In memory of T. A. Stephenson

New Decomposition Pathways for Formyl Complexes of Ruthenium(II)

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The preparation of *trans*-[Ru(CHO)(CO)(dppb)$_2$][SbF$_6$] [dppb = 1,2-bis(diphenylphosphino)-benzene] from hydridic reduction of *trans*-[Ru(CO)$_2$(dppb)$_2$][SbF$_6$]$_2$ is described. The formyl complex decomposes with first-order kinetics ($t_{\frac{1}{2}}$ = 28 min) at 30 °C to give exclusively *trans*-[RuH-(CO)(dppb)$_2$][SbF$_6$]. Detailed studies of the decomposition reaction including the observation of initiation of free-radical polymerization of methyl methacrylate during the reaction lead to the postulation of rate-determining homolytic cleavage of the Ru–CHO bond. The low rate of initiation of polymerization, together with the high isotope effect for the decomposition (k_H/k_D = 2.3) and the failure to observe cross-over products during co-decomposition of *trans*-[Ru(^{13}CHO)-(^{13}CO)(dppb)$_2$][SbF$_6$] and *trans*-[Ru(CDO)(CO)(dppb)$_2$][SbF$_6$], lead to the conclusion that another decomposition pathway, involving concerted H migration and CO loss in a six-co-ordinate complex, operates. These results are compared with those obtained for *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] [dppe = 1,2-bis(diphenylphosphino)ethane].

Formyl complexes of transition elements are of considerable interest since they are likely to be intermediates in homogeneous hydrogenations of carbon monoxide.[1] Although formyl complexes for many transition elements have been isolated,[2] those co-ordinated to catalytically active elements (Rh, Ru, and Co) are comparatively scarce. We have recently reported[3] the isolation and complete characterization of complexes of the form [Ru(CHO)(CO)(P–P)$_2$]$^+$ [P–P = $Ph_2PCH_2CH_2PPh_2$ (dppe), *trans*; or $Ph_2PCH_2PPh_2$ (dppm), *cis*], but find[4] that these complexes decompose above 0 °C in solution to give [RuH(CO)$_n$(P–P)$_2$]$^+$ (n = 1, P–P = dppe; n = 2, P–P = dppm). This has meant that further study of their reaction chemistry is very difficult.

Extensive studies of the decomposition reactions of these formyl complexes have shown that, for dppe, reversible dissociation of an Ru–P bond is followed by rate-determining hydride migration.[4] Subsequent reactions involve loss of CO and reco-ordination of the free phosphorus atom to give *cis*-[RuH(CO)(dppe)$_2$]$^+$ (see Scheme 1) which isomerises to the *trans* isomer in a slower step. Since the first step of the decomposition reaction involves rupture of an Ru–P bond, we have also synthesized osmium formyl complexes and find, as expected, that they are very much more inert than their ruthenium analogues.[5]

In an attempt to reduce the lability of related formyl complexes of ruthenium, we have studied the hydridic reduction of the complex *trans*-[Ru(CO)$_2$(dppb)$_2$]$^{2+}$ [dppb = 1,2-bis-(diphenylphosphino)benzene] reasoning that the lack of free rotation around the backbone C–C bond for dppb, which is facile for monodentate dppe, should reduce the equilibrium constant (K) for the first step of Scheme 1, hence the overall rate of decomposition of the formyl should also be reduced. We now report the results of these studies for which a preliminary communication has appeared.[6]

Results

Preparative Studies.—The salt *trans*-[Ru(CO)$_2$(dppb)$_2$]-[SbF$_6$]$_2$ can be prepared by reaction of [RuCl$_2$(dppb)$_2$] {obtainable from [RuCl$_2$(PPh$_3$)$_3$] and excess of dppb} with AgSbF$_6$ under carbon monoxide {*cf.* the preparation of [Ru(CO)$_2$(P–P)$_2$][SbF$_6$]$_2$[7]}. The white crystalline dicarbonyl dication reacts smoothly with K[BH(OPr^i)$_3$] to give *trans*-[Ru(CHO)(CO)(dppb)$_2$][SbF$_6$] in high yield.

Decomposition Studies.—The formyl complex is indefinitely stable in the solid state at room temperature and in CH_2Cl_2 or CH_3NO_2 solution at −30 °C, but decomposes in solution at room temperature to give, exclusively, *trans*-[RuH(CO)-(dppb)$_2$][SbF$_6$]. The decomposition reaction follows first-order kinetics for at least three half-lives and the formyl complex has a half-life ($t_{\frac{1}{2}}$) of 28 min at 30 °C. A kinetic isotope effect (k_H/k_D) of 2.3 is observed in the decomposition of *trans*-[Ru(CDO)(CO)(dppb)$_2$][SbF$_6$] [prepared using Li(BDEt$_3$)].

Decomposition of *trans*-[Ru(CHO)(CO)(dppb)$_2$][SbF$_6$] in the presence of methyl methacrylate (mma), which is known[8] to undergo free-radical induced polymerization, affords poly-(methyl methacrylate) (pmma), although the amount and number-average molecular weight of the polymer formed suggest that only *ca.* 2% of decomposing molecules initiate polymerization. In contrast, no polymer is formed in an identical experiment using *trans*-[Ru(CHO)(CO)(dppe)$_2$]-[SbF$_6$].

Co-decomposition of *trans*-[Ru(CDO)(CO)(dppb)$_2$]$^+$ and *trans*-[Ru(^{13}CHO)(^{13}CO)(dppb)$_2$]$^+$ produces *trans*-[RuH(^{13}CO)(dppb)$_2$]$^+$ as the only detectable hydride-containing product; the cross-over product *trans*-[RuH(CO)-(dppb)$_2$]$^+$ is not detected.

Finally, we have no evidence for the formation of any radicals other than Bu$^t_2$NO$^\bullet$ from the decomposition of *trans*-[Ru(CHO)(CO)(dppb)$_2$]$^+$ in the presence of Bu^{t}NO, although a similar reaction using *trans*-[Ru(CHO)(CO)(dppe)$_2$]$^+$ produced *trans*-[Ru(Bu^{t}NO)(CO)(dppe)$_2$]$^{+\bullet}$ (e.s.r. evidence).[9]

Discussion

A comparison of the decomposition characteristics of *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$][4] and *trans*-[Ru(CHO)(CO)-(dppb)$_2$][SbF$_6$] is shown in the Table. The main differences are the slower rate and marginally higher isotope effects for

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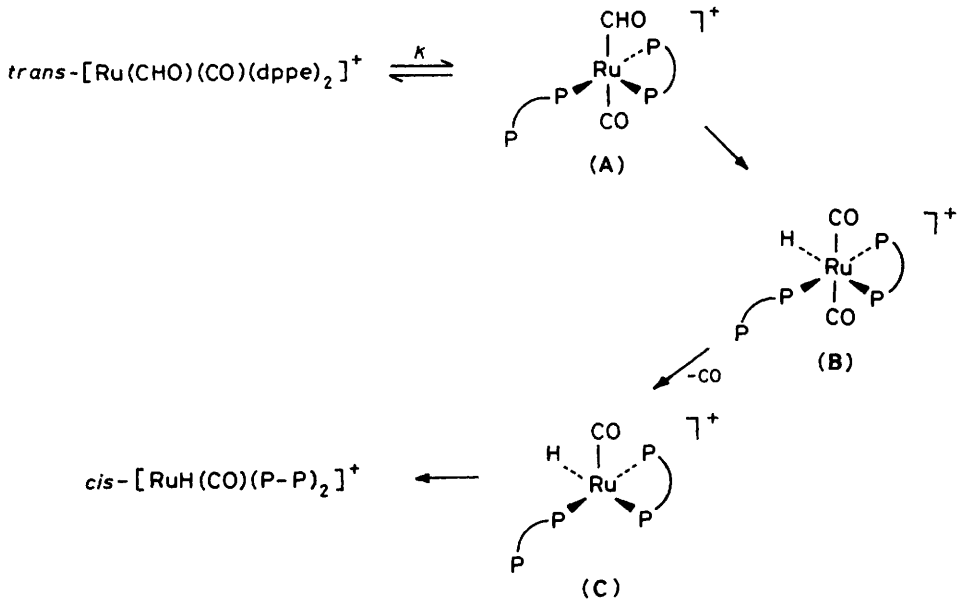
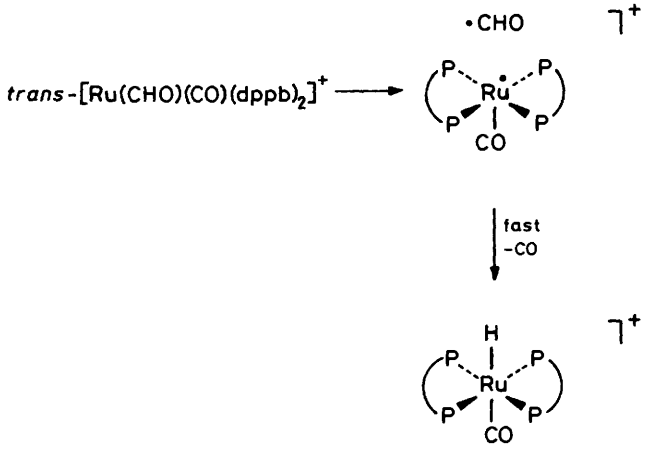
Table. Comparison of decomposition of *trans*-[Ru(CHO)(CO)(P–P)$_2$]$^+$ (P–P = dppb or dppe)

	[Ru(CHO)(CO)(dppb)$_2$]$^+$	[Ru(CHO)(CO)(dppe)$_2$]$^+$
Primary product	*trans*-[RuH(CO)(dppb)$_2$]$^+$	*cis*-[RuH(CO)(dppe)$_2$]$^+$
$t_{\frac{1}{2}}$/min at 30 °C	28	9.25
k/s^{-1}	4×10^{-4}	12×10^{-4}
k_H/k_D	2.3	1.8
Bu^{t}NO	No trapped radicals	*trans*-[Ru(Bu^{t}NO)(CO)(dppe)$_2$]$^{\cdot+}$
Methyl methacrylate	pmma	No polymer



Scheme 1. Mechanism of decomposition of *trans*-[Ru(CHO)(CO)(dppe)$_2$]$^+$, P–P = dppe



Scheme 2. Decomposition of *trans*-[Ru(CHO)(CO)(dppb)$_2$]$^+$ *via* homolytic cleavage of the M–C bond, P–P = dppb

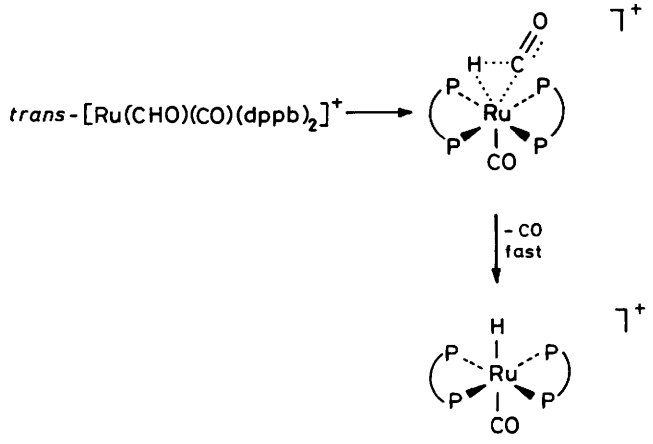
decomposition of *trans*-[Ru(CHO)(CO)(dppb)$_2$][SbF$_6$] and the fact that the primary products have different stereochemistries. In addition, differences occur in decomposition reactions carried out in the presence of mma or Bu^{t}NO.

The formation of pmma on decomposition of *trans*-[Ru(CHO)(CO)(dppb)$_2$][SbF$_6$] in the presence of mma strongly suggests that a free-radical mechanism is available for decomposition of *trans*-[Ru(CHO)(CO)(dppb)$_2$]$^+$. Such a mechanism, involving homolytic cleavage of the Ru–C(formyl) bond, is shown in Scheme 2. This mechanism would also account for the selective formation of *trans*-[RuH(CO)(dppb)$_2$]$^+$ as the primary decomposition product.

Analysis of the polymer formed suggests that only *ca.* 2% of radicals initiate polymerization when the decomposition is carried out at room temperature and the failure to observe cross-over products on co-decomposition of *trans*-[Ru(CDO)(CO)(dppb)$_2$]$^+$ and *trans*-[Ru(^{13}CHO)(^{13}CO)(dppb)$_2$]$^+$ is consistent with this observation, since ^{1}H n.m.r. spectra of the hydride region would be insufficiently sensitive to pick up 2% of *trans*-[RuH(CO)(dppb)$_2$]$^+$, particularly as *trans*-[Ru(^{13}CHO)(^{13}CO)(dppb)$_2$]$^+$ was only *ca.* 96% enriched.

There are two possible explanations of these results. Either the formyl complex decomposes as in Scheme 2 but H$^\bullet$ transfer from CHO$^\bullet$ to [Ru(CO)(dppb)$_2$]$^{\cdot+}$ is so fast that it generally occurs before CHO$^\bullet$ or H$^\bullet$ escapes the solvent cage, or two decomposition mechanisms operate at 30 °C, that of Scheme 2 being the less favourable.

We have argued previously[4] that the isotope effect k_H/k_D of 1.8 observed on decomposition of *trans*-[Ru(CXO)(CO)(dppe)$_2$]$^+$ (X = H or D) is primary and that the low value can be attributed to the presence of a three-centred transition state and movement of a heavy atom (O) during formation of this transition state. It seems highly unlikely that the isotope effect of 2.3 observed for *trans*-[Ru(CXO)(CO)(dppb)$_2$]$^+$ is secondary, particularly as the formyl radical is known to be bent (H–C–O 129.4°)[10] and hence it is unlikely that substantial movement of the X atom will occur during cleavage of the Ru–CXO bond. We therefore conclude that there are two decomposition pathways of similar rate at 30 °C available for the decomposition of *trans*-



Scheme 3. Proposed major pathway for decomposition of *trans*-$[Ru(CHO)(CO)(dppb)_2]^+$, P–P = dppb

$[Ru(CHO)(CO)(dppb)_2]^+$ and that the slightly less favourable one of these involves homolytic cleavage of the Ru–CHO bond.

It remains to identify the more favourable pathway for decomposition of *trans*-$[Ru(CHO)(CO)(dppb)_2]^+$. Scheme 1 might account for some of the observed phenomena, but would not explain the failure to observe *cis*-$[RuH(CO)(dppb)_2]^+$ as the primary product, particularly as isomerization of *cis*- to *trans*-$[RuH(CO)(dppe)_2]^+$ involves[4] preliminary cleavage of an Ru–P bond, and hence the overall rate of isomerization would be expected to be lower for $[RuH(CO)(dppb)_2]^+$ than for $[RuH(CO)(dppe)_2]^+$. It is possible that the *trans* isomer could be formed as the primary product by isomerization of the five-co-ordinate intermediate, $[RuH(CO)(dppb)_2]^+$ [analogous to (**A**) in Scheme 1], but we have presented evidence that, at least for $[RuH(CO)(dppe)_2]^+$, this isomerization is very slow.[4]

The failure to observe* *trans*-$[Ru(Bu^tNO)(CO)(dppb)_2]^+$ on decomposition of *trans*-$[Ru(CHO)(CO)(dppb)_2]^+$ would also appear to rule out dissociation of a phosphorus atom as being mechanistically significant, since we believe[9] that the analogous product for dppe is formed by co-ordination of Bu^tNO to intermediate (**B**) (Scheme 1) followed by expulsion of CHO$^\bullet$, pseudo-rotation of the five-co-ordinate intermediate to place CO and Bu^tNO into the sterically favoured mutually *trans* positions, and reco-ordination of the unbound phosphorus atom.

We therefore propose that the major pathway for decomposition of *trans*-$[Ru(CHO)(CO)(dppb)_2]^+$ involves a concerted transfer of H to ruthenium and loss of CO *via* a three-centred transition state (Scheme 3). Such a mechanism would be expected to have a low primary isotope effect since the rate-determining step involves a three-centred transition state and movement of the oxygen atom. It would also lead directly to *trans*-$[Ru(CHO)(CO)(dppb)_2]^+$ as is observed. Clearly, such a mechanism is also available for decomposition of *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$ and its rate would be expected to be similar for the two complexes. Assuming that the radical mechanism accounts for rather little of the decomposition† of *trans*-$[Ru(CHO)(CO)(dppb)_2]^+$, the rate of concerted CO loss for *trans*-$[Ru(CHO)(CO)(dppb)_2]^+$ will be (3—4) $\times 10^{-4}$ s^{-1}, *i.e.* up to 30% of the rate of decomposition of *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$. Some *trans*-$[RuH(CO)(dppe)_2]^+$ should then be observed as a primary product from *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$. Unfortunately, it is difficult to detect whether or not this is the case since *trans*-$[RuH(CO)(dppe)_2]^+$ is formed as a secondary product from *cis*-$[RuH(CO)(dppe)_2]^+$ at an appreciable rate.[4]

We conclude that the use of dppb in place of dppe stabilizes complexes of the form *trans*-$[Ru(CHO)(CO)(P\text{–}P)_2]^+$ by suppressing Ru–P bond rupture, but that this allows new decomposition pathways summarized in Schemes 2 and 3 to be revealed which have rates at room temperature which are comparable to one another and only slightly lower than that of the reaction of Scheme 1.

* The failure to observe trapped H$^\bullet$ or CHO$^\bullet$ presumably arises from the low concentration of these species escaping from the solvent cage and from the low concentration of Bu^tNO present in solution.

† It is not possible to quantify the relative rates of the two decomposition pathways although 3% is a lower limit for the relative rate of the free-radical pathway. The observed isotope effect, and the failure to observe trapped radicals, however, suggest that the free-radical pathway probably accounts for $<10\%$ of the decomposition reaction.

Experimental

Microanalyses were by Elemental Microanalysis Ltd. and the University of Liverpool. I.r. spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 577 grating spectrometer and n.m.r. spectra on a Brüker Associates WM250 spectrometer, operating in the Fourier-transform mode with (for ^{31}P) proton-noise decoupling.

All solvents were dried before use by distillation from CaH_2 (CH_2Cl_2, Me_2CO, $MeNO_2$) or sodium diphenylketyl [diethyl ether and light petroleum (b.p. 40—60 °C)]. All reactions were carried out under nitrogen using standard Schlenk-line and catheter tubing techniques. Complexes were stored under nitrogen, although they were air-stable unless otherwise stated.

The complex $[RuCl_2(PPh_3)_3]$ was prepared by a standard method;[11] hydride donors were from Aldrich (1 mol dm^{-3} in Et_2O) and *o*-$C_6H_4(PPh_2)_2$ from Strem.

(*a*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*benzene*]*dichlororuthenium*(II).—The complex $[RuCl_2(PPh_3)_3]$ (1.92 g, 2.00 mmol) was refluxed with a slight excess of 1,2-bis(diphenylphosphino)benzene (1.96 g, 4.2 mmol) in acetone (50 cm^3) for 2 h. The resulting yellow solid was filtered off, washed with acetone (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3), and finally dried *in vacuo*, yield 2.12 g (100%) (Found: C, 68.0; H, 4.5. $C_{60}H_{48}Cl_2P_4Ru$ requires C, 67.7; H, 4.5%).

(*b*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*benzene*]*dicarbonylruthenium*(II) *Hexafluoroantimonate–Dichloromethane* (2/1).—The salt $AgSbF_6$ (0.72 g, 2.1 mmol) was added to a carbon monoxide-saturated solution of *trans*-$[RuCl_2(dppb)_2]$ (1.06 g, 1 mmol) in dichloromethane (70 cm^3). The solution was pressurized to 3 atm (*ca.* 3 × 10^5 Pa) with carbon monoxide in a Fisher-Porter bottle and stirred at 80 °C for 36 h. The resulting pale suspension was filtered to remove AgCl. The AgCl was washed with warm CH_2Cl_2 (2 × 15 cm^3) and these washings were combined with the filtrate. After evaporation to half volume, diethyl ether was added and the solution cooled to −30 °C. The resultant white microcrystalline product was filtered off and dried *in vacuo*. The yield of product after recrystallization from dichloromethane–diethyl ether was 0.99 g (65%) (Found: C, 47.9; H, 3.3; P, 8.1. $C_{62}H_{48}F_{12}O_2P_4RuSb_2 \cdot 0.5CH_2Cl_2$ requires C, 48.0; H, 3.1; P, 8.0%). Spectroscopic data: i.r. ν(C≡O) 2 025s cm^{-1}; n.m.r. (CD_3NO_2):^{31}P, δ 43.0 (s); ^1H, δ 5.32 (CH_2Cl_2).

The salt *trans*-$[Ru(^{13}CO)_2(dppb)_2][SbF_6]_2$ was similarly prepared from $AgSbF_6$ (0.34 g, 1 mmol), *trans*-$[RuCl_2(dppb)_2]$ (0.52 g, 0.49 mmol), and ^{13}CO, in 55% yield.

(*c*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*benzene*]*carbonylformylruthenium*(II) *Hexafluoroantimonate–Dichloromethane* (2/1).—To a solution of *trans*-$[Ru(CO)_2(dppb)_2][SbF_6]_2$ (0.61 g, 0.4 mmol) in CH_2Cl_2 (25 cm^3) at −35 °C was added

$K[BH(OPr^i)_3]$ in thf (tetrahydrofuran) (0.8 cm^3, 0.8 mmol) and the solution stirred for 5 h. The black solution was then filtered into diethyl ether (200 cm^3), pre-cooled to −35 °C, and subsequently stored at −30 °C for 24 h. The resulting grey solid was filtered off at −35 °C and dried *in vacuo*. Analytically pure samples of the complex were obtained by dissolving the crude material in CH_2Cl_2 (25 cm^3) at −35 °C, filtering, adding diethyl ether pre-cooled to −35 °C to the filtrate until incipient crystallization, and allowing the resulting solution to stand at −35 °C for several days. The white crystalline product was collected and dried *in vacuo*. Yield 0.31 g (60%) (Found: C, 54.4; H, 3.7; Cl, 4.6; P, 9.1. $C_{62}H_{49}F_6O_2P_4RuSb\cdot0.5CH_2Cl_2$ requires C, 55.2; H, 3.7; Cl, 5.2; P, 9.1%). N.m.r.: ^1H, δ 5.32 (s, CH_2Cl_2), 11.45 (qnt, *J* 6 Hz, CHO); ^{31}P, δ 56.6 (s). I.r.: 2 558w [ν(C–H)], 1 990s [ν(C≡O)], and 1 602s cm^{-1} [ν(C=O)].

The following were similarly prepared: *trans*-$[Ru(^{13}CHO)(^{13}CO)(dppb)_2][SbF_6]$ from *trans*-$[Ru(^{13}CO)_2(dppb)_2][SbF_6]_2$ (0.30 g, 0.2 mmol) in CH_2Cl_2 (25 cm^3) and $K[BH(OPr^i)_3]$ in thf (0.4 cm^3, 0.4 mmol) over a period of 5 h in 50% yield; i.r. 1 940s [ν(C≡O)] and 1 560s cm^{-1} [ν(C=O)]; *trans*-$[Ru(CDO)(CO)(dppb)_2][SbF_6]$ from *trans*-$[Ru(CO)_2(dppb)_2][SbF_6]_2$ (0.61 g, 0.4 mmol) and $Li(BDEt_3)$ in thf (0.8 cm^3, 0.8 mmol) over a period of 8 h, in 55% yield; i.r. 1 990s [ν(C≡O)], 1 925w [ν(C–D)], 1 598s [ν(C=O)], and 1 039m cm^{-1} [δ(C–D)].

(*d*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*benzene*]*carbonylhydridoruthenium*(II) *Hexafluoroantimonate*.—This was isolated from the decomposition of *trans*-$[Ru(CHO)(CO)(dppb)_2][SbF_6]$ (0.26 g, 0.2 mmol) in CH_2Cl_2 (25 cm^3) at room temperature for 4 d. The product was precipitated with excess of diethyl ether and then recrystallized from CH_2Cl_2–diethyl ether in 92% yield (Found: C, 58.0; H, 4.1; P, 9.5. $C_{61}H_{49}F_6OP_4RuSb$ requires C, 58.2; H, 3.9; P, 9.9%). N.m.r.: ^1H, δ −4.0 [qnt, J_{PH} 20 Hz, Ru–H]; ^{31}P, δ 63.3 (s).

Decomposition Studies.—(*i*) *Kinetics of decomposition of formyl complexes*. A saturated solution of either *trans*-$[Ru(CHO)(CO)(dppb)_2][SbF_6]$ or *trans*-$[Ru(CDO)(CO)(dppb)_2][SbF_6]$ was prepared in CH_2Cl_2 (10 cm^3) pre-cooled to −30 °C. The solution was then filtered at −30 °C and subsequently transferred to a solution i.r. cell. The cell was then placed in the spectrometer and the intensity of the formyl ν(C=O) absorption monitored with time. A plot of ln(absorbance) *versus* time gave a straight line from which both the rate constant, *k*, and the half-life, $t_{\frac{1}{2}}$, were calculated. Although the cell was not thermostatted, a thermocouple placed in the solution inside the cell registered 30 ± 1 °C throughout the experiment after the initial warm-up period.

(*ii*) *Decomposition of trans*-$[Ru(^{13}CHO)(^{13}CO)(dppb)_2][SbF_6]$ *in the presence of trans*-$[Ru(CDO)(CO)(dppb)_2][SbF_6]$. The complexes (0.1 g of each) were dissolved together in CD_2Cl_2 (1.5 cm^3) pre-cooled to −30 °C, transferred to an n.m.r. tube, and sealed under nitrogen. The solution was then allowed to warm to room temperature and was left at this temperature for 1 d. The ^1H and ^{31}P n.m.r. spectra of the solution were then recorded.

(*iii*) *Decomposition of formyl complexes in the presence of methyl methacrylate*. Solid *trans*-$[Ru(CHO)(CO)(dppb)_2][SbF_6]$ (0.104 g) was added to a freshly distilled, degassed mixture of CH_2Cl_2 (5 cm^3) and methyl methacrylate (1.5 cm^3). The resulting solution was stirred overnight under N_2. The volume was then reduced by half and the solution was poured into a large excess of light petroleum. The solid white pmma was then collected, washed with light petroleum, and dried at 100 °C to constant weight (yield 0.256 g, *i.e.* 0.152 g of pmma $M_N \simeq 18\,000$).*

Polymer was also produced using *trans*-$[Ru(CHO)(CO)(dppb)_2][SbF_6]$ (0.013 g, 0.1 mmol) in CH_2Cl_2–mma (10 cm^3, 1:1) but not from *trans*-$[Ru(CHO)(CO)(dppe)_2][SbF_6]$ (0.012 g, 0.1 mmol) in CH_2Cl_2–mma (10 cm^3, 1:1).

(*iv*) *Decomposition of trans*-$[Ru(CHO)(CO)(dppb)_2][SbF_6]$ *in the presence of* $(Bu^tNO)_2$. The dimer $(Bu^tNO)_2$ (0.0065 g, 10 mol excess) was dissolved in CH_2Cl_2 (2 cm^3) and stored in the dark for 5 min to ensure minimum decomposition of Bu^tNO. The solution was then transferred onto a sample of *trans*-$[Ru(CHO)(CO)(dppb)_2][SbF_6]$ (0.011 g) at room temperature and the e.s.r. spectrum of the resulting solution recorded.

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* The percentage of radicals inducing polymerization was calculated from the number of ends of polymer molecules ($2 \times \text{yield}/M_N = 1.6 \times 10^{-6}$) relative to the number of moles of formyl (8×10^{-5}). This gives an upper limit by assuming that termination is always by coupling of growing polymer chains.

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