportunity to hydrogen bond with the alcohol. Moreover, since the

R_FCO_2 group trans to triphenylphosphine should be the most labile, it may be preferentially lost as free acid. This eventuality can be accommodated by a mechanism essentially similar to that given in Scheme II and does not invalidate this discussion. We are unable to ascertain whether the step **c–d** involves simultaneous or sequential carboxylic acid loss and hydride migration. If the latter situation prevails then the following complexes could be intermediates in the reaction cycle



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^{13}C Nuclear Magnetic Resonance Studies of Organoplatinum(II) Complexes Containing Substituted Pyridine Ligands

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^{13}C NMR data are reported for the series of platinum(II) compounds *trans*-[$LPtCl_2(NC_5H_4$-4X)] (L = ethylene, styrene, di-*tert*-butylacetylene, or carbon monoxide; NC_5H_4-4X = a series of para-substituted pyridines), *trans*-[$ZPt(NC_5H_4$-4X)$(PMe_2Ph)_2]BF_4$ (Z = CH_3, $CH_3C{\equiv}C$), and [Cl(2-methoxy-5-cyclooctenyl)Pt(NC_5H_4-4X)]. These complexes provide examples of olefins, acetylenes, carbonyls, alkyls and acetylides bonded to platinum(II) in trans position to a para-substituted pyridine. Small changes in the δC and $^1J_{^{195}Pt-^{13}C}$ data of the directly bound carbon atoms as X is varied have been interpreted in terms of slight fluctuations in the σ-donor component of these platinum–carbon bonds (regardless of ligand type). The spectra of the 2-methoxy-5-cyclooctenyl complexes also demonstrate the presence of two geometrical isomers in solution contrary to previous reports.

Introduction

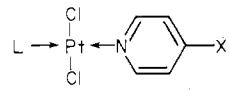
A large amount of data have been published recently regarding the ^{13}C NMR spectra of organometallic compounds of the transition elements.[1-24] Interpretation of the reported chemical shifts is difficult because several parameters determine these values. In fact, a recent, short overview of the subject[25] concluded that it was not possible to satisfactorily explain the chemical shifts of directly bound carbon nuclei attached to transition metals using current theories. A study of trends in ^{13}C NMR data obtained from series of closely related compounds[1,2,5,24] should lead to more meaningful rationalizations. However even this approach has been only partially successful because changing only one ligand on the metal still has both an electronic and a steric effect, and in many cases, even the mode of bonding is altered.

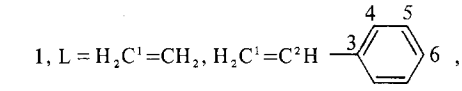
In an attempt to circumvent these problems, we have considered series of organometallic complexes with para-substituted pyridines NC_5H_4-X as ligands. As these para substituents are varied, there should be no change in the steric parameters of the pyridine ligands near the metal, such that the *mode* of the bonding between the metal and the nitrogen should remain essentially unchanged. Thus, the only change experienced by the metal (and the trans metal–carbon bond) when the para substituent is varied will be electronic in origin.

This work considers the ^{13}C NMR data obtained for the series of platinum(II) complexes **1–4**. Platinum is an ideal metal for ^{13}C NMR studies because: (i) ^{195}Pt (33% natural abundance) couples strongly with directly bonded carbon nuclei, and (ii) it is possible to synthesize a large variety of stable platinum–carbon bonds. The series of compounds **1–4** provide examples of acetylene, olefin, carbon monoxide, methyl, and acetylide groups bound to platinum(II) in the trans position to NC_5H_4-X.

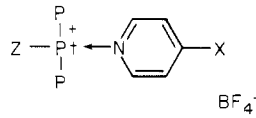
Experimental Section

Complexes of type **1** were prepared using the methods of Orchin et al.[26-29] Compounds of type **2**[2,30-32] and the dimer **3**[33] were prepared

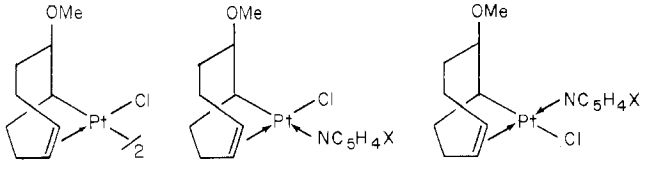




1, L = $H_2C^1{=}CH_2$, $H_2C^1{=}C^2H$, $(C^3H_3)_3C^2C^1{\equiv}CC(CH_3)_3$, $C^1{\equiv}O$



2, P = PMe_2Ph; Z = C^1H_3, $C^1{\equiv}C^2{-}C^3H_3$



3 4a 4b

X = NMe_2, O-*n*-Bu, Me, H, Cl, CO_2Me, COMe, CN

by standard methods. The complexes **4a** and **4b** were not isolated from solution; however, several of them have been characterized.[34]

The ^{13}C NMR spectra were measured at ca. 35 °C on either Varian XL-100-15 or CFT-20 spectrometers operating in the Fourier transform mode at 25.2 and 20.0 MHz, respectively. All the spectra (except **1**, L = CO) were determined with noise modulated proton decoupling.

Results

Data for complexes of type **1** are recorded in Table I.[35] Only spectral data where $^3J_{Pt-C}$ coupling to the β carbons of the pyridines is observed (ca. 35–40 Hz) are completely reliable. The complexes were recrystallized several times to remove excess pyridine which, if present, can catalyze the