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PHOSPHINE SUBSTITUTION AND PHOSPHINE INDUCED REDUCTIVE ELIMINATION REACTIONS: SYNTHESIS OF ZEROVALENT RUTHENIUM FLUOROPHOSPHINE COMPLEXES FROM HYDRIDO(ACETATO)TRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

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Summary

Substitution of PPh_3 from the bidentate acetatohydridoruthenium(II) complex $RuH(CH_3OCO)(PPh_3)_3$ with various ligands, L, leads to unidentate acetatohydrido compounds with replacement of one, two or all PPh_3 ligands depending on L (L = t-BuNC, PF_2NMe_2, $P(OCH_2)_3CMe$, $P(OMe)_3$, dppe). On the other hand acetic acid elimination from $RuH(CH_3OCO)(PPh_3)_3$ occurs with fluorophosphines to yield zerovalent ruthenium complexes RuL'_5 ($L' = PF_2NMe_2$, $PF_2NC_4H_8$), $RuL_4(PPh_3)$ ($L' = PF_3$) and $RuL_3(PPh_3)_2$ ($L' = PF_3$).

Introduction

Hydrido-transition metal complexes have attracted considerable attention over the past two decades [1—4], and their importance in numerous catalytic processes has been described [4,5—8]. Recently the chemistry of hydrido complexes of the platinum group metals ruthenium, rhodium and iridium has been reviewed [9].

Oxidative addition and reductive elimination are key steps in a number of homogeneous catalytic processes [10—15], and recently Cole—Hamilton and Wilkinson [16] showed that the elimination of an alkane from alkylhydridotriphenylphosphineruthenium(II) complexes involves the abstraction of an *ortho*-hydrogen of a phenyl ring attached to phosphorus. Likewise in contrast to earlier reports [17,18] $RuH_2(PPh_3)_4$ reacts with ethylene to give the hydrido-*ortho*-metallated ruthenium(II) complex rather than the zerovalent complex $Ru(PPh_3)_3(C_2H_4)$.

In view of the report that prolonged treatment of $RuH(CH_3OCO)(PPh_3)_3$ (I) with carbon monoxide gives the zerovalent ruthenium complex $Ru(CO)_3$-

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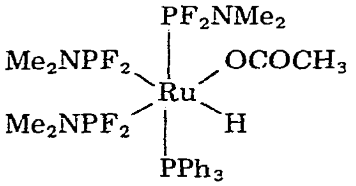
$(PPh_3)_2$ [19] via reductive elimination of acetic acid, we decided to study the generality of this type of reaction by treating I with a wider range of ligands *.

Results and discussion

The nature of the product from the reaction between $RuH(CH_3OCO)(PPh_3)_3$ (I) and PF_2NMe_2 was found to depend on the reaction conditions. Treatment of I with an excess of PF_2NMe_2 at room temperature led to the displacement of two triphenylphosphine ligands and the formation of the yellow hydridoruthenium(II) complex $RuH(CH_3OCO)(PPh_3)(PF_2NMe_2)_3$ (II), whereas at 95°C further displacement of PPh_3 and reductive elimination of CH_3CO_2H occurred to give the white zerovalent complex $Ru(PF_2NMe_2)_5$ (III).

$$RuH(CH_3OCO)(PPh_3)_3 \rightarrow \underset{(II)}{RuH(CH_3OCO)(PPh_3)(PF_2NMe_2)_3} \rightarrow \underset{(III)}{Ru(PF_2NMe_2)_5}$$

These observations clearly show that phosphine displacement reactions precede the reductive elimination step and the formation of the zerovalent metal complex is presumably favoured by the presence of the fluorophosphine ligands.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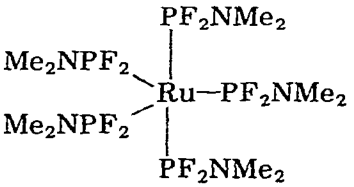
(III)

In related studies we have shown that fluorophosphine ligands can readily induce reactivity between two ligands attached to the same transition metal (e.g. allyl and H or Cl on Pd^{II} or Rh^{III}) [20,21] leading to a reduction in the fomal oxidation state of the metal.

The presence of six ligands attached to ruthenium in II strongly suggests that the acetato group has changed from bidentate in I to monodentate in II and a band at 1630 cm^{-1} is assigned as $\nu(OCO)_{asym}$ [22]. Complex II can exist in four possible isomeric forms and NMR evidence (vide infra) supports the presence mainly of the isomer shown above in which each PF_2NMe_2 is *trans* to a different ligand. The $^{31}P\{^1H\}$ NMR spectrum of II exhibits a doublet for the PPh_3 resonance (coupling to *trans*-PF_2NMe_2) of multiplets (coupling to *cis*-PF_2NMe_2 ligands) and overlapping 1-2-1 triplet patterns for the three types of PF_2NMe_2 ligands. The complexity of the spectrum precludes a full analysis but approximate chemical shift and coupling constant data are summarised in Table 1. The low symmetry of II leads to the presence of non-isochronous fluorine nuclei on each individual PF_2NMe_2 ligand giving rise to a complex spectrum. We found a similar type of behaviour in other PF_2NMe_2-Ru^{II} complexes

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* For a preliminary account of part of this work see ref. 37.

TABLE 1

^{31}P NMR CHEMICAL SHIFT AND COUPLING CONSTANT DATA FOR SOME HYDRIDO RUTHENIUM(II) COMPLEXES [a]

Compound	$\delta(P')$ [b]	$\delta(PPh_3)$ [b]	$^2J(P'_{cis}RuPPh_3)$ [c]
$RuH(CH_3OCO)(t\text{-}BuNC)_2(PPh_3)_2$	—	90.4	—
$RuH(CH_3OCO)(PF_2NMe_2)_3(PPh_3)$ [d,e]	—38.1 —23.2 —19.7	101.4	36.6
$RuH(CH_3OCO)[P(OCH_2)_3CMe]_3(PPh_3)$	~8.5 11.4	96.3	41.5 48.8
$RuH(X)(dppe)_2$	75.1 [f] 77.7 [g]	—	—
$RuH(CH_3OCO)(dppe)(PPh_3)$ [h]	53.1 66.9	92.5	24.4

[a] CH_2Cl_2 solution. [b] ppm relative to TMP. [c] Hz. [d] $^2J(PPh_3RuP_{trans})$ 402.8 Hz. [e] $^1J(PF)$ 1050, 1070, and 1080 Hz. [f] X = CH_3OCO. [g] X = Cl. [h] $^2J(PPh_3Ru\overline{P})_{trans}$) 290.6 Hz.

described elsewhere [23,24]. The proton NMR spectrum of II shows in addition to the PPh_3 and CH_3OCO resonances a high field hydride resonance consisting of a widely spaced doublet ($^2J(PRuH_{trans})$) of multiplets and the chemical shift value; the large phosphorus—hydrogen coupling constant strongly suggests that the group *trans* to H is a fluorophosphine ligand. The methyl protons of PF_2NMe_2 ligands appear as three doublets of triplets (coupling to P and F). Close inspection of their intensities shows that they are not quite equal, suggesting that a small amount of another isomer of II may be present.

The characterisation of III was unambiguously determined by mass spectroscopy and NMR spectroscopy. The most intense line in the mass spectrum of III for the parent ion occurs at *m/e* 667 ($^{102}Ru(PF_2NMe_2)_5$ 667.0) and the intensity pattern of the other isotopic parent ions agreed exactly with expectation. The fragmentation pattern corresponds to successive loss of NMe_2 and PF_2 fragments giving stepwise formation of $Ru(PF_2NMe_2)_n^+$ and $RuPF_2(PF_2NMe_2)_{n-1}^+$ ions ($n = 5 \rightarrow 1$). While this work was in progress the isolation of the analogous iron compound $Fe(PF_2NMe_2)_5$ (14% yield) was reported using metal vapour synthesis [25] and the product was identified mainly by mass spectroscopy, but only ^1H NMR data are available.

The $^{31}P\{^1H\}$ and ^{19}F NMR spectra of III are characteristic of $[AX_2]_5$ spin systems (A = phosphorus, X = fluorine). Although such spin systems are too complicated for a full analysis the observation of a quintet pattern for the centre line of the widely spaced 1-2-1 triplet in the ^{31}P NMR spectrum (Fig. 1) indicates that all five PF_2NMe_2 are identical on the NMR time scale and that an intramolecular exchange process is occurring. Chemical shift and coupling constant data are listed in Table 2. An attempt was made to slow down the rate of intramolecular exchange by cooling III to —85°C but the only change in the ^{19}F NMR spectrum was a broadening of the lines. The ^1H NMR spectrum of III showed a broad band for the Me protons at τ 7.3 ppm which is similar to that observed for $Fe(PF_2NMe_2)_5$ [25].

The analogous piperidinofluorophosphine complex $Ru(PF_2NC_4H_8)_5$ (IV) was

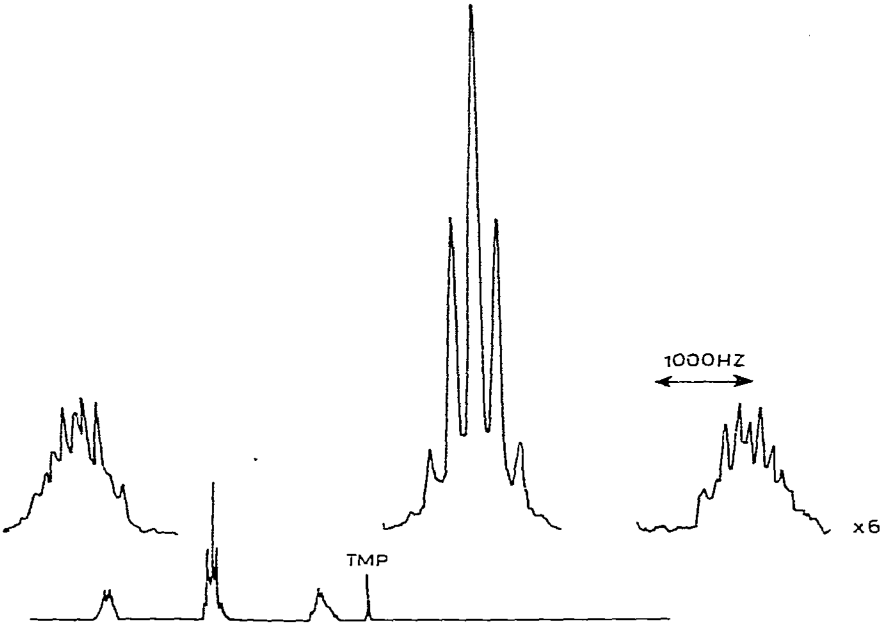


Fig. 1. Proton decoupled ^{31}P NMR spectrum of $Ru(PF_2NMe_2)_5$ (III) at room temperature.

obtained as an oil in a similar way and its ^{31}P and ^{19}F NMR spectra were virtually identical with those of III (Table 2).

The reaction between I and trifluorophosphine in the ratio of 1/3 in CH_2Cl_2 at room temperature gave a high yield of $Ru(PF_3)_3(PPh_3)_2$ (V) and using an excess of PF_3 in benzene at 95°C led to further PPh_3 substitution to afford $Ru(PF_3)_4(PPh_3)$ (VI). It was not possible to remove the last PPh_3 under these conditions, and as described elsewhere [26] $Ru(PF_3)_4(PPh_3)$ was also formed from an excess of PF_3 and $Ru(h^4\text{-}C_4H_6)_2(PPh_3)$. The analogous carbonyl complex $Ru(CO)_4(PPh_3)$ has been obtained [27] by irradiation of $Ru(CO)_5$ solution with PPh_3.

The $^{31}P\{^1H\}$ NMR spectrum of V exhibits a high field quartet pattern for the two magnetically equivalent PPh_3 ligands coupled to the three PF_3 ligands. The low field PF_3 resonance is the A part of an $[AX_3]_3$ spin system with further

TABLE 2

^{19}F AND ^{31}P CHEMICAL SHIFT AND COUPLING CONSTANT DATA FOR FLUOROPHOSPHINE RUTHENIUM(0) COMPLEXES

Complex	$\Phi(F)$ [a,b]	$\delta(P')$ [c]	$\delta(PPh_3)$ [c]	$^2J(PRuP')$ [d]	$[^1J(PF + x\,^3J(PF')]$ [a]
$Ru(PF_2NMe_2)_5$	24.9	−39.5 [e]	—	46.4 [i]	1014 [g]
$Ru(PF_2NC_4H_8)_5$	24.0	−34.5	—	43.9 [i]	1018 [g]
$Ru(PF_3)_4(PPh_3)$	−1.1	−6.3 [f]	101.8	19.8 [j]	1234 [h]
$Ru(PF_3)_3(PPh_3)_2$	4.3	3.9 [e]	96.4	65.9 [k]	1288

[a] $CDCl_3$ solutions. [b] ppm relative to $CFCl_3$. [c] ppm relative to TMP. [d] Hz. [e] CH_2Cl_2 solutions. [f] Benzene solutions. [g] $x = 4$. [h] $x = 3$. [i] Coupling between P′ ligands. [j] $^3J(PPh_3RuPF)$ 9.8 Hz. [k] $^3J(PPh_3RuPF)$ 2.5 Hz.

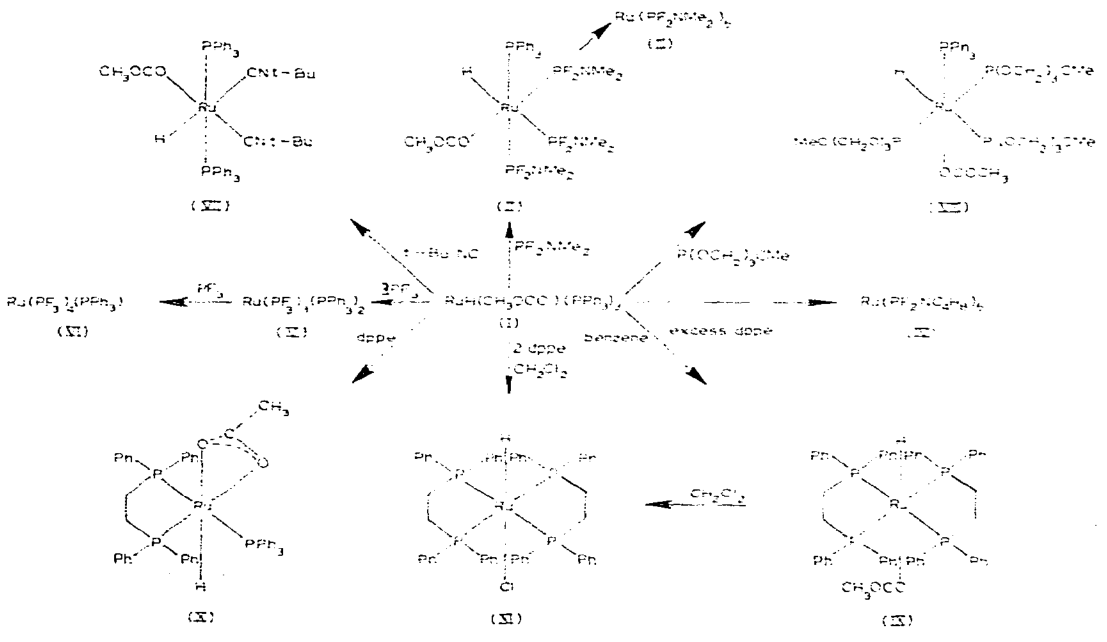
triplet fine structure from coupling to the PPh_3 ligands. The data are consistent with a rapid intramolecular phosphine rearrangement and coupling constant and chemical shift data are summarised in Table 2. No visible change in the spectrum occurred in the ^{31}P NMR spectrum over a range +50 to −55°C. The ^{19}F NMR spectrum showed the expected pattern for the X part of an $[AX_3]_3$ system and is similar in appearance to that reported earlier for $Rh(NO)(PF_3)_3$ [28].

The $^{31}P\{^1H\}$ NMR spectrum of VI showed a high field quintet PPh_3 resonance, each line being split into 13 lines from the twelve equivalent fluorine atoms, while the PF_3 resonance was complex and split into doublets by the PPh_3 ligand. The ^{31}P and ^{19}F NMR spectroscopic data are listed in Table 2.

In contrast to the reductive elimination reactions induced by fluorophosphine ligands, treatment of I with t-butylisonitrile at room temperature resulted in displacement of only one PPh_3 ligand to yield the off-white complex $RuH(CH_3OCO)(t\text{-}BuNC)_2(PPh_3)_2$ (VII). Similarly, the yellow complex $RuH(CH_3OCO)[P(OCH_2)_3CMe]_3(PPh_3)$ (VIII) was obtained from I by treatment with an excess of the cage phosphite in refluxing CH_2Cl_2.

Complete displacement of PPh_3 from I without reductive elimination of acetic acid occurs with an excess of bis(diphenylphosphinoethane) (dppe), to afford $RuH(CH_3OCO)(dppe)_2$ (IX), while the intermediate complex $RuH(CH_3OCO)(PPh_3)(dppe)$ (X) was obtained using a strict 1/1 ratio of dppe.

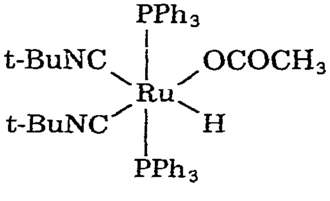
The above substitution reactions are summarised in Scheme 1 and the complexes were found to dissolve in common organic solvents with the exception of IX which is only slightly soluble in chlorinated solvents when a reaction occurs to give $RuHCl(dppe)_2$ (XI) as the main species in solution. Previously



Scheme 1. Some reactions of $RuH(CH_3OCO)(PPh_3)_3$ with various ligands.

Meek and coworkers [29] have briefly reported IX without any experimental details.

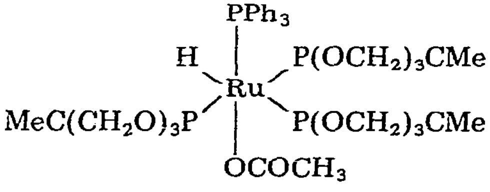
The structure of VII shown below was assigned on the basis of its ^{1}H and ^{31}P NMR spectra. The ^{1}H NMR spectrum exhibits in addition to the expected resonances of PPh_3, CH_3OCO and t-BuNC a high field triplet pattern for the hydride resonance (^2J(HRuP) 17 Hz) indicating the two PPh_3 ligands are equivalent and mutually *cis*- to the hydride ligand. The chemical shift (τ 17.9 ppm) is typical for complexes in which the hydride is *trans* to a neutral ligand rather than to an anionic group.



(VII)

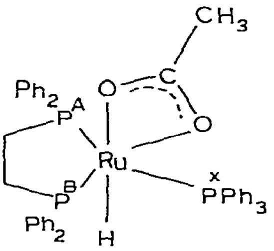
Confirmation of the proposed structure comes from the proton decoupled ^{31}P NMR spectrum which shows a singlet. In the related $RuHCl(CO)(CNR)(PPh_3)_2$ [30] (R = *p*-tolyl) complex Roper et al. reported a triplet hydride pattern (^2J(HRuP) 19 Hz) in the ^{1}H NMR spectrum, indicative of *trans*-PPh_3 groups. Recently we assigned a similar structure to $RuH(CF_3OCO)(PF_3)_2(PPh_3)_2$ [31] on the basis of NMR studies and confirmed the stereochemistry of $RuCl_2(PF_3)_2(PPh_3)_2$ by a single crystal X-ray crystallographic study [32]. The IR spectrum of VII exhibits a strong ν(CN) band at 2130 cm^{-1} (cf. 2140 cm^{-1} for $RuHCl(CO)(CNR)(PPh_3)_2$ [30]) and a band at 1620 cm^{-1} is assigned to $\nu(OCO)_{asym}$.

The $^{31}P\{^1H\}$ NMR spectrum of VIII exhibits a high field overlapping doublet of triplets for the PPh_3 ligand and a complex low field multiplet for the coordinated $P(OCH_2)_3CMe$ ligands. The data suggest an $[AB_2X]$ spin system but a complete analysis was not carried out and only approximate coupling constant data are listed in Table 1. The hydride resonance of VIII appears as a doublet of multiplets, the large splitting being characteristic of a hydride *trans* to a phosphite ligand (Table 3).



(VIII)

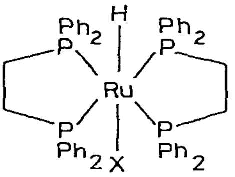
Complex X ($RuH(CH_3OCO)(PPh_3)(dppe)$) is most probably six-coordinate with a bidentate acetato group as in I and the $^{31}P\{^1H\}$ NMR spectrum shows an [ABX] pattern (A and B = $Ph_2PCH_2CH_2PPh_2$, X = PPh_3). The assignments are listed in Table 1 and the large coupling constant $^2J(P_ARuP_X)$ 290.6 Hz suggests



(X)

that they are in mutually *trans*-positions as indicated in the above structure. Confirmation of the proposed structure comes from the ^{1}H NMR spectrum which exhibits the high field hydride resonance as an overlapping doublet of doublets of doublets from coupling to the three magnetically inequivalent phosphine nuclei. The hydride chemical shift (τ 28.9 ppm) is typical for hydride *trans* to an anionic ligand. In general (Table 3) we find that the resonances of hydride *trans* to phosphine occur at 10 ppm to lower field than hydride *trans* to the anionic ligand. The IR spectrum of X exhibits a band at 1980 cm^{-1} (ν(Ru—H)) and a band at 1540 cm^{-1} for $\nu(OCO)_{asym}$ lies within the range expected for bidentate carboxylate complexes [22].

The ^{1}H NMR spectrum of IX could not be obtained since it proved to be insoluble in non-chlorinated solvents and reacted with the latter to replace the



(X:X = OCOCH$_3$;
XI:X = Cl)

acetato group by a chloride ligand. This ready exchange was unexpected but was confirmed by refluxing I with dppe in CH_2Cl_2 to give mainly XI. The high field quintet pattern in the ^{1}H NMR spectrum of XI occurred at (τ 28.8 ppm) which is typical of hydride *trans* to an anionic ligand and is consistent with the *trans* structure shown above where all four phosphorus nuclei are magnetically equivalent.

The ^{31}P{^{1}H} NMR spectrum of XI exhibits a strong singlet at 77.7 ppm (rel. TMP) and an additional weaker singlet at 75.1 ppm may be due to the complex X. In one experiment X was made in benzene solution and then dissolved in $CHCl_3$ and its ^{13}P NMR immediately recorded. Both the above singlets were observed together with much weaker lines (<5%) similar in appearance to those reported by Ittel et al. [33] for the *cis*-hydrido complex RuH(Np)(dmpe)$_2$ (Np = 2-naphthyl) which is an ABCDX spin system.

TABLE 3

^{1}H NMR CHEMICAL SHIFTS [a] AND COUPLING CONSTANT DATA [b] FOR SOME HYDRIDO RUTHENIUM(II) COMPLEXES

Complex	Solvent	τ(Ru—H)	^2J(HRuP) [b]		Other ^{1}H resonances
			cis	*trans*	
$RuH(CH_3OCO)(t\text{-}BuNC)_2(PPh_3)_2$	CD_2Cl_2	17.9	17.0	—	2.5—2.7m(phenyl) 8.85s(CH_3OCO, 9.4s(t-Bu)
$RuH(CH_3OCO)(PF_2NMe_2)_3(PPh_3)$ [c,d]	CD_2Cl_2	14.9	—	~160	2.2—2.7m(phenyl) 6.95d, t, 7.34d, t, 7.68d, t(NMe_2) 8.7s(CH_3OCO)
$RuH(CH_3OCO)[P(OCH_2)_3CMe]_3(PPh_3)$	$CDCl_3$	17.6	—	~117	1.4—1.9m(phenyl) 5.05s, 5.5s, 5.95s(OCH_2) 8.35s, 8.45s, 8.52s(Me) 8.7s(CH_3OCO)
$RuH(CH_3OCO)(PPh_3)(dppe)$ [e]	$CDCl_3$	28.9	[e]	—	2.1—2.95m(phenyl) 7.0—7.9(br)(C_2H_4) 9.00(CH_3OCO)
$RuHX(dppe)_2$	$CDCl_3$	28.7	19.0	—	2.6—3.1m(phenyl) 7.1—8.1(br)(C_2H_4)

[a] Relative to TMS(τ 10). [b] Hz. [c] $^3J(PNCH)$ 11 Hz. [d] $^4J(FPNCH)$ 3.0 Hz. [e] $^2J(P_BRuH)$ 39.0, $^2J(P_ARuH) = {}^2J(P_XRuH) = 19.5$ Hz.

Experimental

General procedures were as described elsewhere [34]. ^1H NMR spectra were recorded on a Perkin—Elmer R32 instrument operating at 90 MHz, ^{19}F NMR spectra were recorded on either a Jeol PFT 100 Fourier transform or Perkin—Elmer R32 spectrometer operating at 84.6 MHz. ^{31}P NMR spectra were recorded on a Jeol PFT 100 Fourier transform spectrometer operating at 40.49 MHz. IR spectra in the range 4000—250 cm^{-1} were recorded on a Perkin—Elmer 457 spectrophotometer. Mass spectra were recorded on an AEI MS9 spectrometer. $RuH(CH_3OCO)(PPh_3)_3$ was obtained as described in the literature [35].

Preparation of $RuH(CH_3OCO)(PF_2NMe_2)_3(PPh_3)$

A mixture of $RuH(CH_3OCO)(PPh_3)_3$ (0.350 g, 0.369 mmol), PF_2NMe_2 (0.223 g, 1.90 mmol) and CH_2Cl_2 (15 cm^3) was sealed off in an ampoule and shaken at room temperature for 6 h. The ampoule was opened under a nitrogen atmosphere and after removal of solent the oily product was washed with hexane (20 cm^3) to give the yellow solid complex acetatohydridotris(dimethylaminodifluorophosphine)(triphenylphosphine)ruthenium(II) (Found: C, 44.5; H, 5.3; N, 4.7. $C_{26}H_{37}F_6N_3O_2P_4Ru$ calcd.: C, 41.0; H, 4.9; N, 5.5%). IR spectrum 3060w, 2015w(br), 1630m(br), 1585w, 1570vw, 1305s, 1180s, 1155m(sh), 1110w, 1090m, 1070w, 1025w, 990vs, 950w(sh), 905vw, 850m(sh), 835vs, 805vs, 790vs(br); 750s, 700s(br), 620vw, 545m(sh), 525vs(br), 460vw, 425m, 390vw, 360m, 320vw, 280w(br) cm^{-1} (Nujol mull).

Preparation of $RuH(CH_3OCO)(P(OCH_2)_3CMe)_3(PPh_3)$

A solution of $RuH(CH_3OCO)(PPh_3)_3$ (0.697 g, 0.736 mmol) in CH_2Cl_2 (25 cm^3) and $P(OCH_2)_3CMe$ (0.654 g, 4.4 mmol) was heated under reflux for 6 h. Evaporation of the yellow solution to dryness, followed by stirring in hexane (30 cm^3) overnight, gave the yellow powder, acetatohydridotris(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)(triphenylphosphine)ruthenium(II) (0.588 g, 0.677 mmol, 92%). M.p. 102°C. (Found: C, 49.3; H, 5.9. $C_{35}H_{46}O_5P_4Ru$ calcd.: C, 48.4; H, 5.3%). IR spectrum: 3050w, 1940w(br), 1625w(br), 1585w, 1570w, 1345w, 1310w(br), 1180s, 1090m, 1055m(sh), 1045m(sh), 1020vs(br), 960m, 930s, 860s, 790vs(br), 765s, 745s, 730s, 700s, 685w(sh), 650vs, 620vw, 520s, 460w, 425m, 375m, 345m cm^{-1} (Nujol mull).

Preparation of $RuH(CH_3OCO)(dppe)_2$

A solution of $RuH(CH_3OCO)(PPh_3)_3$ (1.315 g, 1.38 mmol) in benzene (50 cm^3) and an excess of $Ph_2PCH_2CH_2PPh_2$ (3.316 g, 8.322 mmol) was heated under reflux for 4 h. The greenish-yellow solid found was filtered off, washed with hexane, dried in vacuo and identified as acetatohydridobis(bis(diphenylphosphino)ethane)ruthenium(II) (0.98 g, 1.02 mmol 73%). M.p. 217°C (dec). (Found: C, 67.5; H, 6.1. $C_{54}H_{52}O_2P_4Ru$ calcd.: C, 67.8; H, 5.5%). IR spectrum: 3050w, 2040w, 1605s, 1590m(sh), 1565m(sh), 1545w(sh), 1330m, 1315w(sh), 1280w, 1240vw, 1190w, 1155w, 1100s, 1070w, 1030w, 1005w, 985vw(br), 920vw(br), 890m, 850vw, 830m, 810w, 745s, 730w, 700s, 685m, 650w, 620w, 540s, 525s, 490s, 480m, 435m, 420m, 400vw, 390w, 320m, 310vw cm^{-1} (Nujol mull).

Preparation of $RuH(CH_3OCO)(PPh_3)(dppe)$

In a similar way to the above $RuH(CH_3OCO)(PPh_3)_3$ (1.026 g, 1.082 mmol) and dppe (0.431 g, 1.082 mmol) gave the yellow solid acetatohydrido(bis(diphenylphosphino)ethane)(triphenylphosphine)ruthenium(II) (0.850 g, 1.034 mmol; 95%). M.p. 162—164° C (dec). (Found: C, 67.5; H, 6.0. $C_{46}H_{43}O_2P_3Ru$ calcd.: C, 67.2; H, 5.3%). IR spectrum: 3060w, 1980m, 1590w, 1580w, 1540m, 1315w, 1280w, 1240vw, 1190w, 1160vw, 1120vw, 1098s, 1085w, 1030w, 1003w, 945w, 882w, 850vw, 818m, 784vw, 755m, 747s, 727m, 700vs, 685s, 775w(sh), 648w, 619w, 550m(sh), 542vs, 528vs, 520m(sh), 507m, 493w, 462w, 441m, 427m, 405w, 373w, 340vw(br), 284vw(br) cm^{-1} (Nujol mull).

Reaction of $RuH(CH_3OCO)(PPh_3)_3$ *with dppe in* CH_2Cl_2

$RuH(CH_3OCO)(PPh_3)_3$ (0.400 g, 0.422 mmol) was heated under reflux with dppe (0.336 g, 0.870 mmol) in CH_2Cl_2 (35 cm^3) for 5 h to afford the greenish-yellow product (0.38 g, 0.401 mmol, 96%). M.p. 138° C formulated as chlorohydridobis(bis(diphenylphosphino)ethane)ruthenium(II) (containing a small amount of the acetato complex IX. (Found: C, 65.3; H, 5.2; Cl, 3.9. $C_{52}H_{49}ClP_4Ru$ calcd.: C, 66.8; H, 5.3; Cl, 3.9%). IR spectrum: 3060w, 2040w, 1605w(sh), 1580m(br), 1550w(sh), 1530vw(sh), 1315vw, 1280vw(br), 1190m, 1160w, 1120vw, 1100s, 1075w, 1030w, 1005w, 980vw(br), 930vw(br), 890m, 855vw, 830m, 785w, 745s, 730w, 700s, 675m, 650w, 625w, 540s, 520m, 495s, 430m, 400vw, 390vw, 315w cm^{-1} (Nujol mull).

Preparation of $Ru(PF_3)_3(PPh_3)_2$

A mixture of $RuH(CH_3OCO)(PPh_3)_3$ (2.272 g, 2.40 mmol), trifluorophosphine (0.666 g, 0.757 mmol) and CH_2Cl_2 (50 cm^3) was sealed off in an ampoule and warmed from —196° C to room temperature where a rapid reaction occurred and the colour of the solution changed from orange to pale yellow. The mixture was shaken overnight and removal of solvent and acetic acid gave a pale-yellow oil which was washed with hexane (3 × 10 cm^3) and recrystallisation from CH_2Cl_2/hexane gave colourless crystals of tris(trifluorophosphine)bis(triphenylphosphine)ruthenium(0) (1.996 g, 2.25 mmol, 93.6%); M.p. 170° C (dec). (Found: C, 48.4; H, 3.7. $C_{36}H_{30}F_9P_5Ru$ calcd.: C, 48.7; H, 3.4%). IR spectrum 3063w, 1588w, 1573w, 1485m, 1438m, 1315vw, 1268vw, 1230vw, 1191mw, 1162vw, 1091m, 1080vw(sh), 1031vw, 1003mw, 976vw, 927vw, 892w, 866vw(sh), 853w(sh), 827s, 816m(sh), 804vs, 782w(sh), 751m, 705w(sh), 699m, 686w(sh), 620vw, 549vw(sh), 521vs, 513w(sh), 462vw(sh), 456mw, 429mw, 412w, 407w, 388w cm^{-1} (Nujol mull).

Preparation of $Ru(PF_3)_4(PPh_3)$

In a similar manner to that above using an excess of PF_3 at 95° C led to formation of an oil which after treatment with $CoCl_2$ (in EtOH) to remove PPh_3 gave tetrakis(trifluorophosphine)(triphenylphosphine)ruthenium(0) as a colourless oil.

Preparation of $Ru(PF_2NMe_2)_5$ *and* $Ru(PF_2NC_4H_8)_5$

The above complexes were obtained from $RuH(CH_3OCO)(PPh_3)_3$ and an excess of aminodifluorophosphine ligand. $Ru(PF_2NMe_2)_5$ was obtained as a white solid and $Ru(PF_2NC_4H_8)_5$ as a pale yellow oil and their formulation was confirmed by ^{19}F, ^{1}H and ^{31}P NMR spectroscopy and mass spectroscopy (see text) *.

Preparation of $RuH(CH_3OCO)(t\text{-}BuNC)_2(PPh_3)_2$

t-BuNC (0.2 g, 2.4 mmol) was condensed into a solution of $RuH(CH_3OCO)(PPh_3)_3$ (0.300 g, 0.316 mmol) in CH_2Cl_2 (15 cm^3) in an evacuated glass ampoule which was then sealed and warmed from —196°C to room temperature. After shaking the mixture for 6 h removal of the volatiles gave an oil which was washed with hexane (15 cm^3) to give the off-white solid complex acetatohydridobis(t-butylisonitrile)bis(triphenylphosphine)ruthenium(II) (0.190 g, 0.223 mmol; 57%). (Found: C, 66.0; H, 6.9; N, 4.1. $C_{36}H_{42}N_2O_2P_2Ru$ calcd.: C, 67.7; H, 6.2; N, 3.3%). IR spectrum: 3050w, 2185m(sh), 2130s(br), 1620m(br), 1315w(br), 1240w, 1200m(br), 1160vw, 1120vw, 1100m, 1030w, 975vw(br), 850vw(br), 790w(br), 750m, 725w, 700s, 685m, 615vw(br), 590w, 555m, 525s, 515m(sh), 495w(sh), 470w, 430vw cm^{-1} (Nujol mull).

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* Since completion of this work a brief report by Timms and King [36] on the direct synthesis of $Ru(PF_2NMe_2)_5$ has appeared.

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