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PROPIONYL COMPLEXES OF RUTHENIUM DERIVED FROM THE REACTION OF ETHYLENE WITH $RuHCl(CO)_2(PPh_3)_2$

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Summary

$RuHCl(CO)_2(PPh_3)_2$ reacts with ethylene under mild conditions (25 psi, 80°C) to yield a propionyl derivative $RuCl(C[O]C_2H_5)(CO)(PPh_3)_2$ which is believed to be coordinatively unsaturated. Unlike the acetyl analogue, $RuCl(C[O]C_2H_5)(CO)(PPh_3)_2$ does not isomerize to $RuCl(C_2H_5)(CO)_2(PPh_3)_2$ in solution. Under one atmosphere of carbon monoxide, $RuCl(C[O]C_2H_5)(CO)(PPh_3)_2$ exists in equilibrium with two species believed to be $RuCl(C[O]C_2H_5)(CO)_2(PPh_3)_2$ and $[Ru(C[O]C_2H_5)(CO)_3(PPh_3)_2]Cl$. $RuCl(C[O]C_2H_5)(CO)(PPh_3)_2$ reacts with CO/ $AgClO_4$ to give *mer*-$[Ru(C[O]C_2H_5)(CO)_3(PPh_3)_2]ClO_4$, *p*-tolylisocyanide (RNC) and $NaClO_4$ to give *cis*-$[Ru(C[O]C_2H_5)(CO)(CNR)_2(PPh_3)_2]ClO_4$, and hydrochloric acid to yield the hydroxycarbene complex, $RuCl_2(CO)(C[OH]C_2H_5)(PPh_3)_2$.

Introduction

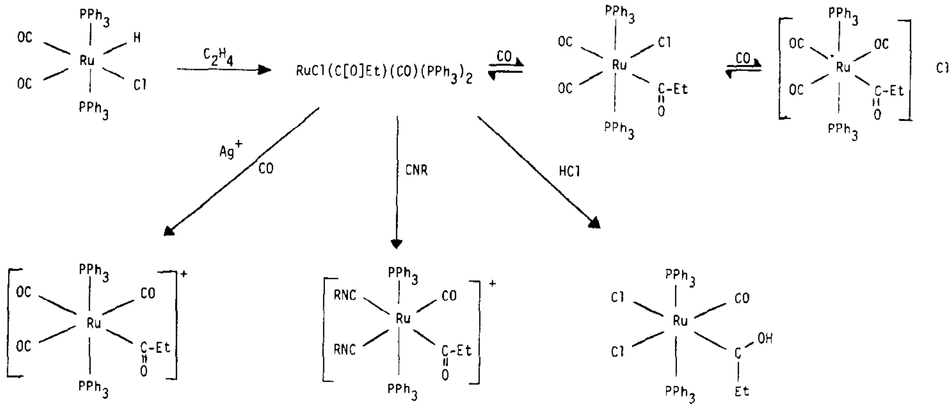
A number of organoruthenium carbonyl complexes have been observed to participate in facile alkyl or aryl to acyl equilibria. For example, the complexes $RuRX(CO)_2(PPh_3)_2$ (R = *p*-tolyl, X = Cl, Br, I) are in equilibrium with the *dihapto*-acyl complexes $Ru(\eta^2\text{-}C[O]R)(CO)(PPh_3)_2$ in solution [1]. Similarly, $RuI(\eta^2\text{-}C[O]CH_3)(CO)(PPh_3)_2$ isomerises reversibly on dissolution in CH_2Cl_2 to $Ru(CH_3)I(CO)_2(PPh_3)_2$ [2]. A similar but five coordinate acyl complex, $RuX(C[O]CH_3)(CO)(PMe_2Ph)_2$ (X = Cl, Br), has been proposed as an intermediate in the rapid interconversion of $RuX(CH_3)(CO)_2(PMe_2Ph)_2$ and $RuX(C[O]CH_3)(CO)L(PMe_2Ph)_2$ in the presence of ligands L (= CO and PMe_2Ph) [3].

Interestingly enough, however, in the ruthenium systems described to date, there do not appear to be any examples in which the acyl form seems to be preferred in both the solid state and solution. In view of the manifestly greater tendency of longer chain alkyl groups to undergo migratory insertion reactions [4,5,6], it was of interest to us to attempt the synthesis of complexes such as $RuX(C_2H_5)(CO)_2(PPh_3)_2$ and to compare their chemistry with that of their ruthenium [1,2] and osmium [1,5,7] analogues. We report herein the preparation of a number of propionyl and related complexes derived from the unusual insertion reaction of $RuHCl(CO)_2(PPh_3)_2$ and C_2H_4.

Results and discussion

Infrared and ^1H NMR data for new complexes are summarized in Table 1.

In benzene solution, $RuHCl(CO)_2(PPh_3)_2$ reacts with ethylene under modest pressure to yield a yellow solution. Upon addition of ethanol and removal of the benzene under reduced pressure, a yellow solvated solid is obtained which, on recrystallization from dichloromethane/ethanol, gives well-formed bright yellow crystals of stoichiometry, $RuHCl(CO)_2(PPh_3)_2 \cdot C_2H_4 \cdot CH_2Cl_2$. Solid state infrared spectra and elemental analysis of this material show it to be a propionyl derivative, $RuCl(C[O]Et)(CO)(PPh_3)_2 \cdot CH_2Cl_2$ (Scheme 1). The propionyl ligand exhibits characteristic maxima at 1643vs (ν(C=O)), 1418w, 1073m, 918m and 865s cm^{-1}. In the ν(CO) region, a number of maxima may be observed depending on the work-up and crystallinity of the sample. Most commonly seen are bands at 1957vs, 1926s and 1900s. Regardless of the number and position of ν(CO) bands, however, all samples exhibit the same spectrum in dichloromethane solution. In such solutions, two bands are observed at 1948vs and 1920s cm^{-1} with acyl ν(C=O) occurring at 1640s cm^{-1}. The ^1H NMR spectrum of $RuCl(C[O]Et)(CO)(PPh_3)_2 \cdot CH_2Cl_2$ confirms the presence of the ethyl group (2.38 q, 2H, 0.36 t, 3H; ^3J(HH) 7.2 Hz) and dichloromethane (5.25 s, 2H). The lack of coupling of the methylene quartet to phosphorus confirms that the propionyl ligand remains unchanged in solution. Hence, there is no evidence for the isomeric complex $RuCl(C_2H_5)(CO)_2(PPh_3)_2$ in this system, unlike the methyl analogue [2], in keeping with the enhanced thermodynamic stability of propionyl complexes [6]. This system also illustrates the enhanced tendency of ruthenium alkyls to undergo migration reactions by comparison to their osmium analogues. Thus $OsCl(C_2H_5)(CO)_2(PPh_3)_2$ is quite stable, undergoing only an acid assisted migratory insertion reaction in the presence of HCl, wherein the acyl ligand is converted to an hydroxy carbene group [5].



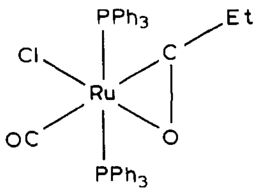
SCHEME 1. Synthesis and reactions of $RuCl(C[O]Et)(CO)(PPh_3)_2$.

Examples of the direct migratory insertion of ethylene into labile, unsaturated hydride complexes such as $[PtH(acetone)(PPh_2Me)_2]^+$ [8], $PtHCl(PPh_3)_2/SnCl_2$ [9] and $RhHCl_2(PPh_3)_2$ [10] under mild conditions have been reported. They are to our knowledge, however, unknown when the substrate is a supposedly inert, octahedral d^6 complex such as $RuHCl(CO)_2(PPh_3)_2$. It seems logical to assume that the initial step in the formation of the propionyl complex is the dissociation of PPh_3, followed by recoordination of the PPh_3 at some point in the reaction path, subsequent to the initial migratory insertion reaction needed to generate the ethyl group. Since any sensible reaction mechanism based on this premise involves unstable, 16 electron intermediates, it is perhaps not surprising that added PPh_3 is needed in order to optimize isolated yields of $RuCl(C[O]Et)(CO)(PPh_3)_2$ although, qualitatively, the reaction appears to be slowed.

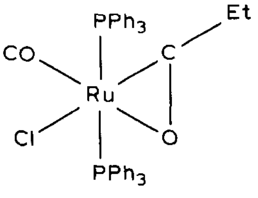
Although the ligand set in $RuCl(C[O]Et)(CO)(PPh_3)_2$ is known with some certainty, the same cannot be said of the structure of this complex, either in solution or the solid state. In solution, a single point molecular weight determination in dichloromethane indicated that the complex is monomeric. We have no good explanation of what processes may have contributed to the rather low value of 531 obtained (cf. 746 reqd). We believe that the complex is also monomeric in the solid state, but attempts to verify this by X-ray crystallography failed owing to rapid decomposition of the complex in the X-ray beam. The far infrared spectrum of $RuCl(C[O]Et)(CO)(PPh_3)_2$ exhibits only one strong band at 284 cm^{-1} with a weaker component at 272 cm^{-1}. Terminal Ru–Cl stretching vibrations typically occur in the range 310–270 cm^{-1} when *trans* to a carbonyl group and 230–270 cm^{-1} when *trans* to tertiary phosphine or arsine donors [11]. Although the number of closely related species in limited, dimers of octahedral ruthenium(II) bridged by chlorides tend to exhibit $\nu(RuCl)$ in the 250–260 cm^{-1} range [12]. Hence it seems reasonable to exclude dimeric, chloro-bridged structural assignments for $RuCl(C[O]Et)(CO)(PPh_3)_2$.

The most obvious assignment for the structure of this complex would be as an η^2-propionyl derivative I, occurring as a mixture of isomers Ia and Ib.

There are, however, some problems with this assignment. Most damaging is the



(Ia)



(Ib)

rather high value of $\nu(C{=}O)$ of 1643 cm^{-1} by comparison to those observed for analogous $RuI(\eta^2\text{-}C[O]Me)(CO)(PPh_3)_2$ (1599 cm^{-1}) and $RuI(\eta^2\text{-}C[O]p\text{-tolyl})(CO)(PPh_3)_2$ (1550 cm^{-1}). The value of 1643 cm^{-1} is more in keeping with a mono-hapto formulation. In addition, the bright yellow colour of the propionyl complex is uncharacteristic for 6-coordinate Ru^{II}. $RuI(\eta^2\text{-}C[O]p\text{-tolyl})(CO)(PPh_3)_2$ for example, is described as being pale yellow [1], as is $RuI(\eta^2\text{-}C[O]CH_3)(CO)(PPh_3)_2$ [10]. These latter two complexes also exist in only one isomeric form, unlike the

TABLE 1

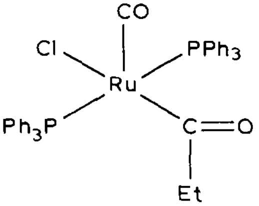
INFRARED [a] AND ^{1}H NMR [b] DATA FOR NEW COMPLEXES

Compound	ν(CO)	ν(C=O)	Others	$\delta(^1H)$ (assignment)
$RuCl(C[O]Et)(CO)(PPh_3)_2$	1957vs, 1926s, 1900s (1948vs, 1920s)	1643vs (1640s)	ν(RuCl), 284s, 272w	0.36, t, 3H; 2.39, q, 2H, ^3J(HH) 7.2 (C_2H_5) 7.41, m, 30H (Ph)
mer-$[Ru(C[O]Et)(CO)_3(PPh_3)_2]ClO_4$	2129m, 2059vs, 2040vs 1996m, 1989m (2124w, 2050vs, 1985m)	1624s (1632s)	–	0.30, t, 3H; 1.90, q, 2H, ^3J(HH) 6.7 (C_2H_5) 7.55, m, 30H (Ph)
cis-$[Ru(C[O]Et)(CNR)_2(CO)(PPh_3)_2]ClO_4$	1996vs (2007vs)	1603s	ν(CN), 2187s, 2154vs (2185s, 2142vs)	0.30, t, 3H; 2.01, q, 2H, ^3J(HH) 6.8 (C_2H_5) 2.33, 2.31, 6H (tol-CH_3); 7.45, m, 38H (Ph)
cis-$RuCl_2(C[OH]Et)(CO)(PPh_3)_2$	1967s, 1956vs (1970vs)	–	ν(RuCl), 253s, 240vs ν(OH), 3500 w,br	0.02, t, 3H, 2.33, q, 2H, ^3J(HH) 6.7 (C_2H_5) 15.15, s, 1H(OH); 7.37, m, 30H (Ph)

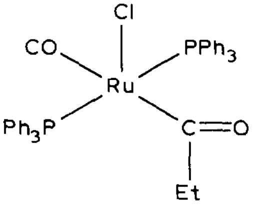
[a] Recorded as Nujol mulls. Dichloromethane solution values in parentheses (ν in cm^{-1}). [b] $CDCl_3$ solutions. Internal TMS standard (δ in ppm, J in Hz).

propionyl complex isolated in this study. If the dihapto-acyl formulation is rejected for these reasons, the remaining possibilities are various 5-coordinate structures based upon the trigonal bipyramid and square pyramid. There is an ample theoretical and practical basis for eliminating structures based on the trigonal bipyramid for five coordinate d^6 complexes [4,6,14]. In particular, X-ray crystal structures of complexes such as $RuCl_2(PPh_3)_3$ [14c], $RhCl_2(COCH_2CH_2Ph)(PPh_3)_2$ [6], $RhMeI_2(PPh_3)_2$ [6] and $[RhI(L)(COC_2H_5)(mdt)]^-$ (L = CO, PPh_3; mdt = maleonitriledithiolate) [6] all reveal square pyramidal geometries.

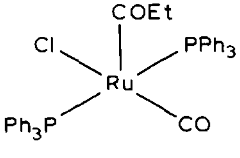
For $RuCl(C[O]Et)(CO)(PPh_3)_2$, there exist three possible structures based upon the square pyramid, IIa–IIc, with the vacant coordination site being blocked



(IIa)



(IIb)



(IIc)

possibly by either the dichloromethane solvent molecule, or a phenyl hydrogen atom [14c]. The possibility also exists for blocking of the vacant coordination by β or γ hydrogens of the propionyl group, as observed in the acetyl complex $Mo(C[O]CH_3)(S_2CNMe_2)(CO)(PMe_3)_2$ [15]. However, the absence of any P–H coupling in the ethyl ^1H NMR signals of the propionyl complex tends to argue against any interaction of this type. Structures with *cis*-phosphines have been ruled out by the ^{31}P NMR studies to be discussed below.

There is little to choose between the structures IIa–IIc, although the evidence we have to date does seem to favour $RuCl(C[O]Et)(CO)(PPh_3)_2$ existing as an equilibrium mixture of only two of these isomeric forms. The most compelling piece of evidence is the existence of two solution $\nu(CO)$ values separated by 28 cm^{-1}. The only other form of isomerism possible is rotational isomerism of the propionyl ligand and it is difficult to believe that rotational isomers of any of IIa–IIc would exhibit such widely differing values of $\nu(CO)$. The low temperature ^{31}P NMR spectrum of $RuCl(C[O]Et)(CO)(PPh_3)_2$ also indicates the presence of at least two isomers. At 20°C in CD_2Cl_2, the ^{31}P NMR spectrum of the acyl complex exhibits a sharp singlet at 31.30 ppm. This signal remains a singlet at −40°C but at −80°C it splits into two somewhat broader singlets of 31.49 and 30.57 ppm. The most logical interpretation of this evidence is that $RuCl(C[O]Et)(CO)(PPh_3)_2$ consists of two rapidly interconverting geometrical isomers, both possessing a *trans* arrangement of phosphine ligands, as expected on steric grounds. Rotational isomerism cannot be responsible for the two low temperature ^{31}P NMR signals since rotational isomers of IIa–IIc will all exhibit essentially equivalent environments for the phosphorus nuclei. It seems natural to suspect that one of the isomers involved in this equilibrium is IIc in view of the number of five-coordinate acyl complexes exhibiting square pyramidal geometry with apical acyl groups [6]. However, if there is any sort of interaction between the propionyl group and the vacant coordination site, this may favour the presence of IIa and IIb. The rapid interconversion of isomers observed for $RuCl(C[O]Et)(CO)(PPh_3)_2$ also must account for the observation of only one ethyl environment in the ^1H NMR spectrum of the complex down to $-40°C$.

The chemistry of $RuCl(C[O]Et)(CO)(PPh_3)_2$ is certainly consistent with the presence or availability of a vacant coordination site. For example, when CO is bubbled into a yellow dichloromethane solution of the acyl complex, a colour change to pale yellow takes place. Infrared spectra of such solutions show maxima at 2050, 1984, 1948, 1921, 1641 and 1604 cm^{-1}. Similarly, reacting $RuCl(C[O]Et)(CO)(PPh_3)_2$ with CO under 40 psi pressure in acetone suspension yields a cream product with a particularly complex pattern of carbonyl absorptions in the infrared. Bands are seen at 2107m, 2047vs, 2039vs, 1995vs, 1985vs, 1971vs and 1925s cm^{-1} with acyl bands observed at 1639w and 1599s. One more likely explanation for these observations would be that carbonylation under these conditions yields (inter alia) a mixture of *mer*-$[Ru(CO)_3(C[O]Et)(PPh_3)_2]Cl$, $RuCl(C[O]Et)(CO)_2(PPh_3)_2$ and the starting material. Any manipulation of these mixtures in dichloromethane results in immediate gas evolution and only $RuCl(C[O]Et)(CO)(PPh_3)_2$ can be isolated. High field ^1H NMR spectra of $RuCl(C[O]Et)(CO)(PPh_3)_2$ under an atmosphere of CO at room temperature indicate the presence of two principal products along with two minor products. The ethyl resonances of the two major products (-0.16 t; 1.57 q and 0.22 t; 2.27 q) occur in the approximate ratio of 2/1 and the signals are broadened, especially the pair at 0.22 and 2.27 ppm. Despite the pale yellow colour of the solution at this temperature and the infrared evidence, no signals attributable to the starting material were identifiable. $^{31}P\{^1H\}$ NMR spectra of the same solutions show a sharp singlet at 27.57 ppm and a very broad peak at ca. 26 ppm. On cooling to $-40°C$, this spectrum sharpened considerably to give two singlets at 27.71 and 25.22 ppm in addition to a number of very minor singlets, one of which corresponded to $RuCl(C[O]Et)(CO)(PPh_3)_2$. At this temperature, the solution was virtually colourless and when ^1H NMR spectra were obtained we were still unable to positively identify the presence of starting material, although it was obvious that the two principal products formed were now present in approximately equal amounts. A reasonable interpretation of these data is provided by assuming that the following equilibria occur in solution:

$$RuCl(C[O]Et)(CO)(PPh_3)_2 + CO \rightleftharpoons RuCl(C[O]Et)(CO)_2(PPh_3)_2$$

$$RuCl(C[O]Et)(CO)_2(PPh_3)_2 + CO \rightleftharpoons mer\text{-}[Ru(C[O]Et)(CO)_3(PPh_3)_2]Cl$$

of which only the second is slow on the NMR time scale. The minor products observed may result from similar equilibria involving PPh_3 substitution. If this interpretation is correct then the lower field ^1H NMR signals and the higher field ^{31}P NMR signal must be due to $RuCl(C[O]Et)(CO)_2(PPh_3)_2$.

If $[Ru(C[O]Et)(CO)_3(PPh_3)_2]Cl$ is indeed a product of the above carbonylation, it must exist as a rather tight ion pair since performing the reaction in the presence of $NaClO_4$ does not produce any $[Ru(C[O]Et)(CO)_3(PPh_3)_2]ClO_4$. Similarly, dichloromethane solutions of $RuCl(C[O]Et)(CO)(PPh_3)_2$ show only a very minor increase in conductivity when saturated with CO (0.086 to 0.22 $cm^2\ \Omega^{-1}\ equiv^{-1}$). *mer*-$[Ru(C[O]Et)(CO)_3(PPh_3)_2]ClO_4$ can, however, be synthesized by adding a solution of $RuCl(C[O]Et)(CO)(PPh_3)_2$ to CO saturated acetone containing one equivalent of $AgClO_4$. $[Ru(C[O]Et)(CO)_3(PPh_3)_2]ClO_4$ is very similar to its osmium analogue spectroscopically [5] but is much more sensitive to CO loss, necessitating the presence of CO during recrystallization and other manipulations in solution. The complex also reacts very readily with Cl^-, even bulk NaCl, regenerating the starting material.

$RuCl(C[O]Et)(CO)(PPh_3)_2$ also reacts with *p*-tolylisocyanide (CNR) in a 1/2 molar ratio to generate *cis*-$[Ru(C[O]Et)(CNR)_2(CO)(PPh_3)_2]^+$ which can be isolated as its ClO_4^- salt. Adding the isocyanide in a 1/1 ratio results only in a mixture of the cation and starting material. No evidence for $RuCl(C[O]Et)(CO)(CNR)(PPh_3)_2$ could be found. In view of the fact that $OsCl(Et)(CO)_2(PPh_3)_2$ undergoes an acid assisted migration to generate the hydroxycarbene complex $OsCl_2(CO)(C[OH]Et)(PPh_3)_2$, it was of interest to see whether or not a similar product could be obtained from $RuCl(C[O]Et)(CO)(PPh_3)_2$. The acyl complex reacts, with decolourization, with a vast excess of HCl(aq) in CH_2Cl_2/ethanol solution. Evaporation gives $RuCl_2(CO)(C[OH]Et)(PPh_3)_2$ analogous to its osmium counterpart but considerably more susceptible to dehydrochlorination. Washing the white solid with ethanol, for example, results in partial regeneration of $RuCl(C[O]Et)(CO)(PPh_3)_2$. Spectroscopically, $RuCl_2(CO)(C[OH]Et)(PPh_3)_2$ is very similar to the osmium analogue, although here it is possible to detect the OH proton in the ^1H NMR at 15.15 ppm. Adding D_2O to this solution simply effects the elimination of hydrogen chloride and regeneration of the acyl complex.

Experimental

General

Infrared spectra were recorded on a Perkin–Elmer 283B grating spectrophotometer equipped with a 3500 Data Station, either as Nujol mulls on KBr plates or as CH_2Cl_2 solutions in NaCl cells. ^1H and $^{31}P\{^1H\}$NMR spectra were recorded on a Varian Associates CFT 20 spectrometer in $CDCl_3$ solutions with TMS as internal calibrant or on the Nicolet 360 MHz instrument of the Atlantic Region Magnetic Resonance Centre. Melting points were obtained with a Fisher-Jones apparatus and are uncorrected. Elemental analyses were performed by the Canadian Microanalytical Service Ltd., British Columbia and molecular weight measurements were performed by Galbraith Laboratories Inc., Knoxville, Tennessee. $RuHCl(CO)_2(PPh_3)_2$ was prepared as previously described [16]. All solvents were appropriately dried and distilled before being stored over Linde type 4A molecular sieves. All preparative procedures were performed under an atmosphere of prepurified nitrogen even though most complexes were found to be air stable. Reactions under pressure were performed in a Fisher-Porter aerosol compatibility bottle fitted with a pressure head consisting of an inlet valve, pressure gauge and pressure relief valve set at 120 psi. All complexes were subject to vacuum drying at 60°C before the recording of physical and analytical data, unless otherwise noted.

Warning. Although the perchlorate salts isolated in this study did not prove to be hazardous, the reader should be aware of the potential hazards associated with perchlorate salts, especially in the presence of the free acid.

Preparation of complexes

$RuCl(C[O]C_2H_5)(CO)(PPh_3)_2 \cdot CH_2Cl_2$

$RuHCl(CO)_2(PPh_3)_2$ (3.00 g, 4.17 mmol) and triphenylphosphine (1.10 g, 4.19 mmol) in benzene (100 ml) were subjected to ethylene (25 psi) at 80°C for 3 h. On cooling and venting, ethanol (100 ml) was added and the benzene removed by evaporation under reduced pressure. The yellow product was removed by filtration and recrystallized from dichloromethane/ethanol to give the product as well-formed, bright yellow crystals (3.08 g, 89%). M.p. 150°C. Analysis prior to drying indicated that slow loss of solvent occurred on standing. Thus for the solvate: Anal. Found: C, 59.57; H, 4.55; Cl, 10.56. $C_{41}H_{37}Cl_3O_2P_2Ru$ calcd.: C, 59.24; H, 4.49; Cl, 12.79%.

After prolonged drying (2–3 days) the majority of the solvate can be removed. Anal. Found: C, 63.81; H, 4.60; Cl, 5.09. $C_{40}H_{35}ClO_2P_2Ru$ calcd.: C, 64.38; H, 4.73; Cl, 4.75%. $M = 531$ (calcd. 746), Λ_M 0.086 cm^2 Ω^{-1} equiv^{-1}.

Reaction of $RuCl(C[O]C_2H_5)(CO)(PPh_3)_2 \cdot CH_2Cl_2$ *with CO in acetone*

$RuCl(C[O]C_2H_5)(CO)(PPh_3)_2$ (0.30 g, 0.36 mmol) suspended in acetone (10 ml) was subjected to CO pressure (40 psi) for 5 min, after which time the suspension had turned white. Filtration produced 0.2 g of pale cream product. Evaporation of the filtrate produced bright yellow crystals of the starting material.

mer-$[Ru(C[O]C_2H_5)(CO)_3(PPh_3)_2]ClO_4$

$RuCl(C[O]C_2H_5)(CO)(PPh_3)_2 \cdot CH_2Cl_2$ (0.30 g, 0.36 mmol) was dissolved in the minimum volume of dichloromethane and added to a solution of $AgClO_4$ (0.075 g, 0.36 mmol) in acetone whilst bubbling CO through the reaction mixture. The yellow colour of the parent acyl was immediately discharged and a precipitate of AgCl formed. After filtering through Celite, ethanol (50 ml) was added to the solution and the dichloromethane removed under reduced pressure. A pale yellow solution resulted which turned colourless when exposed briefly to CO and deposited fine white needles, which were recrystallized from dichloromethane/ethanol in similar fashion (0.21 g, 67%). M.p. d 130–135°C. Anal. Found: C, 58.63; H, 4.25; P, 7.13. $C_{42}H_{35}P_2O_8ClRu$ calcd.: C, 58.24; H, 4.07; P, 7.15%. Λ_M 49.5 cm^2 Ω^{-1} equiv^{-1}.

cis-$[Ru(C[O]C_2H_5)(CO)(CNR)_2(PPh_3)_2]ClO_4$

To $RuCl(C[O]C_2H_5)(CO)(PPh_3)_2$ (0.30 g, 0.36 mmol) dissolved in a minimum of dichloromethane was added a solution of *p*-tolylisocyanide in dichloromethane (9.40 ml, 10.0 mg ml^{-1}, 0.80 mmol). To the resultant colourless solution was added a solution of $NaClO_4$ (0.15 g) in 20 ml of ethanol. The faint precipitate of NaCl formed was removed by filtration through Celite and the resultant solution evaporated to ca. 10 ml. Seeding of the solution by scratching produced colourless crystals of the product. Recrystallization was from dichloromethane/ethanol (0.30 g, 80%). M.p. d > 170°C with gas evolution. Anal. Found: C, 64.27; H, 4.83; N, 2.72; P, 5.82. $C_{56}H_{49}N_2P_2O_6ClRu$ calcd.: C, 64.40; H, 4.73; N, 2.68; P, 5.93%. Λ_M 62.5 cm^2 Ω^{-1} equiv^{-1}.

cis-$RuCl_2(C[OH]C_2H_5)(CO)(PPh_3)_2 \cdot 0.5(CH_2Cl_2)$

$RuCl(C[O]C_2H_5)(CO)(PPh_3)_2$ (0.26 g, 0.31 mmol) was dissolved in 20 ml of dichloromethane. To this solution was added 20 ml ethanol and 2 ml of concentrated hydrochloric acid. The yellow colour of the acyl complex was immediately discharged and, on evaporation under reduced pressure, a mass of white needles was obtained. Recrystallization was from dichloromethane/ethanol/hydrochloric acid (0.24 g, 93%). Evidence for the formation of the hemi-solvate comes from the ^1H NMR spectrum at 5.25 ppm (s, 1H). M.p. 225–227°C (dec). Anal. Found: C, 59.27;

H, 4.69; Cl, 12.55. $C_{40}H_{36}Cl_2O_2P_2Ru(CH_2Cl_2)_{0.5}$ calcd.: C, 58.95; H, 4.52; Cl, 12.89%. Λ_M 0.17 $cm^2\ \Omega^{-1}\ equiv^{-1}$.

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