Reactions of Ruthenium Formyl and Related Complexes with Nitroxide Spin Traps

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Reactions of the complexes *trans*-$[Ru(CHO)(CO)(dppe)_2][SbF_6]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), *cis*-$[Ru(CHO)(CO)(dppm)_2][SbF_6]$ (dppm = $Ph_2PCH_2PPh_2$), or *trans*-$[Os(CHO)(CO)(dppe)_2][SbF_6]$ with Bu^tNO give $Bu^t_2NO^{\cdot}$ and *trans*-$[M(Bu^tNO)(CO)(P\text{–}P)_2]^{\cdot+}$ (M = Ru, P–P = dppe or dppm; M = Os, P–P = dppe), the structures of which have been elucidated by e.s.r. and labelling (^{13}C, ^2H) studies. *cis*- or *trans*-$[RuH(CO)(dppe)_2]^+$ gives only $Bu^t_2NO^{\cdot}$, whilst *trans*-$[Ru(CO)_2(dppe)_2]^{2+}$ gives a mixture of *trans*-$[Ru(CO)_2(dppe)\{Ph_2PCH_2CH(Bu^tNO)PPh_2\}]^{\cdot 2+}$ and a radical with the trap bound to a carbonyl carbon atom. The decomposition products of *cis*-$[Ru(CHO)(CO)(dppm)_2]^+$ give a radical with the trap bound to the back-bone carbon atom of a chelating dppm ligand, whilst dppe and dppm both give radicals where the Bu^tNO group is bound to a phosphorus atom. The mechanisms of some of these reactions are discussed.

During the course of investigations[1] into the modes of decomposition of cationic formyl complexes of ruthenium, we attempted to use the spin-trapping technique,[2–4] which has previously been used with other transition-metal complexes,[5] *e.g.* manganese carbonyls,[6] in order to discover whether or not free radicals were involved in the decomposition. In all cases radicals were observed. However, since they were also observed on reaction with analogous formyl complexes of osmium, which are stable towards thermal decomposition under the conditions employed, we conclude that a radical mechanism does not constitute the major pathway for decomposition of the cationic ruthenium formyls. Rather, we believe that the radical traps help to form the radicals and we now report the results of these investigations.

Results and Discussion

Two spin traps were employed in attempting to identify radicals trapped during the decomposition reaction of ruthenium formyls: (*i*) *N*-benzylidene-t-butylamine *N*-oxide (phenyl-*N*-t-butyl nitrone, pbn), since it is very easily used and is believed to be a very mild reagent with a low tendency to generate radicals, and (*ii*) 2-methyl-2-nitrosopropane (mnp) for its trapping efficiency and the high information content of the e.s.r. spectra of its spin adducts. The even more efficient trap, nitrosodurene (2,3,5,6-tetramethylnitrosobenzene) gave very low concentrations of radicals, presumably because it is less reactive than pbn or mnp, so was not extensively used in this study.

Spin Trapping with N-*Benzylidene-t-butylamine* N-*Oxide*.—The spin trap pbn was used in a series of preliminary experiments to determine whether free radicals are involved in the decomposition of $[Ru(CHO)(CO)(dppe)_2][SbF_6]$ [dppe = 1,2-bis(diphenylphosphino)ethane]. When the latter decomposed thermally in dichloromethane in the presence of pbn a spin adduct was formed having the expected e.s.r. spectrum comprising a 1 : 1 : 1 triplet of 1 : 1 doublets. Coupling constants were found to be $a^N = 1.463 \pm 0.005$ mT and $a^H = 0.300 \pm 0.001$ mT at 20 °C; these values are not particularly informative but they could arise from the trapping of carbon-, phosphorus- or oxygen-centred radicals.[5]

Spin Trapping with 2-Methyl-2-nitrosopropane (*mnp*).—The success of the trapping experiments with pbn led us to use the more specific spin trap mnp to study the decomposition of a series of ruthenium formyl complexes; the results are given below.

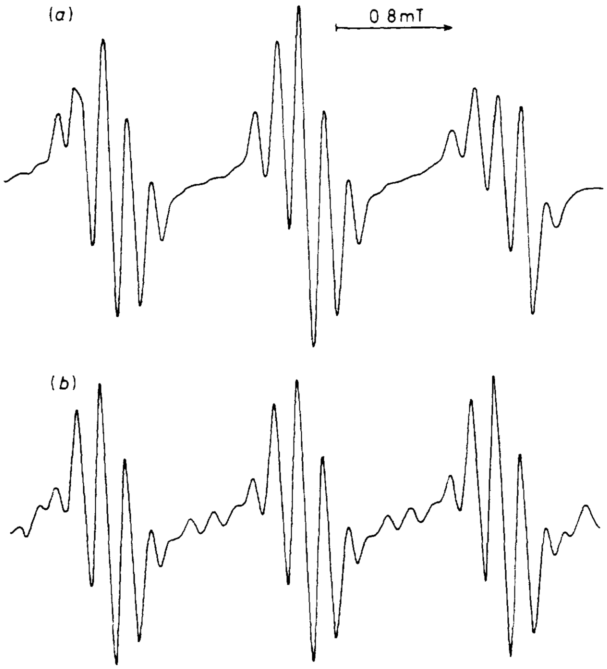

Figure 1. First derivative *X*-band e.s.r. spectrum of a solution of *trans*-$[Ru(CHO)(CO)(dppe)_2][SbF_6]$ and mnp in CH_2Cl_2 at 20 °C. (*a*) Experimental spectrum and (*b*) computer simulated spectrum. Note that some of the weak outer lines have been omitted

trans-$[Ru(CHO)(CO)(dppe)_2][SbF_6]$. This salt was mixed with solid mnp and then dichloromethane added. The e.s.r. spectrum of the solution increased in intensity over a period of 2 h at room temperature. The spectrum (see Figure 1) comprised a 1 : 1 : 1 triplet superimposed on a 1 : 1 : 1 triplet of 1 : 4 : 6 : 4 : 1 quintets. There are clearly two radicals having identical *g* factors and similar values of a^N. The quintet is likely to arise from coupling to four equivalent phosphorus nuclei. Weak lines falling between the main groups of lines can be attributed to hyperfine coupling to magnetic ruthenium isotopes. The computer simulation [Figure 1(*b*)] was achieved by ignoring the 1 : 1 : 1 triplet (from $Bu^t_2NO^{\cdot}$) since the central

Table. Radicals trapped by Bu^{t}NO from various compounds [a]

Precursor	a^N/mT	Mult.	a^H/mT	Mult.	Other couplings (Mult.)				Assignment
					^{101}Ru	^{99}Ru	^{189}Os	^{13}C	
trans-[Ru(CHO)(CO)(dppe)$_2$]$^+$	1.379(4)	3	0.163(5)	5	0.417(6)	0.287(4)			*trans*-[Ru(Bu^{t}NO)(CO)(dppe)$_2$]$^{\cdot +}$
Figure 1	1.563	3							Bu$^t_2$NO$^{\cdot}$
trans-[Ru(CDO)(CO)(dppe)$_2$]$^+$	1.379(5)	3	0.161(7)	5					*trans*-[Ru(Bu^{t}NO)(CO)(dppe)$_2$]$^{\cdot +}$
									Bu$^t_2$NO$^{\cdot}$
trans-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$]$^+$	1.379(8) [b]	3	0.175	5	0.417(6)	0.287(4)		0.052(2)	*trans*-[Ru(Bu^{t}NO)(CO)(dppe)$_2$]$^{\cdot +}$
Figure 2	1.568 [c]	3							Bu$^t_2$NO$^{\cdot}$
trans-[Os(CHO)(CO)(dppe)$_2$]$^+$	1.384(12)	3	0.162(6)	5			0.469(4)		*trans*-[Os(Bu^{t}NO)(CO)(dppe)$_2$]$^{\cdot +}$
	1.571	3							Bu$^t_2$NO$^{\cdot}$
trans-[Ru(CO)$_2$(dppe)$_2$]$^{2+}$	1.054(3)	3	1.175(3)	2					(B), Scheme 2
Figure 3	0.800(2)	3							See text
cis-[RuH(CO)(dppe)$_2$]$^+$	1.569	3							Bu$^t_2$NO$^{\cdot}$
trans-[RuH(CO)(dppe)$_2$]$^+$	1.568	3							Bu$^t_2$NO$^{\cdot}$
cis-[Ru(CHO)(CO)(dppm)$_2$]$^+$	1.574 [d]	3	1.048	3					See text
Figure 4	1.340 [e]		0.079	5					*trans*-[Ru(Bu^{t}NO)(CO)(dppm)$_2$]$^{\cdot +}$
cis-[Ru(CDO)(CO)(dppm)$_2$]$^+$	1.538(34)	3	1.045(19)	3					See text
	1.570	3							Bu$^t_2$NO$^{\cdot}$
cis-[Ru(^{13}CHO)(^{13}CO)(dppm)$_2$]$^+$	1.568(10)	3	1.037(10)	3					
	1.569	3							Bu$^t_2$NO$^{\cdot}$
cis-[RuH(CO)$_2$(dppm)$_2$]$^+$ + *trans*-[RuCl(CO)(dppm)$_2$]$^+$	1.575(5)	3	1.048(9)	3				0.058(2)	See text
Figure 5									
dppe	1.165(8)	3							
	1.375(5)	3	3.916(5)						See text
	1.688(2)	3							
	1.575(3)	3							Bu$^t_2$NO$^{\cdot}$
dppm	1.573(2)	3							Bu$^t_2$NO$^{\cdot}$
	1.333(5)	3	6.400(3)	2					See text
			0.184(6)	2					

[a] The g values of all the spin adducts are typical of nitroxide radicals, *e.g.* for Bu$^t_2$NO$^{\cdot}$, g factor = 2.006. For the stability of the radicals see Experimental section. Errors are in parentheses. Mult. = multiplicity of signal. [b] A linewidth of 0.07 and a relative concentration of 85% was used for the computer simulated spectrum. [c] A linewidth of 0.07 and a relative concentration of 15% was used for the computer simulated spectrum. [d] A linewidth of 0.055 and a relative concentration of 80% was used for the computer simulated spectrum. [e] A linewidth of 0.055 and a relative concentration of 20% was used for the computer simulated spectrum.

group of lines is undistorted. The values of the hyperfine coupling constants and of linewidths used in the simulation of this and other spectra are shown in the Table. The heights of the satellite lines in the computed spectrum are greater than those in the experimental since no allowance was made for the expected quadrupolar broadening; $I(^{101}\mathrm{Ru}) = \frac{5}{2}$ and $I(^{99}\mathrm{Ru}) = \frac{3}{2}$. These lines were, however, confirmed as arising from hyperfine coupling to Ru since reaction of the analogous *trans*-[Os(CHO)(CO)(dppe)$_2$][SbF$_6$] with mnp under identical conditions gave Bu$^t_2$NO$^{\cdot}$ and a radical very similar to that obtained with the ruthenium complex (Table) but with different satellites caused by coupling to ^{189}Os ($I = \frac{3}{2}$, abundance = 16.1 atom %).

In order to identify these radicals more fully, identical reactions were carried out using *trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] and *trans*-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$][SbF$_6$]. For the deuterioformyl complex, the e.s.r. spectrum of the trapped radical was identical with that obtained from its protio-analogue, although more Bu$^t_2$NO$^{\cdot}$ was formed, whilst for the ^{13}C (92%) labelled complex the spectrum, Figure 2, showed hyperfine coupling to one carbon atom ($a^C = 0.052$ mT).*

The basic quintet structure of the radical trapped on reaction of *trans*-[Ru(CHO)(CO)(dppe)$_2$]$^+$ with mnp suggests coupling to four equivalent phosphorus atoms and the observed coupling constant is similar to that obtained[5] for mnp adducts of manganese carbonyl phosphine complexes ($a^{^{55}\mathrm{Mn}} = 1.1$ mT) when allowance is made for the higher magnetic moment of ^{55}Mn. The coupling to ^{13}C in the ^{13}C-labelled radical is small and suggests a carbonyl group *trans* to the nitroxide. We therefore assign the structure as (A) in Scheme 1.

Since neither of the decomposition products of *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$], *cis*- and *trans*-[RuH(CO)(dppe)$_2$]$^+$, nor the starting material from which it is synthesised, *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$, give the same ruthenium-based radical on reaction with mnp (see below), we conclude that this radical arises directly from the formyl and a tentative mechanism for its formation is shown in Scheme 1. The first step, cleavage of a Ru–P bond, is known[1] from decomposition studies to be a facile process and since hydrogen migration is blocked by co-ordination of the spin trap, we assume that homolytic cleavage of the Ru–C bond of the formyl is the next most facile process. From an *X*-ray structure determination,[7] we believe that this Ru–C bond is longer and therefore weaker than those observed in neutral or anionic metal formyl complexes. It is probable that the five-co-ordinate intermediate formed rapidly isomerises so that re-chelation of the phosphorus atom gives the thermodynamically favoured *trans* isomer of the product.

Both *cis*- and *trans*-[RuH(CO)(dppe)$_2$]$^+$ give only Bu$^t_2$NO$^{\cdot}$ as the radical product from reaction with mnp, whilst *trans*-

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* Although this small coupling is not immediately apparent, it manifests itself in the form of shoulders on most of the smaller peaks of the quintets in the spectrum of the ^{13}C derivative (Figure 2) and in a greater experimental linewidth (0.11 mT) for the ^{13}C-labelled compound than for the ^{12}C derivative (0.07 mT).

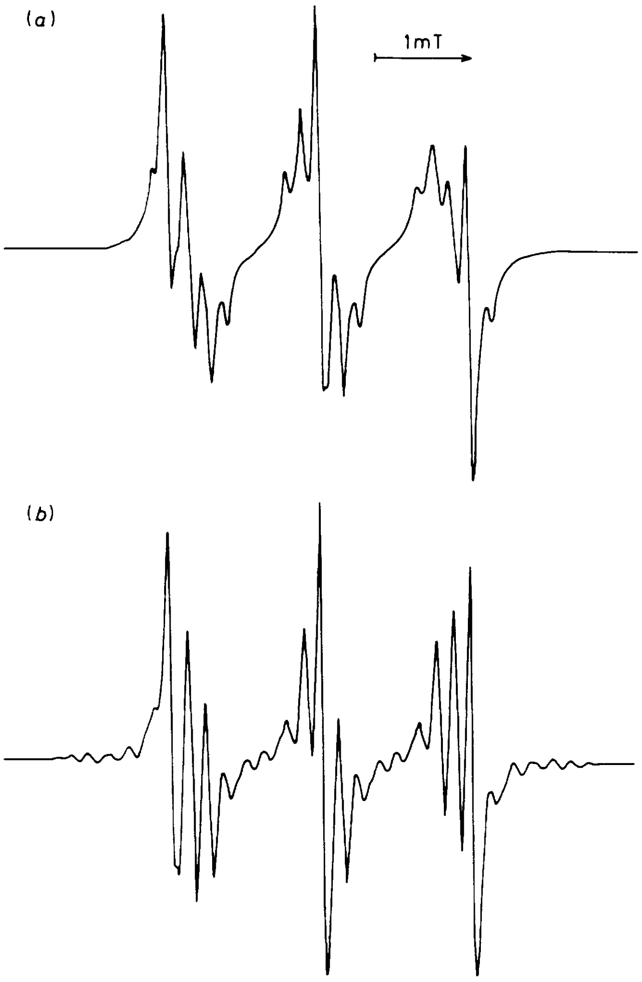
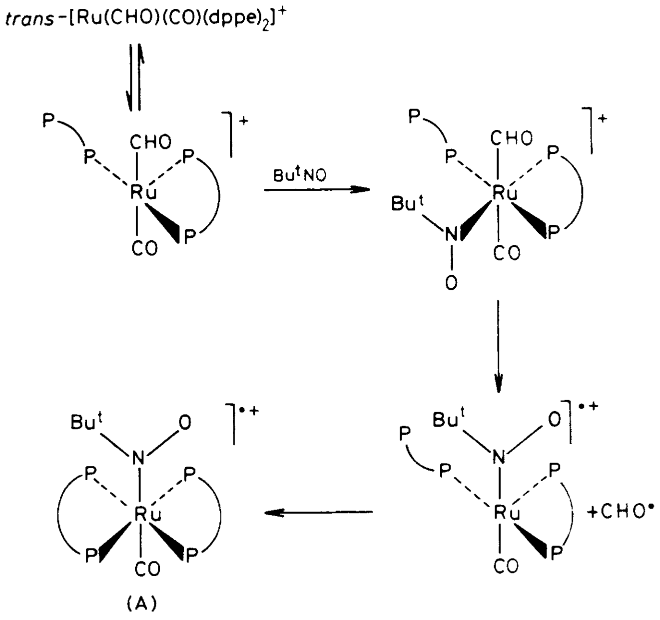


Figure 2. First derivative *X*-band e.s.r. spectrum of a solution of *trans*-$[\mathrm{Ru(^{13}CHO)(^{13}CO)(dppe)_2][SbF_6]}$ and mnp at 23.9 °C. (*a*) Experimental spectrum and (*b*) computer simulated spectrum

$[\mathrm{Ru(CO)_2(dppe)_2}]^{2+}$ gives two new radicals in low concentration (see Figure 3 and Table). One of these shows coupling to nitrogen and one phosphorus atom, the value of a^{P} (1.75 mT) is lower than expected for direct attachment of the nitroxide to phosphorus (see later), but could arise from attachment of mnp to an α-carbon atom of dppe [(B), Scheme 2]. Indeed, a^{P} is similar to that found when mnp is attached to the backbone carbon atom of dppm [dppm = bis(diphenylphosphino)methane] (see later). The less abundant radical shows only a small coupling to nitrogen consistent with mnp being adjacent to a carbonyl group;[5] in this situation long-range couplings are not observed.[3]

For $[\mathrm{Ru(CO)_2(dppe)_2}]^{2+}$ to generate radicals, one of four processes must occur: oxidation or reduction of the metal, abstraction of halide from the solvent, or loss of H˙ from a dppe ligand. Clearly, for the radical shown in (B) (Scheme 2) loss of H˙ has occurred, but we do not have sufficient information to comment on the mode of formation of the other radical or on its structure.

cis-$[\mathrm{Ru(CHO)(CO)(dppm)_2][SbF_6]}$. *cis*-$[\mathrm{Ru(CHO)(CO)(dppm)_2][SbF_6]}$ is considerably less stable than *trans*-$[\mathrm{Ru(CHO)(CO)(dppe)_2][SbF_6]}$ and decomposes in $\mathrm{CH_2Cl_2}$ in the presence of mnp to give two radicals, the second derivative e.s.r. spectrum of which is shown in Figure 4. Clearly one of these radicals is *trans*-$[\mathrm{Ru(Bu^tNO)(CO)(dppm)_2}]^{\cdot +}$ since its



Scheme 1. Proposed mechanism of formation of *trans*-$[\mathrm{Ru(Bu^tNO)(CO)(dppe)_2}]^{\cdot +}$ from *trans*-$[\mathrm{Ru(CHO)(CO)(dppe)_2}]^{+}$ and $\mathrm{Bu^tNO}$; P–P = dppe

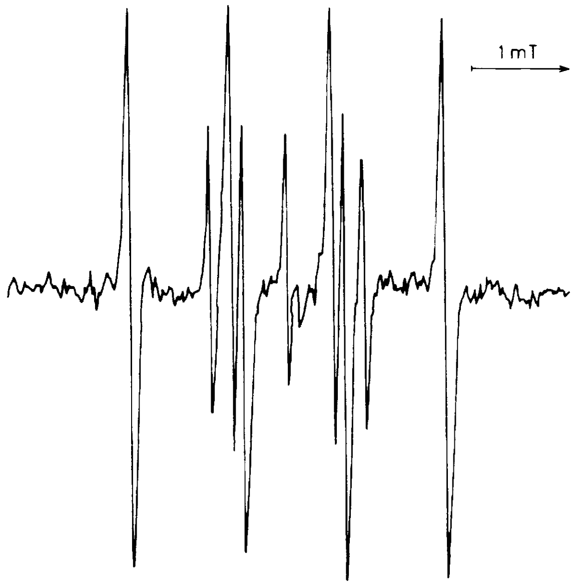


Figure 3. First derivative *X*-band e.s.r. spectrum of a solution of *trans*-$[\mathrm{Ru(CO)_2(dppe)_2][SbF_6]_2}$ and mnp in $\mathrm{CH_2Cl_2}$ at 20 °C

e.s.r. spectrum is similar to that of *trans*-$[\mathrm{Ru(Bu^tNO)(CO)(dppe)_2}]^{\cdot +}$ apart from a smaller value for a^{P}. This difference in coupling is similar to those observed[8] for metal phosphorus coupling constants in the ^{31}P n.m.r. spectra of for example, $[\mathrm{PtMe_2L}]$, $[\mathrm{PtCl_2L}]$, and $[\mathrm{W(CO)_4L}]$ (L = dppe or dppm) and can be attributed to different degrees of strain in the four- and five-membered rings.

The second, more abundant, radical (80% of radical species present) shows coupling to nitrogen and to two equivalent phosphorus atoms. The spectrum of this species is identical whether generated from *cis*-$[\mathrm{Ru(CHO)(CO)(dppm)_2}]^{+}$, *cis*-$[\mathrm{Ru(CDO)(CO)(dppm)_2}]^{+}$, or *cis*-$[\mathrm{Ru(^{13}CHO)(^{13}CO)(dppm)_2}]^{+}$ although in the last two cases much more $\mathrm{Bu^t_2NO^{\cdot}}$ and no *trans*-$[\mathrm{Ru(Bu^tNO)(CO)(dppm)_2}]^{\cdot +}$ are observed.

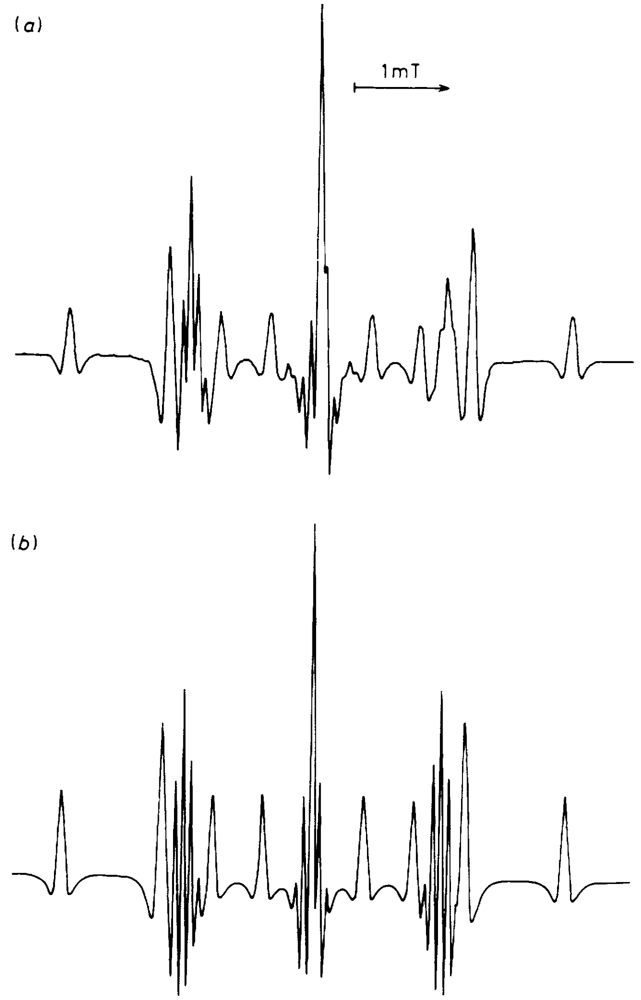


Figure 4. Second derivative *X*-band e.s.r. spectrum of a solution of *cis*-[Ru(CHO)(CO)(dppm)$_2$][SbF$_6$] and mnp in CH$_2$Cl$_2$ one hour after mixing at 20 °C. (*a*) Experimental spectrum and (*b*) computer simulated spectrum

Interestingly, the same radical, with coupling to nitrogen and two equivalent phosphorus atoms (Figure 5) is formed from a mixture of *cis*-[RuH(CO)$_2$(dppm)$_2$]$^+$ and *trans*-[RuCl(CO)(dppm)$_2$]$^+$, which are decomposition products of *cis*-[Ru(CHO)(CO)(dppm)$_2$]$^+$, under similar conditions.[1] The satellites observed in this spectrum can be assigned to ^{13}C coupling with the α-carbons of the Bu^t group.[5] The apparent lack of coupling of the electron to ruthenium, ^{13}C in the ^{13}CO labelled derivative or to ^{1}H suggests that the trap is not bound directly to the metal. However, since the same radical is not formed from free dppm (see below) we believe that the trap must be bound to a dppm molecule attached to ruthenium and, so that it is equally coupled to both phosphorus atoms, we propose that it is bound to the back-bone carbon atom of a bidentate dppm ligand. Although the lack of coupling to the remaining methine proton is somewhat surprising, minimizing steric repulsions between the phenyl rings of the dppm and the t-butyl group of the mnp forces the methine proton and the N–C(butyl) bond to be mutually *syn* (see Figure 6). In this arrangement, large couplings to phosphorus but approximately zero coupling to hydrogen would be expected.[9,10]

1,2-*Bis*(*diphenylphosphino*)*ethane and bis*(*diphenylphosphino*)*methane*. Reaction of dppe with mnp in CH$_2$Cl$_2$ at room temperature gives three radicals. Two of these, which are unstable and give Bu$^t{}_2$NO$^\bullet$ on standing, show coupling only to nitrogen, whilst the third, more stable radical shows coupling to nitrogen and to one other spin $\frac{1}{2}$ nucleus (a^{P} = 3.916 mT). With dppm, mnp gives Bu$^t{}_2$NO$^\bullet$ and a radical with coupling to nitrogen and two spin $\frac{1}{2}$ nuclei (a^{P} = 6.4 mT and a^{P} = 0.184 mT). The very large couplings observed with dppe or dppm suggest direct binding of the spin trap to phosphorus and the smaller coupling observed for dppm is probably due to the remote phosphorus atom. Whether the radical comes from a redox process or loss of H$^\bullet$ from the back-bone of the diphosphine is not clear, but since mnp is attached directly to phosphorus we think it unlikely that H$^\bullet$ abstraction has occurred.

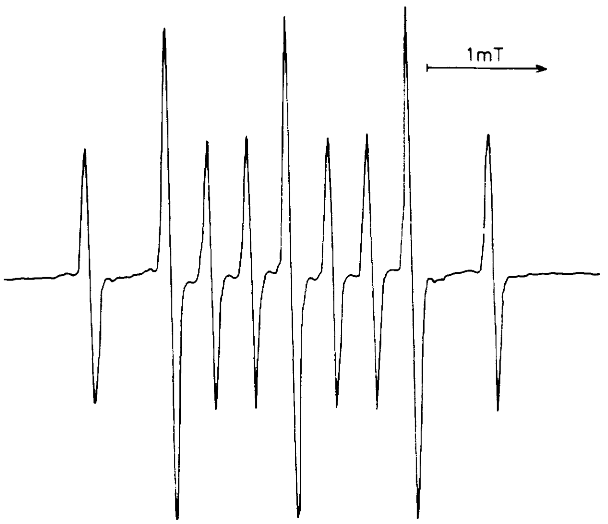


Figure 5. First derivative *X*-band e.s.r. spectrum of a mixture of *cis*-[RuH(CO)$_2$(dppm)$_2$][SbF$_6$] and *trans*-[RuCl(CO)(dppm)$_2$]-[SbF$_6$] and mnp in CH$_2$Cl$_2$ at 20 °C

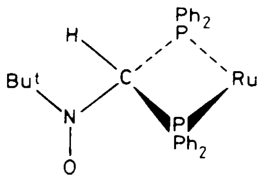


Figure 6. Orientation of Bu^{t}NO attached to the back-bone carbon atom of chelating dppm

Mechanism of Formation of the Radicals.—The mechanism of formation of the ruthenium bound radicals has been discussed above, but the formation of radicals from [Ru(CO)$_2$-(dppe)$_2$]$^{2+}$ and from mixtures of [RuH(CO)$_2$(dppm)$_2$]$^+$ and [RuCl(CO)(dppm)$_2$]$^+$ is more difficult to explain. In both cases, the major radicals appear to have mnp attached to a back-bone carbon atom of the diphosphine and a plausible mechanism involves abstraction of H$^\bullet$ from this carbon atom to give Bu^{t}NHO$^\bullet$ and a radical which is trapped by Bu^{t}NO.* Bu^{t}NHO$^\bullet$ is not observed as a product presumably because, since this and other nitroxide radicals are known [11] to be good hydride abstractors, it would rapidly give Bu^{t}NH(OH)

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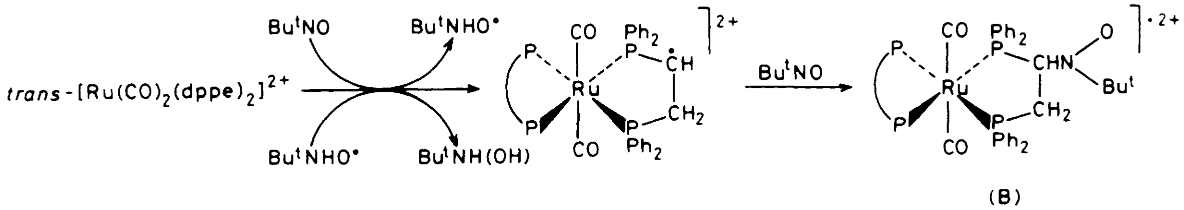
* We note that the methylene C–H bonds of the dppe ligand can also be activated by the metal.[1]



Scheme 2. Proposed mechanism of formation of *trans*-[Ru(CO)$_2$(dppe){Ph$_2$PCH$_2$CH(Bu^{t}NO)PPh$_2$}]$^{•2+}$ from *trans*-[Ru(CO)$_2$(dppe)$_2$]$^{2+}$ and Bu^{t}NO; P–P = dppe

and another ruthenium based radical for trapping by Bu^{t}NO. This is shown for [Ru(CO)$_2$(dppe)$_2$]$^{2+}$ in Scheme 2.

Finally, Bu$^t{}_2$NO$^•$ is evidently produced by a metal promoted reaction in a number of the systems that we have studied but we have insufficient evidence on which to base a mechanism for its formation.

Experimental

2-Methyl-2-nitrosopropane (mnp) was purchased from Lancaster Synthesis and used without further purification. The white solid is a dimer which dissociates in solution to give the blue monomer.[12] *N*-Benzylidene-t-butylamine *N*-oxide was prepared by a three-step synthesis: *N*-t-butylbenzamide, prepared by the condensation of benzaldehyde with t-butylamine,[13] was converted to 2-t-butyl-3-phenyloxaziridine using *m*-chloroperoxybenzoic acid.[14,15] Subsequent refluxing for three days in dry acetonitrile [14] yielded the impure nitrone. Purification and recrystallisation from light petroleum (b.p. 40—60 °C) containing decolourising charcoal afforded the nitrone as white needles.

For the spin-trapping experiments all manipulations were performed under sodium light, and samples were kept in the dark before and in between the recording of their e.s.r. spectra. All operations were carried out under nitrogen using standard Schlenk-line and catheter-tubing techniques, and all solvents were thoroughly degassed prior to use.

The preparations of *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$[16] and the formyl complexes [Ru(CHO)(CO)(P–P)$_2$][SbF$_6$] [7] (P–P = dppm or dppe) have been reported previously, and *trans*-[Os(CHO)(CO)(dppe)$_2$][SbF$_6$] [17] was made by a similar route. The complexes *cis*- and *trans*-[RuH(CO)(dppe)$_2$][SbF$_6$] were prepared *via* the decomposition of the formyl complex, *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$], and isolated as previously described.[1] Dppm was made by the standard route [18] whilst dppe was purchased from B.D.H. and used without further purification.

The spectra were recorded on a Varian E-4 *X*-band e.s.r. spectrometer. The details of spectrometer calibration, data acquisition, and computer simulations have previously been reported.[19,20]

For the spin-trapping experiments two types of experimental procedure have been employed: (i) the solid complex and trap (pbn or mnp) were first placed into a silica e.s.r. sample tube, into which 0.75 cm^3 of solvent [CH$_2$Cl$_2$ or tetrahydrofuran (thf)] was added. The sample was then sealed and its e.s.r. spectrum recorded at regular intervals; (*ii*) the solid complex was placed into an e.s.r. tube whereas the solid trap (mnp) was dissolved in dichloromethane (0.75 cm^3) in a separate side-arm on the e.s.r. tube. When the characteristic blue colour of the monomer had appeared, the solvent was decanted onto the solid complex and the spectrum recorded at intervals.

Reactions.—(*a*) *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] *with* pbn. *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] (0.02 g, 0.017 mmol) and pbn (0.03 g, 0.17 mmol) were dissolved in dichloromethane as in procedure (i). The intensity of the signal increased with time, reaching a maximum after 2 h, and disappearing on standing overnight.

(*b*) *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] *with* mnp. *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] (0.02 g, 0.017 mmol) and mnp (0.015 g, 0.17 mmol Bu^{t}NO monomer) were dissolved in dichloromethane as in procedure (i). The signal appeared within minutes of mixing and rapidly intensified over a period of 3 h. On standing overnight the ruthenium spin adduct disappeared, leaving a strong signal due to Bu$^t{}_2$NO$^•$.

A sample of *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] was prepared in nitromethane (as opposed to dichloromethane), isolated, and then decomposed in thf as above. The e.s.r. spectrum was identical with that obtained when dichloromethane was used as solvent, thus eliminating the possibility of the trap reacting with the solvent to produce radicals.

(*c*) *trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] *with* mnp. *trans*-[Ru(CDO)(CO)(dppe)$_2$][SbF$_6$] (0.02 g) and mnp (0.015 g) were dissolved in dichloromethane as in (i). The signal due to the ruthenium spin adduct again increased in intensity with time; however, the rate of increase was slower than that for the non-deuteriated formyl [see (*b*)]. This result is in agreement with the different rates of decomposition of the formyls.[1] A greater amount of Bu$^t{}_2$NO$^•$ was formed than for the protio-analogue.

(*d*) *trans*-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$][SbF$_6$] *with* mnp. *trans*-[Ru(^{13}CHO)(^{13}CO)(dppe)$_2$][SbF$_6$] (0.02 g) and mnp (0.015 g) were dissolved in dichloromethane as in (i). The signals due to the adducts again increased with time reaching a maximum after 2 h.

(*e*) *cis*-[RuH(CO)(dppe)$_2$][SbF$_6$] *with* mnp. *cis*-[RuH(CO)(dppe)$_2$][SbF$_6$] (0.02 g, 0.017 mmol) and mnp (0.015 g, 0.17 mmol) were dissolved in dichloromethane as in (i). A strong signal due to Bu$^t{}_2$NO$^•$ was immediately observed, rapidly increasing in intensity with time, and indefinitely stable.

(*f*) *trans*-[RuH(CO)(dppe)$_2$][SbF$_6$] *with* mnp. The experimental procedure and results were identical with those in (*e*), this time using *trans*-[RuH(CO)(dppe)$_2$][SbF$_6$] as the metal complex.

(*g*) *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$ *with* mnp. *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$ (0.03 g, 0.021 mmol) and mnp (0.018 g, 0.21 mmol) were dissolved in dichloromethane as in (i). The resultant e.s.r. spectrum showed two spin adducts which were low in concentration, and did not increase in intensity significantly on standing.

(*h*) *cis*-[Ru(CHO)(CO)(dppm)$_2$][SbF$_6$] *with* mnp. *cis*-[Ru(CHO)(CO)(dppm)$_2$][SbF$_6$] (0.03 g, 0.026 mmol) was dissolved in a dichloromethane solution of mnp (0.023 g, 0.26 mmol) as in (ii). The adduct with two equivalent P atoms (see Results and Discussion section) was immediately formed and increased in intensity with time. The second spin adduct with four equivalent P atoms was also formed immediately, but grew in intensity at a greater rate, and over a longer period of time (5 h). Several days after mixing the latter spin adduct was still present, along with a substantial amount of $Bu^t{}_2NO^{\cdot}$ whereas the former adduct had disappeared.

(*i*) *cis*-$[Ru(CDO)(CO)(dppm)_2][SbF_6]$ *with* mnp. *cis*-$[Ru(CDO)(CO)(dppm)_2][SbF_6]$ (0.03 g) was dissolved in a dichloromethane solution of mnp (0.023 g) as in (ii). Only the former spin adduct as in (*h*) was formed, but this time at a slower rate, and with a greater amount of $Bu_2{}^tNO^{\cdot}$ present.

(*j*) *cis*-$[Ru(^{13}CHO)(^{13}CO)(dppm)_2][SbF_6]$ *with* mnp. *cis*-$[Ru(^{13}CHO)(^{13}CO)(dppm)_2][SbF_6]$ (0.03 g) was dissolved in a dichloromethane solution of mnp (0.023 g) as in (ii). The e.s.r. spectrum showed the presence of a spin adduct with two equivalent P atoms, and a large amount of $Bu^t{}_2NO^{\cdot}$. The presence of decomposed trap obscured any possible signals due to the spin adduct with four equivalent P atoms, and hence it was impossible to determine whether the adduct was present.

(*k*) *cis*-$[RuH(CO)_2(dppm)_2][SbF_6]$ *and trans*-$[RuCl(CO)(dppm)_2][SbF_6]$ *with* mnp. *cis*-$[Ru(CHO)(CO)(dppm)_2][SbF_6]$ (0.1 g, 0.086 mmol) was dissolved in dichloromethane (10 cm^3) and stirred for 15 min in the dark. The solution was then filtered, and a solution i.r. spectrum showed the characteristic[1] bands due to $\nu_{C\equiv O}$ of *cis*-$[RuH(CO)_2(dppm)_2]^+$ (2 050vs and 2 010vs cm^{-1}) and *trans*-$[RuCl(CO)(dppm)_2]^+$ (1 978s cm^{-1}). The solution was reduced in volume to *ca.* 2 cm^3 and then a portion (0.75 cm^3) was decanted onto solid mnp (0.025 g) in an e.s.r. tube. The e.s.r. spectrum run immediately showed a high concentration of the spin adduct with two equivalent P atoms and no other radical. The spin adduct was present several days after mixing, the only change being a build-up in concentration of $Bu^t{}_2NO^{\cdot}$.

(*l*) 1,2-*Bis*(*diphenylphosphino*)*ethane with* mnp. Dppe (0.05 g, 0.126 mmol) and mnp (0.01 g, 1.0 mmol) were dissolved in dichloromethane as in (i). Three different spin adducts were observed 15 min after mixing, but after 2 h only one of these remained (1 : 1 doublet of 1 : 1 : 1 triplets), with the added presence of $Bu^t{}_2NO^{\cdot}$.

(*m*) *Bis*(*diphenylphosphino*)*methane with* mnp. Dppm (0.05 g, 0.13 mmol) and mnp (0.1 g, 1.0 mmol) were dissolved in dichloromethane as in (i). Initially $Bu^t{}_2NO^{\cdot}$ was the major product observed, but after 2 h the concentration of spin adducts increased, with an additional signal appearing (1 : 1 doublet of 1 : 1 : 1 triplets of 1 : 1 doublets).

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