Decomposition Reactions of Cationic Ruthenium Formyl Complexes

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trans-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] (dppe = $Ph_2PCH_2CH_2PPh_2$) decomposes in CH_2Cl_2 with first-order kinetics ($t_{\frac{1}{2}}$ = 9.25 min, $k = 11 \times 10^{-4}$ s^{-1}) to give *cis*-[RuH(CO)(dppe)$_2$][SbF$_6$] which subsequently isomerises to the *trans* isomer ($t_{\frac{1}{2}} \simeq 72$ h). A deuterium isotope effect of 1.8 on the decomposition reaction is interpreted as being primary, the low value being attributable to a three-membered cyclic transition state and movement of the oxygen atom during the rate-determining step. A predissociation of a phosphorus atom of a dppe ligand is followed by rate-determining hydride migration for the decomposition, or fluxionality of the five-membered intermediate for the isomerisation. If the isomerisation of *cis*-[RuD(CO)(dppe)$_2$][SbF$_6$] is carried out at low temperature, significant H/D exchange of the deuteride and both phenyl and methylene hydrogen atoms of the dppe ligand is observed. *cis*-[Ru(CHO)(CO)(dppm)$_2$][SbF$_6$] (dppm = $Ph_2PCH_2PPh_2$) gives [RuH(CO)$_2$(dppm)$_2$]-[SbF$_6$] with a unidentate dppm ligand but chelation occurs on photolysis in CH_2Cl_2 to give *trans*-[RuCl(CO)(dppm)$_2$][SbF$_6$] *via trans*-[RuH(CO)(dppm)$_2$][SbF$_6$].

The decomposition reactions of metal formyl complexes have been the subject of a number of recent studies [1] although the intimate details of the mechanism of these decomposition reactions have only been unravelled in a few instances. Thus, kinetic studies in the presence and absence of added phosphite suggest [2] that [Fe(CHO)(CO)$_3${P(OC$_6$H$_3$Me$_2$-3,5)$_3$}]$^-$ decomposes *via* rate-determining loss of phosphite ligand followed by rapid α-hydrogen transfer to give [FeH(CO)$_4$]$^-$. A similar mechanism is assumed to operate for the decomposition of the closely related [Fe(CHO)(CO)$_4$]$^-$ and [Fe(CHO)(CO)$_3${P(OPh)$_3$}]$^-$, although in the latter case the products are [FeH(CO)$_4$]$^-$ and [FeH(CO)$_3${P(OPh)$_3$}] (4 : 1).

For [Mn(CHO)(CO)$_4${C(Ph)O}]$^-$ the rate-determining step is believed [3] to be hydride transfer from the formyl to the benzoyl group probably *via* a cyclic four-membered transition state; subsequent fast steps lead to [Mn(CO)$_5$]$^-$, [Mn(CO)$_5${C(Ph)O}] and $PhCH_2O^-$ as observable products.

For rhenium formyl complexes the decomposition products depend upon the conditions.[4,5] Thus, [Re(cp)(CHO)(NO)(CO)] (cp = η-C$_5$H$_5$) decomposes to [Re(cp)H(NO)(CO)] in dilute solution whilst more concentrated solutions give [(CO)(NO)(cp)Re{C(O)OCH$_2$}Re(cp)(NO)(CO)].

The analogous [Re(cp)(CHO)(NO)(PPh$_3$)] gives [6] a 1 : 1 mixture of [Re(cp)H(NO)L] (L = PPh_3 or CO) if decomposed in hot toluene ($t_{\frac{1}{2}} \simeq 1$ h) but little of these products when decomposed at lower temperatures. In none of these rhenium cases, however, has the rate-determining step been established.

Very recently, Gladysz and co-workers [7] have reported on the decomposition reactions of dinuclear metal formyl complexes, [Mn$_2$(CHO)(CO)$_9$]$^-$, and they conclude that rate-determining metal–metal bond cleavage is followed by hydrogen loss from unreacted formyl and transient [Mn(CHO)(CO)$_4$] to give [Mn$_2$(CO)$_{10}$].

An isotope effect of 1.66 is assigned as secondary rather than primary, although it is accepted that this is an exceptionally high value for a secondary isotope effect.

For polynuclear metal complexes, the observation [8] that deuterioformyl complexes can be detected in certain cases where their protioformyl analogues are insufficiently stable for detection suggests a marked isotope effect and that hydride migration is rate determining.

We now report detailed studies of the decomposition reactions of cationic ruthenium formyls and their deuterio-analogues which give insight into the mechanism by which these reactions occur.

Results and Discussion

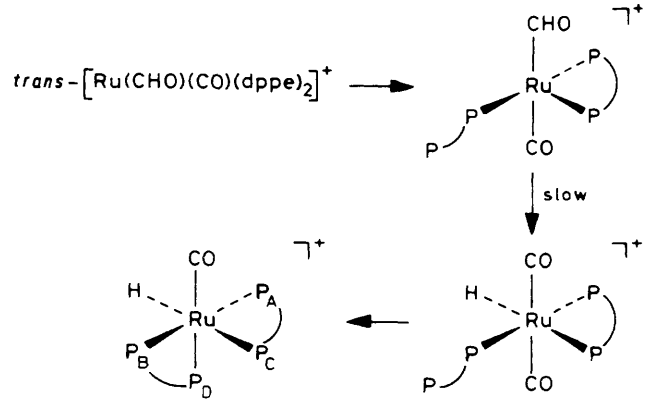
(*a*) 1,2-*Bis*(*diphenylphosphino*)*ethane* (*dppe*) *Complexes*.—*trans*-[Ru(CHO)(CO)(dppe)$_2$][Y] (Y = SbF$_6$ or BEt$_4$) [9] decomposes by first-order kinetics with a half-life of 9.25 min at 30 °C ($k = 11 \times 10^{-4}$ s^{-1}) in CH_2Cl_2 to give *cis*-[RuH(CO)(dppe)$_2$][Y] [10] as the only primary product. A deuterium isotope effect of 1.8 is observed on decomposition of the analogous *trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] under identical conditions. The reaction is somewhat complicated by the fact that *trans*-[Ru(CHO)(CO)(dppe)$_2$]$^+$, prepared from *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$] and Na[BH(OEt)$_3$] or K[BH(OPr^i)$_3$] in CH_2Cl_2, is usually contaminated by significant amounts of *trans*-[RuCl(CO)(dppe)$_2$]$^+$. However, we have been able to rule this out as a decomposition product by careful recrystallisation of the starting formyl or by synthesis of the formyl in tetrahydrofuran (thf). In both cases, decomposition of the product formyl in CH_2Cl_2 leads only to *cis*-[RuH(CO)(dppe)$_2$]$^+$.

In a subsequent and slower step, *cis*-[RuH(CO)(dppe)$_2$]$^+$ isomerises to the *trans* isomer with a half-life of ≃ 72 h at 25 °C.

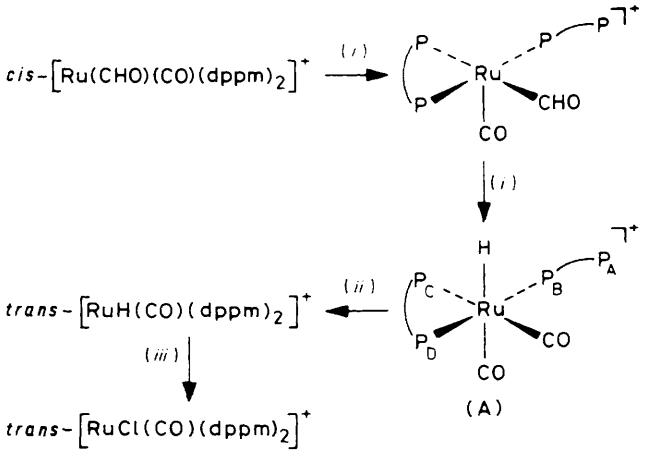
Mechanism of formyl decomposition. The observation of a kinetic isotope effect of 1.8 in the decomposition of the ruthenium formyl complexes suggests that the rate-determining step must involve hydride transfer since it is unlikely that such a large rate difference could be attributed to a secondary isotope effect. Although hydride and deuteride have significantly different *trans* effects in octahedral complexes, it would not be expected that formyl and deuterioformyl ligands would differ significantly in this respect.

The assignment of Gladysz and co-workers [7] of an isotope effect of 1.66 to being secondary rather than primary suggests that this may also be the case for *trans*-[Ru(CHO)(CO)(dppe)$_2$]$^+$ but other experiments (see below) would appear to rule this out.

Although decomposition of *trans*-[Ru(CHO)(CO)(dppe)$_2$]$^+$ in the presence of radical traps [11] does lead to the isolation of trapped metal radicals, the low isotope effect rules out homolytic cleavage of the C–H bond as being rate determining. An alternative radical-based mechanism involving rate-determining cleavage of the M–C bond followed by decomposition of the formed formyl radical and reattack of H$^\cdot$ might allow an isotope effect of the observed magnitude but if free radicals *are* involved, co-decomposition of *trans*-[Ru(^{13}CHO)-



Scheme 1. Proposed mechanism for the decomposition of *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$ in CH_2Cl_2 (P–P = dppe)



Scheme 2. Proposed mechanism for the decomposition of *cis*-$[Ru(CHO)(CO)(dppm)_2]^+$ (P–P = dppm) and for the subsequent photolysis of the decomposition product: (*i*) CH_2Cl_2, 25 °C; (*ii*) u.v. irradiation, CH_2Cl_2, 25 °C, 24 h; (*iii*) u.v. irradiation, CH_2Cl_2, 25 °C, 48 h

$(^{13}CO)(dppe)_2]^+$ and *trans*-$[Ru(CDO)(CO)(dppe)_2]^+$ should lead to scrambling of the labels and formation of $[RuH(^{13}CO)(dppe)_2]^+$, $[RuH(CO)(dppe)_2]^+$, $[RuD(CO)(dppe)_2]^+$, and $[RuD(^{13}CO)(dppe)_2]^+$. In practice, the hydride resonance in the ^1H n.m.r. spectra of solutions obtained from such co-decompositions is identical to that obtained from decomposition of *trans*-$[Ru(^{13}CHO)(^{13}CO)(dppe)_2]^+$ alone. This result rules out the formation of *free* radicals in the system so that if radical species are important, decomposition of the formyl radical and re-attack of H· on the metal must all occur before escape from the solvent cage. We think this unlikely and believe that the radical traps are acting as radical generators since similar trapped metal radicals are obtained from *trans*-$[Os(CHO)(CO)(dppe)_2]^+$ and Bu^{t}NO under conditions where the osmium compound is stable towards decomposition.[11,12]

Since the above arguments rule out a radical decomposition mechanism for *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$, it seems likely that the rate-determining step of the reaction must be hydride migration from CO to Ru in a five-co-ordinate intermediate. This type of migration would be expected to occur *via* a three-centred transition state and since the angle at hydrogen is much less than 180° a small isotope effect would be expected.[13] Movement of the oxygen atom in arriving at the transition state should also lead to a lower than expected isotope effect.[13]

In the only other formyl decomposition reaction where a primary isotope effect has been measured and interpreted, the rate-determining step is believed[3] to involve hydride migration from formyl to benzoyl ligand in $[Mn(CHO)(CO)_4\{C(Ph)O\}]^-$. In this case $k_H/k_D = 3.4$, consistent with a cyclic four-membered transition state.[13] To our knowledge, the only examples of primary kinetic isotope effects as low as those observed in this study, for example in the hydrolysis of the B–H bond of $BHPh_2$·py (py = pyridine) ($k_H/k_D = 1.5$),[14] involve a three-centred cyclic transition state, thus supporting the existence of a similar type of transition state in the decomposition of *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$. Unfortunately, isotope effects on the rate of other α-hydrogen abstraction reactions where a hydride is transferred to the metal, *e.g.* the formation of carbene–hydrides from metal alkyls do not appear to have been measured.[15,16]

It remains then to identify the five-co-ordinate intermediate in which this rate-determining hydride migration occurs. A seven-co-ordinate intermediate, $[RuH(CO)_2(dppe)_2]^+$, can be ruled out since if this were accessible it should be formed directly in the reaction of $[Ru(CO)_2(dppe)_2]^{2+}$ with hydride donors.

We can rule out an initial pre-equilibrium involving CO loss to give transient $[Ru(CHO)(dppe)_2]^+$ since partial decomposition of $[Ru(CDO)(CO)(dppe)_2]^+$ under ^{13}CO should lead to ^{13}CO incorporation into the recovered unreacted formyl. In practice, this is not the case and ^{13}CO is not incorporated into the decomposition product or the recovered formyl complex.

We conclude, therefore, that the mechanism of decomposition of *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$ is as shown in Scheme 1. This involves an initial reversible cleavage of an Ru–P bond to give a five-co-ordinate intermediate in which hydride migration occurs. This is followed by rapid loss of carbon monoxide and re-co-ordination of the free phosphorus atom. We believe that, although the five-co-ordinate intermediates may be fluxional, their rearrangement will be slower than any of the other steps (see below).

(*b*) *Bis(diphenylphosphino)methane (dppm) Complexes.*—Further support for the mechanism of decomposition of *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$ shown in Scheme 1, and in particular for the formation of a unidentate dppe ligand comes from studies of the decomposition of *cis*-$[Ru(CHO)(CO)(dppm)_2]^+$.[9] This complex decomposes almost instantaneously at room temperature in CH_2Cl_2 to give almost exclusively (>95%) $[RuH(CO)_2(dppm)_2]^+$ with mutually *cis* carbonyl groups and a unidentate dppm ligand [(A) in Scheme 2], *via* the mechanism shown in Scheme 2. The isolation of this species containing a unidentate dppm ligand presumably occurs because of the greater ring strain in chelated dppm than in dppe. The relief of this ring strain may also be responsible for the greater rate of decomposition of *cis*-$[Ru(CHO)(CO)(dppm)_2]^+$ than of *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$.

Formation of *trans*-$[RuH(CO)(dppm)_2]^+$ can be achieved by photolysis of $[RuH(CO)_2(dppm)_2]^+$ in CH_2Cl_2 but the hydride is further converted to $[RuCl(CO)(dppm)_2]^+$ under these conditions (see Scheme 2).

Mechanism of Isomerisation of cis-$[RuH(CO)(dppe)_2]^+$.—As pointed out above, *cis*-$[RuH(CO)(dppe)_2]^+$ isomerises to its *trans* isomer in CH_2Cl_2 at room temperature with a half-life of ≃ 72 h. *trans* Isomers of complexes of the form $[RuXY(dppe)_2]^+$ are generally thermodynamically the more stable for steric reasons [17] and, indeed, *cis*-$[RuH(CO)(dppe)_2]^+$

Table 1. Spectroscopic data for ruthenium complexes of *trans* stereochemistry

Complex	$\nu_{C\equiv O}$/cm^{-1}	^{31}P N.m.r. δ [a]	^{31}P N.m.r. J_{PC}/Hz	^{1}H N.m.r. δ [b]	^{1}H N.m.r. J_{PH}/Hz	^{13}C N.m.r. δ [b]	^{13}C N.m.r. J_{PC}/Hz
trans-[RuH(CO)(dppe)$_2$][SbF$_6$]	1 987	62.8(s) [c]		−6.83(quin)	19.5		
trans-[RuH(CO)(dppe)$_2$][BEt$_4$] [d]	1 985	62.8(s) [c]		−6.8(quin)	19.5		
trans-[RuH(^{13}CO)(dppe)$_2$][BEt$_4$] [d]		63.5(d) [e]	8.54	−6.8(dquin)	20.0	201.3(quin) [f]	8.54
trans-[RuD(CO)(dppe)$_2$][SbF$_6$]	1 973	63.9(t) [g]		−7.2(m) [h]			
trans-[RuH(CO)(dppm)$_2$][SbF$_6$]	1 997	−2.29(s) [c]		−3.07(quin)	20.5		
trans-[RuD(CO)(dppm)$_2$][SbF$_6$]	1 984	−2.33(s) [i]		−3.4(m) [h]			
trans-[RuCl(CO)(dppe)$_2$][SbF$_6$]	1 946	40.5(s)					
trans-[RuCl(^{13}CO)(dppe)$_2$][BEt$_4$] [d]		41.7(d)	11.56			198.97(quin)	11.6
trans-[RuCl(CO)(dppm)$_2$][SbF$_6$]	1 974	−13.87(s)					

[a] In p.p.m. to high frequency of external 85% H_3PO_4, in CH_2Cl_2 at 298 K. [b] In p.p.m. relative to internal $SiMe_4$, CH_2 resonances not analysed, in CD_2Cl_2 at 298 K. [c] Splits into a doublet on selective ^{1}H decoupling of phenyl protons only. [d] All $[BEt_4]^-$ compounds have expected ^{1}H and ^{11}B resonances; ^{1}H n.m.r., δ 0.73 (tq, 1 : 1 : 1 : 1, $J_{CH_3CH_2B}$ = 3 Hz), and −0.03 (qq, 1 : 1 : 1 : 1, $J_{CH_3CH_2B}$ = 4.5 Hz), ^{11}B n.m.r., δ −16.11(s) relative to external BF_3·OEt_2. [e] Splits into a further doublet on selective ^{1}H decoupling of phenyl protons only. [f] Splits into a doublet of quintets on selective ^{1}H decoupling of phenyl protons only; J_{CH} = 20 Hz (from ^{1}H spectrum). [g] 1 : 1 : 1 triplet, J_{PD} = 3 Hz. [h] δ(Ru−D) in p.p.m. relative to internal $SiMe_4$, internal ^{7}Li used for lock. [i] Unresolved fine structure present.

appears to be the only *cis* isomer of this kind to have been isolated.

Isomerisation of *cis*-[RuD(CO)(dppe)$_2$]$^+$ shows no significant isotope effect, although the kinetic data are not sufficient to identify an effect of 1.3 or less. However, when the isomerisation is carried out at low temperature, significant exchange of the deuterium atom with the hydrogen atoms [both phenyl (^{2}D, δ 7.38, ν_{C-D} = 2 360 cm^{-1}) and methylene (^{2}D, δ 2.92, ν_{C-D} = 2 318 cm^{-1})] of the dppe ligand occurs. This exchange appears to be intramolecular since the intensity of the C−D stretches in the i.r. spectra appear to correlate with the amount of hydride present, as determined from the ^{31}P n.m.r. spectrum. For the pure [RuD(CO)(dppe)$_2$]$^+$ the resonance appears as a 1 : 1 : 1 triplet (J_{PD} = 3 Hz) whereas if H−D exchange occurs the central resonance has a higher relative intensity. On some occasions this intensity enhancement can be as much as 60% but is usually around 12%.

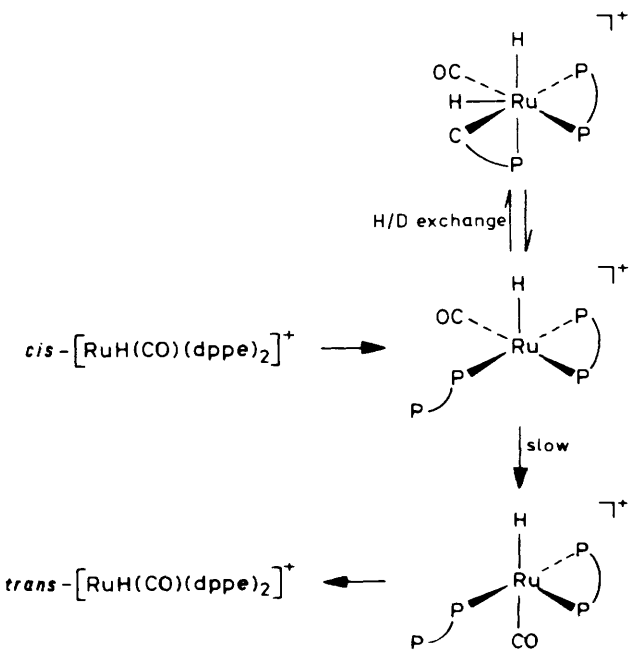
There is no evidence for exchange of the hydridic hydrogen atom with the solvent, since decomposition of *trans*-[Ru(CHO)(CO)(dppe)$_2$]$^+$ in CD_2Cl_2 or of *trans*-[Ru(CDO)(CO)(dppe)$_2$]$^+$ in CH_2Cl_2 gives the expected products apart from the intramolecular H/D exchange described above.

This intramolecular H/D exchange reaction presumably involves internal metallation of C−H bonds and since 20e eight-co-ordinate complexes of ruthenium(IV) are almost certainly inaccessible, these metallations must occur in a five-co-ordinate intermediate such as that shown in Scheme 3. Steric requirements also dictate that metallation of a methylene C−H bond will only occur in a unidentate dppe ligand. We therefore propose the mechanism shown in Scheme 3 for the *cis*–*trans* isomerisation and for the H/D exchange reaction.

The rate-determining step of the isomerisation must be rearrangement of the five-co-ordinate intermediate since (*a*) the *trans* effect of hydride in six-co-ordinate complexes is higher than that of phosphine and we already know (from the formyl decomposition reaction) that cleavage of an Ru−P bond *trans* to phosphorus occurs considerably faster than the rate of the isomerisation reaction, (*b*) the internal metallation reactions leading to H/D exchange as described above most likely occur in the intermediate present before the rate-determining step, and (*c*) significant isotope effects have recently been observed when cleavage of an M−P bond *trans* to hydride or deuteride is rate determining.[18,19]

Spectroscopic Properties.—The i.r., ^{1}H and ^{31}P n.m.r. spectroscopic properties of the complexes isolated during the decomposition studies are collected in Tables 1 and 2, whilst analytical data appear in Table 3. Most of the spectroscopic data require no further comment although the effects of deuteriation on some of the spectral properties are of interest.

Thus, $\nu_{C\equiv O}$ appears at 1 987 cm^{-1} for *trans*-[RuH(CO)(dppe)$_2$]$^+$ but at 1 973 cm^{-1} for its deuterio-analogue. Differences of a similar order of magnitude have been observed in $\nu_{C\equiv O}$[20,21] or $\nu_{C\equiv N}$[21] in a number of complexes where $\nu_{C\equiv O}$ or $\nu_{C\equiv N}$ has the same symmetry as ν_{M-H} and have been attributed to Fermi resonance between $\nu_{C\equiv O}$ and ν_{M-H}. This resonance is of much less importance for $\nu_{C\equiv O}$ and ν_{M-D} since they occur at widely different frequencies. Although we have not been able to assign ν_{M-H} in the i.r. spectrum of *trans*-[RuH(CO)(dppe)$_2$]$^+$, we assume that it must occur at lower frequency than pure $\nu_{C\equiv O}$ on account of the direction of move-



Scheme 3. Proposed mechanism for the isomerisation of *cis*-[RuH(CO)(dppe)$_2$]$^+$ in CH_2Cl_2 and for H/D exchange (P−P = dppe; P−C = unidentate dppe metallated at a phenyl or methylene carbon atom)

Table 2. Spectroscopic data for complexes of *cis* stereochemistry [a]

		^{31}P N.m.r. [b]										^{1}H N.m.r. [c]				
		δ				J/Hz							J/Hz			
Complex	$\nu_{C\equiv O}$/cm^{-1}	P_A	P_B	P_C	P_D	P_AP_B	P_AP_C	P_AP_D	P_BP_C	P_BP_D	P_CP_D	δ	HP_A	HP_B	HP_C	HP_D
(A) [d]	1 970	67.79	58.01	53.34	39.85	210	24.1	16.4	29.7	5.6	24.1	−7.2 (dddd)	19 [e]	22 [e]	70	16 [e]
(B) [f]	2 050, 2 010	−27.7	32.25	−12.8	−2.0	119	0	0	27	199	56	−5.2 (dq)	4.2	17.8	17.8	17.8
(C)	2 048, 2 008	−27.3	32.5	−12.5	−2.2	115	3.4	1.7	28	199	56	−5.2 [g]	0	2.4 [h]	3.4 [h]	2.4 [h]

[a] N.m.r. studies in CH_2Cl_2(^{31}P) or CD_2Cl_2 (^{1}H) at ambient temperature. (A) = *cis*-[RuH(CO)(dppe)$_2$][SbF_6], (B) = *cis*-[RuH(CO)$_2$(dppm)$_2$][SbF_6], (C) = *cis*-[RuD(CO)$_2$(dppm)$_2$][SbF_6]. [b] In p.p.m. to high frequency of external 85% H_3PO_4. [c] In p.p.m. relative to internal $SiMe_4$, hydride proton CH_2 resonances not analysed. [d] For assignments see Scheme 1. [e] Assignments of J_{HP_A}, J_{HP_B}, and J_{HP_D} are arbitrary. [f] For assignments see Scheme 2. [g] ^{2}H resonance. [h] J_{DP} from phosphorus spectrum.

Table 3. Analytical data for ruthenium complexes

	Found (Calc.)/%			
Complex	C	H	P	F
trans-[RuH(CO)(dppe)$_2$][SbF_6]·CH_2Cl_2 [a]	52.0 (52.0)	4.2 (4.1)		9.1 (9.1)
cis-[RuH(CO)(dppe)$_2$][SbF_6]	54.8 (54.7)	4.2 (4.2)		10.0 (9.8)
cis-[RuH(CO)$_2$(dppm)$_2$][SbF_6] [b]	52.9 (53.7)	3.8 (3.9)	10.0 (10.7)	
trans-[RuCl(CO)(dppe)$_2$][SbF_6]·CH_2Cl_2 [a]	50.6 (50.6)	4.0 (3.9)		
trans-[RuCl(CO)(dppm)$_2$][SbF_6]·CH_2Cl_2 [a,c]	49.9 (50.4)	3.8 (3.7)	10.0 (10.0)	

[a] CH_2Cl_2 detected by ^{1}H n.m.r. spectroscopy. [b] Small impurity of *trans*-[RuCl(CO)(dppm)$_2$][SbF_6]·CH_2Cl_2 present; see footnote *a*. [c] Cl, 7.8 (8.6)%.

ment of this band in the deuteride, although substantial mixing of $\nu_{C\equiv O}$ and ν_{Ru-H} makes even this assignment tentative. The need for the two vibrations to have the same symmetry for Fermi resonance to occur is confirmed by the near superimposability of $\nu_{C\equiv O}$ in *cis*-[RuX(CO)(dppe)$_2$]$^+$ (X = H or D).

In the ^{31}P n.m.r. spectrum of [RuH(CO)$_2$(dppm)$_2$]$^+$, long-range coupling of the unbound phosphorus atom to those bound to ruthenium [P_C and P_D of (A) in Scheme 2] is not observed. In the deuterio-analogue, on the other hand, these couplings are readily identifiable. We do not offer any explanation for this phenomenon although we note the change in spin system from AFMR to AFMRX, where X is the deuterium atom (for the hydrido-complex, all protons, including the hydride were decoupled).

Experimental

Microanalyses were by Elemental Microanalysis Ltd. Infrared spectra were recorded as Nujol mulls between CsI plates or as dichloromethane solutions in matched 0.1-mm NaCl plates on a Perkin-Elmer 577 grating spectrometer and ^{1}H n.m.r. spectra on a Varian Associates R34 220-MHz spectrometer. Phosphorus-31, ^{13}C, ^{11}B, ^{1}H, and ^{2}H n.m.r. spectra were recorded at ambient temperature on a JEOL FX90Q spectrometer (City of London Polytechnic) or a Bruker WM250 multinuclear spectrometer (University of Liverpool) operating in the Fourier-transform mode with proton-noise decoupling (^{31}P, ^{13}C, and ^{11}B). Fast atom bombardment (f.a.b.) mass spectra were recorded of glycerine suspensions on a modified MM9 mass spectrometer (I.C.I. Pharmaceuticals Division). Ultraviolet irradiations were of CH_2Cl_2 solutions in silica glass cells using a medium-pressure mercury diffusion lamp (λ = 354 nm).

All solvents were dried using standard methods, and were thoroughly degassed before use. All manipulations were carried out under nitrogen using standard Schlenk-line and catheter-tubing techniques. The preparations of the formyl complexes, [Ru(CXO)(CO)(P–P)$_2$][Y] (X = H or D; P–P = dppm or dppe; Y = SbF_6 or BEt_4), have been reported previously.[9]

(*a*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonylchlororuthenium*(II) *Hexafluoroantimonate*.—Addition of diethyl ether, until incipient precipitation (followed by cooling), to the filtrate obtained from the careful recrystallisation of *trans*-[Ru(CXO)(CO)(dppe)$_2$][SbF_6] (X = H or D), prepared from *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF_6]$_2$ and excess K[BH(OPr^i)$_3$] or Li[$BDEt_3$] in CH_2Cl_2, gave the product as white microcrystals. The yield obtained was dependent upon the reaction time of the formyl synthesis step. Thus in the preparation of *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF_6],[9] the reaction time was only 4 h and the yield of the chlorocarbonyl was only minimal (~5%) whereas the deuterioformyl was prepared in 16 h and the yield of the chlorocarbonyl was significantly higher (~20%). We have so far been unable to obtain a pure sample of the complex (it is either contaminated with the formyl complex or decomposition products, see later), but the assignment is confirmed by f.a.b. mass spectroscopy studies: *m/e* 961, M^+; 898, M^+ − (Cl + CO); 563, M^+ − (Cl + CO + dppe). Peaks show typical Ru and Cl isotope patterns, weights calculated using ^{102}Ru and ^{35}Cl as most abundant isotopes.

(*b*) cis-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonylhydridoruthenium*(II) *Hexafluoroantimonate*.—A solution of recrystallised *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF_6] (0.26 g, 0.22 mmol) in dichloromethane (10 cm^3) was stirred at 0 °C for 16 h. Diethyl ether was then slowly added to the solution until incipient precipitation and the solution cooled to −30 °C overnight. The solid was collected, washed with light petroleum (b.p. 40—60 °C; 2 × 20 cm^3) and dried *in vacuo* (0.17 g, 70%).

(*c*) cis-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonyldeuteridoruthenium*(II) *Hexafluoroantimonate*.—This was

prepared from *trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] (0.21 g, 0.17 mmol) as in (*b*) (0.16 g, 78%).

(*d*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonylhydridoruthenium*(II) *Hexafluoroantimonate–Dichloromethane* (1/1).—A solution of recrystallised *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] (0.28 g, 0.23 mmol) in dichloromethane (30 cm^3) was stirred at ambient temperature for 4 d. Addition of diethyl ether (100 cm^3) followed by recrystallisation of the collected solid yielded the complex as pale gold microneedles (0.22 g, 80%).

(*e*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonylhydridoruthenium*(II) *Tetraethylborate–Dichloromethane* (1/1).—This was prepared from *trans*-[Ru(CHO)(CO)(dppe)$_2$][BEt$_4$] (0.32 g, 0.30 mmol) as in (*d*), as cream microneedles (0.21 g, 60%).

(*f*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonyldeuteridoruthenium*(II) *Hexafluoroantimonate–Dichloromethane* (1/1).—This was prepared from *trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] (0.23 g) as in (*d*), as pale gold microneedles.

Decomposition of *trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] (0.22 g) in dichloromethane (25 cm^3) at 0 °C over a period of 14 d results in significant incorporation of deuterium in the methylene protons of the dppe backbone (see text). F.a.b. mass spectra: *m/e* 928, M^+; 898, $M^+ - (CO + D)$; 563, $M^+ - (CO - D - dppe)$, using ^{102}Ru as most abundant ruthenium isotope.

(*g*) *Decomposition Products of trans*-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$][BEt$_4$].—*trans*-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$][BEt$_4$] (0.05 g) was dissolved in degassed CD_2Cl_2 (0.75 cm^3) at −30 °C and sealed in an n.m.r. tube. After the low-temperature ^{13}C n.m.r. spectrum had been recorded, the solution was allowed to warm to room temperature and left for several days. The ^{31}P, ^{1}H, and ^{13}C n.m.r. spectra were then recorded (see Tables 1 and 2). Of interest was the presence of free carbon monoxide, indicated by a characteristic [22] singlet at δ 183.5 p.p.m. in the ^{13}C n.m.r. spectrum.

(*h*) cis-*Bis*[*bis*(*diphenylphosphino*)*methane*]*dicarbonylhydridoruthenium*(II) *Hexafluoroantimonate*.—*cis*-[Ru(CHO)(CO)(dppm)$_2$][SbF$_6$] (0.38 g, 0.33 mmol) and dichloromethane (20 cm^3) were stirred in the dark for 15 min. The resulting solution was then filtered, and the yellow filtrate reduced *in vacuo* to *ca.* 10 cm^3. Diethyl ether was added until incipient precipitation and the solution cooled to −30 °C for 16 h. Recrystallisation of the solid from CH_2Cl_2–diethyl ether afforded the complex as pale yellow microcrystals (0.25 g, 66%).

(*i*) cis-*Bis*[*bis*(*diphenylphosphino*)*methane*]*dicarbonyldeuteridoruthenium*(II) *Hexafluoroantimonate*.—This was prepared as in (*h*) from *cis*-[Ru(CDO)(CO)(dppm)$_2$][SbF$_6$] (0.4 g), as pale yellow microcrystals (0.24 g).

(*j*) trans-*Bis*[*bis*(*diphenylphosphino*)*methane*]*carbonylchlororuthenium*(II) *Hexafluoroantimonate–Dichloromethane* (1/1).—A solution of *cis*-[RuH(CO)$_2$(dppm)$_2$][SbF$_6$] was prepared as in (*h*) above, and the volume reduced to 5 cm^3. Its solution i.r. spectrum was recorded ($\nu_{C\equiv O}$ at 2 050 and 2 010 cm^{-1}). The solution was then photolysed (u.v. irradiation) for 2 d and the change in the solution i.r. spectrum monitored. After 1 d the solution had paled and the predominant species was *trans*-bis[bis(diphenylphosphino)methane]carbonylhydridoruthenium(II) hexafluoroantimonate ($\nu_{C\equiv O}$ at 2 008 cm^{-1}, CH_2Cl_2 solution), whereas after 2 d the major species was *trans*-[RuCl(CO)(dppm)$_2$][SbF$_6$] ($\nu_{C\equiv O}$ at 1 982 cm^{-1}, CH_2Cl_2 solution). The yellow-green solution was left to stand for a further 2 d, before diethyl ether was added to precipitate the product. Recrystallisation from CH_2Cl_2–diethyl ether afforded the product as pale yellow analytically pure microcrystals (0.14 g, 50%).

The product can also be made by an identical route from *cis*-[Ru(CDO)(CO)(dppm)$_2$][SbF$_6$].

(*k*) trans-*Bis*[*bis*(*diphenylphosphino*)*methane*]*carbonylhydridoruthenium*(II) *Hexafluoroantimonate–Dichloromethane* (1/1).—Addition of diethyl ether to the photolysed (1 d) solution obtained as in (*j*) gave the product as a cream powder, contaminated with varying amounts of *trans*-[RuCl(CO)(dppm)$_2$][SbF$_6$]. The complex is unstable in CH_2Cl_2, converting to *trans*-[RuCl(CO)(dppm)$_2$][SbF$_6$] over a period of 2 d.

(*l*) trans-*Bis*[*bis*(*diphenylphosphino*)*methane*]*carbonyldeuteridoruthenium*(II) *Hexafluoroantimonate–Dichloromethane* (1/1).—This was prepared as in (*k*) from *cis*-[Ru(CDO)(CO)(dppm)$_2$][SbF$_6$] as a cream powder; the product was contaminated with substantial amounts of *trans*-[RuCl(CO)(dppm)$_2$][SbF$_6$].

(*m*) *Partial Decomposition of trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] *under* ^{13}CO.—*trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] (0.21 g, 0.17 mmol) was dissolved in dichloromethane (15 cm^3) at −30 °C in a 100-cm^3 glass pressure bottle. The vessel was sealed, cooled to −196 °C, evacuated and four samples (21 cm^3 at 0.5 atm) of ^{13}CO (92 atom %) were introduced into the vessel as has been previously described.[9] The solution was allowed to warm to room temperature, and then stirred at that temperature for 2 h. The pressure was released and 50 cm^3 of diethyl ether added to the reaction vessel to precipitate the complexes. The solid was then collected and dried *in vacuo*. The i.r. spectrum showed the characteristic bands due to the formyl complex plus the formyl decomposition products (*ca.* half the formyl complex had decomposed). There were no bands present due to $\nu_{^{13}C\equiv O}$ or $\nu_{^{13}C=O}$.

(*n*) *Mixed Decomposition of trans*-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$][SbF$_6$] *and trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$].—The recrystallised complexes *trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] (0.15 g) and *trans*-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$][SbF$_6$] (0.15 g) were dissolved in dichloromethane (10 cm^3) at −30 °C. The solution was allowed to warm up and stirred at ambient temperature for 4 d. The solution was then evaporated to dryness *in vacuo* and the ^{1}H n.m.r. spectrum of the sample recorded (CD_2Cl_2); the hydride resonance was identical to that obtained from decomposition of *trans*-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$][SbF$_6$] alone.

(*o*) *Kinetics of Decomposition of trans*-[Ru(CXO)(CO)(dppe)$_2$][SbF$_6$] (X = H *or* D).—*trans*-[Ru(CXO)(CO)(dppe)$_2$][SbF$_6$] (0.1 g) was dissolved in CH_2Cl_2 (10 cm^3) at −30 °C. A portion of this solution was placed into a solution i.r. cell and the height of the $\nu_{C=O}$ vibration was monitored at regular intervals. A plot of log peak height against time was linear after an initiation period of *ca.* 5 min (while the solution warmed) for at least 2.8 half-lives. For X = H and X = D the kinetic study was repeated and found to be reproducible. The temperature of the solution, as measured by a thermocouple inserted into the cell *via* a septum cap was 30 °C. For X = H, $t_{\frac{1}{2}} = 9.25 \pm 0.2$ min; for X = D, $t_{\frac{1}{2}} = 16.4 \pm 1$ min.

(*p*) *Kinetics of Isomerisation of cis*-[RuX(CO)(dppe)$_2$][SbF$_6$] (X = H *or* D).—*trans*-[Ru(CXO)(CO)(dppe)$_2$][SbF$_6$]

($0.1\ cm^3$) was dissolved in CH_2Cl_2 ($2\ cm^3$) containing CD_2Cl_2 ($0.5\ cm^3$) at room temperature. ^{31}P N.m.r. spectra were recorded immediately and then periodically over 140 h. The amount of *cis*-$[RuX(CO)(dppe)_2]^+$ was monitored by integration of its ^{31}P resonances and comparison with the height of a small impurity peak arising from *trans*-$[RuCl(CO)(dppe)_2]^+$. Readings taken in the first 8 h were discarded because of the presence of undecomposed formyl complex but a plot of log [*cis*-$RuH(CO)(dppe)_2^+$] against time was linear up to ~1 half-life. Beyond this a slight upward deviation from linearity was observed after longer times. For X = H a half-life of 72 ± 16 h was obtained whilst for X = D, $t_{\frac{1}{2}} = 73 \pm 8$ h. Identical spectrometer conditions and parameters were employed for the recording of all ^{31}P spectra.

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