# Patterns of Nucleophilic Attack on Ethene Complexes of Ruthenium(II)

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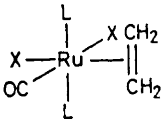
Although reaction of $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$ with the nucleophile $PMe_2Ph$ at 308 K simply results in substitution of the ethene ligand, studies at lower temperatures reveal that the kinetically favoured product is the cation $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3]^+$. Similarly the complexes $[Ru(CO)(\eta-C_2H_4)X_2(AsMe_2Ph)_2]$ (X = Cl or Br) react with $PMe_2Ph$ to yield $[Ru(CO)(CH_2CH_2PMe_2Ph)X(AsMe_2Ph)_2(PMe_2Ph)]^+$ and $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$ reacts with $PMePh_2$ to form $[Ru(CO)(CH_2CH_2PMePh_2)Cl(PMe_2Ph)_2(PMePh_2)]^+$. It appears probable that the first step in these reactions involves nucleophilic attack on the ethene, with subsequent substitution of the halide ion *trans* to the newly formed alkyl ligand. In the case of the nucleophiles L′ = $AsMe_2Ph$, $NH_2CH_2Ph$, $P(OMe)_2Ph$, 4-methylpyridine, and $SMe_2$, there is no evidence of low-temperature attack on the ethene ligand in $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$: on raising the temperature, only the ethene substitution products $[Ru(CO)Cl_2L'(PMe_2Ph)_2]$ are obtained.

SOME time ago, we reported on the preparation [1] and crystal structure [2] of an ethene complex of ruthenium(II), $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$ of structure (I), where X = Cl and L = $PMe_2Ph$. Information on the reactivity of co-ordinated ethene in octahedral complexes of $d^6$ metal ions is in relatively short supply {although $[Fe(\eta-C_5H_5)(CO)_2(\eta-C_2H_4)]^+$ has been well studied [3,4]}, whereas ethene complexes of metal ions of other configurations [particularly palladium(II), where interest has recently been rekindled by the presentation of new evidence relevant to the mechanism of the Wacker process [5]] have received much more attention. We therefore decided to study the reactions of nucleophiles with $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$ and other ethene complexes of ruthenium(II). We hoped that the comparatively high co-ordination number in these complexes might, by hindering direct attack on the metal, favour nucleophilic attack on the ethene ligand.



(I)

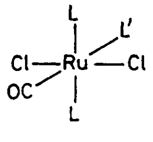
## RESULTS AND DISCUSSION

Details of the i.r. and $^1H$ n.m.r. spectra of the ethene complexes and other previously uncharacterized complexes are given in Table 1, and information about the $^{13}C$ n.m.r. spectra of selected complexes is given in Table 2.

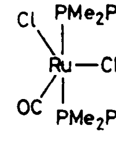
*Preparation of Ethene Complexes*.—Details of the preparation of $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$, which involves treating a solution of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with ethene, have been given previously.[1,2] The presence of the $PMe_2Ph$ ligands, although often useful as a means of obtaining stereochemical information,[6,7] can make n.m.r. spectra very complicated, and the use of analogous complexes containing $AsMe_2Ph$ can provide welcome simplification. The complex *cis*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$ was prepared by the method described by Jenkins *et al.*[6] for *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, using $AsMe_2Ph$ in place of $PMe_2Ph$. The corresponding bromo-complex was obtained by repeating the preparation in the presence of excess of NaBr, and both were converted to their *trans* isomers by u.v. irradiation of their solutions in propanone.[1] The complex *trans*-$[Ru(CO)_2I_2(AsMe_2Ph)_2]$ was prepared by irradiation of a propanone solution of *cis*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$ and NaI. Treatment of $CHCl_3$ solutions of the complexes *trans*-$[Ru(CO)_2X_2(AsMe_2Ph)_2]$ (X = Cl or Br) with ethene yielded the desired products $[Ru(CO)(\eta-C_2H_4)X_2(AsMe_2Ph)_2]$, but we were unable to obtain the corresponding iodo-complex either from the reaction of *trans*-$[Ru(CO)_2I_2(AsMe_2Ph)_2]$ with ethene or by treating $[Ru(CO)(\eta-C_2H_4)Cl_2(AsMe_2Ph)_2]$ with NaI in propanone solution.

Apart from the absence of phosphorus splittings, the ambient temperature $^1H$ and $^{13}C$ n.m.r. spectra of $[Ru(CO)(\eta-C_2H_4)Cl_2(AsMe_2Ph)_2]$ and the $^1H$ spectrum of its bromo-analogue were very similar to those of $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$, and we concluded that they also possessed structure (I), where L = $AsMe_2Ph$ and X = Cl or Br.

*Reactions of the Ethene Complexes with the Nucleophiles* $PMe_2Ph$ *and* $PMePh_2$.—In the initial experiment, $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$ was treated with an equimolar quantity of $PMe_2Ph$ in benzene solution at 308 K. Proton n.m.r. spectra recorded during the reaction revealed the presence of an increasing quantity of free ethene and the formation of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ [structure (II), where L = L′ = $PMe_2Ph$].[1] Thus the complex was undergoing nucleophilic substitution at the metal rather than addition to the alkene. On the basis of earlier studies of substitution reactions of complexes $[Ru(CO)Cl_2L'(PMe_2Ph)_2]$,[1] the likely mechanism is a dissociative one, with loss of ethene being followed by attack on the five-co-ordinate species $[Ru(CO)Cl_2-$



(II)



(III)

TABLE 1

Infrared [a] and $^1$H n.m.r. spectra [b] of complexes

| Complex | $\nu$(C–O)/cm$^{-1}$ | $\delta$/p.p.m. | Assignment |
|---|---|---|---|
| *cis*-$[\mathrm{Ru(CO)_2Cl_2(AsMe_2Ph)_2}]$ | 2 053 | 1.93 (s) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  | 1 992 |  |  |
| *cis*-$[\mathrm{Ru(CO)_2Br_2(AsMe_2Ph)_2}]$ | 2 052 | 2.02 (s) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  | 1 998 |  |  |
| *trans*-$[\mathrm{Ru(CO)_2Cl_2(AsMe_2Ph)_2}]$ | 2 012 | 1.84 (s) | $\mathrm{As}Me_2\mathrm{Ph}$ |
| *trans*-$[\mathrm{Ru(CO)_2Br_2(AsMe_2Ph)_2}]$ | 2 006 | 1.95 (s) | $\mathrm{As}Me_2\mathrm{Ph}$ |
| *trans*-$[\mathrm{Ru(CO)_2I_2(AsMe_2Ph)_2}]$ | 1 998 | 2.10 (s) | $\mathrm{As}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)}(\eta\text{-}\mathrm{C_2H_4})\mathrm{Cl_2(PMe_2Ph)_2}]$ | 1 963 | 2.27 (t, 4) | $\mathrm{C_2H_4}$ |
|  |  | 2.14 (t, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 2.13 (t, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)}(\eta\text{-}\mathrm{C_2H_4})\mathrm{Cl_2(AsMe_2Ph)_2}]$ | 1 968 | 2.46 (s, 4) | $\mathrm{C_2H_4}$ |
|  |  | 2.00 (s, 12) [c] | $\mathrm{As}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)}(\eta\text{-}\mathrm{C_2H_4})\mathrm{Br_2(AsMe_2Ph)_2}]$ | 1 973 | 2.52 (s, 4) | $\mathrm{C_2H_4}$ |
|  |  | 2.15 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 2.10 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3]Cl}$ | 1 924 | 2.20 (br, 2) | $\mathrm{CH_2C}H_2\mathrm{PMe_2Ph}$ |
|  |  | 1.97 (d, 6) | $\mathrm{CH_2CH_2P}Me_2\mathrm{Ph}$ |
|  |  | 1.50 (t, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.49 (t, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.42 (d, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 0.64 (br, 2) | $\mathrm{C}H_2\mathrm{CH_2PMe_2Ph}$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3][ClO_4]}$ | 1 920 | 2.05 (br, 2) | $\mathrm{CH_2C}H_2\mathrm{PMe_2Ph}$ |
|  |  | 1.87 (d, 6) | $\mathrm{CH_2CH_2P}Me_2\mathrm{Ph}$ |
|  |  | 1.42 (c, 18) [d] | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 0.60 (br, 2) | $\mathrm{C}H_2\mathrm{CH_2PMe_2Ph}$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Cl(AsMe_2Ph)_2(PMe_2Ph)]Cl}$ | 1 917 | 2.20 (br, 2) | $\mathrm{CH_2C}H_2\mathrm{PMe_2Ph}$ |
|  |  | 1.90 (d, 6) | $\mathrm{CH_2CH_2P}Me_2\mathrm{Ph}$ |
|  |  | 1.50 (d, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.39 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 1.35 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 0.80 (br, 2) | $\mathrm{C}H_2\mathrm{CH_2PMe_2Ph}$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Cl(AsMe_2Ph)_2(PMe_2Ph)][ClO_4]}$ | 1 920 | 2.10 (br, 2) | $\mathrm{CH_2C}H_2\mathrm{PMe_2Ph}$ |
|  |  | 1.66 (d, 6) | $\mathrm{CH_2CH_2P}Me_2\mathrm{Ph}$ |
|  |  | 1.53 (d, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.37 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 1.33 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 0.80 (br, 2) | $\mathrm{C}H_2\mathrm{CH_2PMe_2Ph}$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Br(AsMe_2Ph)_2(PMe_2Ph)]Br}$ [e] | 1 920 | 2.32 (br, 2) | $\mathrm{CH_2C}H_2\mathrm{PMe_2Ph}$ |
|  |  | 1.81 (d, 6) | $\mathrm{CH_2CH_2P}Me_2\mathrm{Ph}$ |
|  |  | 1.60 (d, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.40 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 1.35 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 0.83 (br, 2) | $\mathrm{C}H_2\mathrm{CH_2PMe_2Ph}$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Br(AsMe_2Ph)_2(PMe_2Ph)][ClO_4]}$ | 1 919 | 2.00 (br, 2) | $\mathrm{CH_2C}H_2\mathrm{PMe_2Ph}$ |
|  |  | 1.60 (d, 6) | $\mathrm{CH_2CH_2P}Me_2\mathrm{Ph}$ |
|  |  | 1.58 (d, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.40 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 1.35 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
|  |  | 0.92 (br, 2) | $\mathrm{C}H_2\mathrm{CH_2PMe_2Ph}$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMePh_2)Cl(PMe_2Ph)_2(PMePh_2)]Cl}$ [f] |  | 2.20 (d, 3) | $\mathrm{CH_2CH_2P}Me\mathrm{Ph_2}$ |
|  |  | 1.95 (d, 3) | $\mathrm{P}Me\mathrm{Ph_2}$ |
|  |  | 1.26 (t, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.20 (t, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 0.67 (br, 2) | $\mathrm{C}H_2\mathrm{CH_2PMePh_2}$ |
| $[\mathrm{Ru(CO)Cl(PMe_2Ph)_3][ClO_4]}$ | 1 969 | 1.75 (br, 12) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.45 (d, 6) | $\mathrm{P}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)Cl(PMe_2Ph)_4][ClO_4]}$ | 1 954 | 1.65 (br) | $\mathrm{P}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)Cl_2(AsMe_2Ph)(PMe_2Ph)_2}]$ [g] | 1 974 | 1.73 (t, 12) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.06 (s, 6) | $\mathrm{As}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)Cl_2(NH_2CH_2Ph)(PMe_2Ph)_2}]$ [g] | 1 950 | 6.04 (br, 2) | $\mathrm{N}H_2\mathrm{CH_2Ph}$ |
|  |  | 2.84 (br, 2) | $\mathrm{NH_2C}H_2\mathrm{Ph}$ |
|  |  | 2.02 (t, 12) | $\mathrm{P}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)Cl_2(4\text{-}MeC_5H_4N)(PMe_2Ph)_2}]$ [g] | 1 966 | 2.18 (s, 3) | $4\text{-}Me\mathrm{C_5H_4N}$ |
|  |  | 1.75 (t, 12) | $\mathrm{P}Me_2\mathrm{Ph}$ |
| $[\mathrm{Ru(CO)Cl_2(PMe_2Ph)_2(SMe_2)}]$ [f,g] |  | 1.86 (t, 12) | $\mathrm{P}Me_2\mathrm{Ph}$ |
|  |  | 1.50 (s, 6) | $\mathrm{S}Me_2$ |

[a] In $\mathrm{CHCl_3}$ solution. Only bands in the C–O stretching region are listed. [b] In $\mathrm{CDCl_3}$ solution. Resonances due to aromatic protons are not included. Multiplicities and relative areas of resonances are given in parentheses after the chemical-shift values: s = singlet, d = doublet, t = triplet, br = broad, c = complex multiplet. [c] Accidental superimposition of two resonances. [d] Three largely superimposed resonances. [e] Spectrum recorded at 279 K. [f] Not isolated. [g] Isomer (II).

TABLE 2

Carbon-13 n.m.r. spectra of selected complexes [a]

| Complex | δ/p.p.m. | Assignment | Coupling constant/Hz | Assignment |
|---|---|---|---|---|
| $[\mathrm{Ru(CO)}(\eta\text{-}\mathrm{C_2H_4})\mathrm{Cl_2(PMe_2Ph)_2}]$ | 194.0 (t) | CO | 12.0 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | 58.6 (s) | $\mathrm{C_2H_4}$ | | |
| | 13.6 (t) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 35.0 | $\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$ |
| | 11.6 (t) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 35.0 | $\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$ |
| $[\mathrm{Ru(CO)}(\eta\text{-}\mathrm{C_2H_4})\mathrm{Cl_2(AsMe_2Ph)_2}]$ | 193.4 (s) | CO | | |
| | 55.2 (s) | $\mathrm{C_2H_4}$ | | |
| | 9.4 (s) | $\mathrm{As}\mathit{Me}_2\mathrm{Ph}$ | | |
| | 7.9 (s) | $\mathrm{As}\mathit{Me}_2\mathrm{Ph}$ | | |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3}][\mathrm{ClO_4}]$ | 202.8 (dt) | CO | 10.0 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | | | 15.0 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | 28.4 (d) | $\mathrm{CH_2}\mathit{C}\mathrm{H_2PMe_2Ph}$ | 33.7 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | 17.1 (d) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 22.5 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | 14.7 (t) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 29.0 | $\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$ |
| | 14.5 (t) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 29.0 | $\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$ |
| | 6.2 (d) | $\mathrm{CH_2CH_2P}\mathit{Me}_2\mathrm{Ph}$ | 54.2 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | −0.2 (ddt) | $\mathit{C}\mathrm{H_2CH_2PMe_2Ph}$ | 69.0 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | | | 16.6 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | | | 7.3 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Cl(AsMe_2Ph)_2(PMe_2Ph)}][\mathrm{ClO_4}]$ | 201.5 (dd) | CO | 9.8 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | | | 2.0 | $\lvert {}^4J(\mathrm{P{-}C}) \rvert$ |
| | 29.5 (d) | $\mathrm{CH_2}\mathit{C}\mathrm{H_2PMe_2Ph}$ | 32.2 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | 17.5 (d) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 23.4 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | 10.0 (s) [b] | $\mathrm{As}\mathit{Me}_2\mathrm{Ph}$ | | |
| | 6.0 (d) | $\mathrm{CH_2CH_2P}\mathit{Me}_2\mathrm{Ph}$ | 54.7 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | −2.3 (dd) | $\mathit{C}\mathrm{H_2CH_2PMe_2Ph}$ | 68.9 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | | | 16.1 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Br(AsMe_2Ph)_2(PMe_2Ph)}]$-$[\mathrm{ClO_4}]$ [c] | 201.1 (dd) | CO | 10.2 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | | | 2.4 | $\lvert {}^4J(\mathrm{P{-}C}) \rvert$ |
| | 30.7( d) | $\mathrm{CH_2}\mathit{C}\mathrm{H_2PMe_2Ph}$ | 32.2 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | 18.5 (d) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 23.4 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | 10.9 (s) | $\mathrm{As}\mathit{Me}_2\mathrm{Ph}$ | | |
| | 10.4 (s) | $\mathrm{As}\mathit{Me}_2\mathrm{Ph}$ | | |
| | 5.6 (d) | $\mathrm{CH_2CH_2P}\mathit{Me}_2\mathrm{Ph}$ | 54.7 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | −3.6 (dd) | $\mathit{C}\mathrm{H_2CH_2PMe_2Ph}$ | 68.0 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | | | 16.0 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| $[\mathrm{Ru(CO)Cl(PMe_2Ph)_3}][\mathrm{ClO_4}]$ | 199.9 (dt) | CO | 16.0 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | | | 12.8 | $\lvert {}^2J(\mathrm{P{-}C}) \rvert$ |
| | 17.9 (d) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 37.1 | $\lvert {}^1J(\mathrm{P{-}C}) \rvert$ |
| | 14.8 (t) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 31.2 | $\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$ |
| | 12.3 (t) | $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$ | 33.0 | $\lvert {}^1J(\mathrm{P{-}C}) + {}^3J(\mathrm{P{-}C}) \rvert$ |

[a] Spectra were recorded on $\mathrm{CDCl_3}$ solutions of the complexes. Resonances due to phenyl carbon atoms are not included. Multiplicities are given in parentheses after the chemical-shift values. [b] Accidental superimposition of two resonances. [c] Spectrum recorded at 273 K.

$\mathrm{(PMe_2Ph)_2}]$ of structure (III) in the kinetically favoured position *trans* to CO. We felt, however, that this result did not rule out the possibility that at lower temperatures, where dissociation of the ethene ligand would be a much slower process, we might observe nucleophilic attack on the ethene instead.

The reaction between equimolar quantities of $[\mathrm{Ru(CO)}(\eta\text{-}\mathrm{C_2H_4})\mathrm{Cl_2(PMe_2Ph)_2}]$ and $\mathrm{PMe_2Ph}$ was therefore repeated, in $\mathrm{CDCl_3}$ solution, at 287 K. Although the substitution reaction observed at 308 K still occurred, with liberation of ethene and formation of $[\mathrm{Ru(CO)Cl_2(PMe_2Ph)_3}]$, it was clear that some other product was also being formed. In addition, we found that when all the added $\mathrm{PMe_2Ph}$ had been consumed some of the original ethene complex still remained, suggesting that formation of the alternative product required more than one molecule of $\mathrm{PMe_2Ph}$. Accordingly, we repeated the reaction, again in $\mathrm{CDCl_3}$ solution, at 279 K and using a 2 : 1 molar ratio of $\mathrm{PMe_2Ph}$ to ethene complex. This time no ethene was liberated and no $[\mathrm{Ru(CO)Cl_2(PMe_2Ph)_3}]$ was formed, and both $\mathrm{PMe_2Ph}$ and the ethene complex were completely consumed in the formation of the alternative product. By changing the solvent to either propanone or chlorobenzene, we were able to isolate this product as a white solid (showing by redissolving it in $\mathrm{CDCl_3}$ and recording its $^1$H n.m.r. spectrum that it was the same product as that formed in $\mathrm{CDCl_3}$). Elemental analysis gave results compatible with the empirical formula $\mathrm{Ru(CO)(C_2H_4)Cl_2(PMe_2Ph)_4}$, and we tentatively assigned the structure $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3}]\mathrm{Cl}$ to the complex, implying that, of the two molecules of $\mathrm{PMe_2Ph}$ required for the reaction, one had attacked the ethene and the other had displaced a chloride ligand. Evidence for the ionic nature of the product was provided by its ready reaction with $\mathrm{Na[ClO_4]}$ in propanone solution to yield $[\mathrm{Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3}][\mathrm{ClO_4}]$. The perchlorate salt was also obtained in high yield simply by carrying out the original reaction in the presence of $\mathrm{Na[ClO_4]}$.

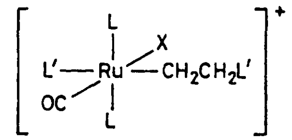
The complexes $[\mathrm{Ru(CO)}(\eta\text{-}\mathrm{C_2H_4})\mathrm{X_2(AsMe_2Ph)_2}]$ (X = Cl or Br) also reacted with $\mathrm{PMe_2Ph}$ in propanone at 279 K, giving products for which analytical evidence suggested the formulae $[Ru(CO)(CH_2CH_2PMe_2Ph)X(AsMe_2Ph)_2(PMe_2Ph)]X$. Again the corresponding perchlorate salts could be obtained (and in better yields than those for the halide salts) by including $Na[ClO_4]$ in the reaction mixtures.

Once isolated, almost all the complexes were sufficiently long-lived in $CDCl_3$ solution at ambient temperature for n.m.r. spectra to be obtained. The more easily isolated perchlorate salts were used in preference to the halide salts for $^{13}C$ n.m.r. spectroscopy.

The $^1H$ n.m.r. spectrum of the complex thought to be $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3]Cl$ contained in the region characteristic of methyl protons in coordinated $PMe_2Ph$ the standard pattern [6] of two triplets and a doublet which is characteristic of a *mer* arrangement of three $PMe_2Ph$ ligands where the Ru–P bonds to the mutually *trans* pair of ligands do not lie in a plane of symmetry. A more unusual feature was the wide doublet $[^2J(P-H) = 13.5$ Hz$]$ centred at $\delta$ 1.97. This large coupling constant is typical for protons in a methyl group attached to a phosphorus atom bearing a positive charge: we found, for example, that a spectrum of $[PMe_2EtPh]Br$ recorded under identical conditions included a doublet resonance with $^2J(P-H) = 15.0$ Hz for the methyl protons. This was useful evidence that nucleophilic attack on the ethene had occurred, with the formation of the ligand $-CH_2CH_2PMe_2Ph^+$. Unfortunately the resonances for the two pairs of methylene protons appeared as featureless humps centred at $\delta$ 2.20 and 0.64. Within the limits imposed by the stability of the complex in solution, variation in temperature had little effect on the appearance of these resonances, and it could simply have been that the complexity of the proton–proton and proton–phosphorus couplings made it impossible to discern the expected fine structure.

The $^1H$ n.m.r. spectrum of $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3][ClO_4]$ was very similar to that of the chloride salt, leaving no doubt that the two contained the same cation. In the $^{13}C$ spectrum, the pattern of methyl carbon resonances included the expected two triplets and one doublet for the *mer* arrangement of three $PMe_2Ph$ ligands, and a wider doublet $[^1J(P-C) = 54.2$ Hz$]$ at $\delta$ 6.2 for the methyl carbon atoms in the $-CH_2CH_2PMe_2Ph^+$ ligand. The magnitude of the coupling constants for the doublet of triplets resonance for the carbonyl carbon atom $[^2J(P-C) = 10.0$ and 15.0 Hz respectively$]$ demonstrated that the carbonyl ligand was *cis* to all three $PMe_2Ph$ ligands, since a typical value for $^2J(P-C)$ when CO and $PMe_2Ph$ are mutually *trans* in a ruthenium(II) complex is *ca.* 90 Hz.[8] There was evidence of a further small doublet splitting due to long-range coupling to the phosphorus nucleus in the $-CH_2CH_2PMe_2Ph^+$ ligand.

The only significant splitting of the resonance for the methylene carbon atom adjacent to phosphorus in the $-CH_2CH_2PMe_2Ph^+$ ligand was from the phosphorus atom to which it was directly attached $[^1J(P-C) = 33.7$ Hz$]$, whereas the methylene carbon atom attached to the metal gave a resonance (a doublet of doublets of triplets) split by all the phosphorus nuclei in the molecule. The triplet splitting $[^2J(P-C) = 7.3$ Hz$]$ was clearly due to the mutually *trans* pair of $PMe_2Ph$ ligands. The values of the coupling constants $^2J(P-C)$ for the doublet splittings were 16.6 and 69.0 Hz. Since the value of the coupling constant $^2J(P-C)$ for the β-carbon atom in the ethyl group in $[PMe_2EtPh]Br$ is only *ca.* 7 Hz, we assumed that the 16.6 Hz splitting was due to the phosphorus nucleus in the $-CH_2CH_2PMe_2Ph^+$ ligand, so the large doublet splitting was evidently caused by the remaining $PMe_2Ph$ ligand. Given the big difference between the magnitudes of the doublet and triplet splittings by the three $PMe_2Ph$ ligands, we concluded that the $-CH_2CH_2PMe_2Ph^+$ ligand was positioned *trans* to the unique $PMe_2Ph$ ligand. This fixed the structure of the cation as (IV), where $L = L' = PMe_2Ph$ and $X = Cl$.



(IV)

The $^1H$ n.m.r. spectra of the complexes $[Ru(CO)(CH_2CH_2PMe_2Ph)X(AsMe_2Ph)_2(PMe_2Ph)]Y$ $(X = Cl, Y = Cl$ or $ClO_4$; $X = Br, Y = Br$ or $ClO_4)$ were all similar. Comparison with the spectra of the complexes $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3]Y$ $(Y = Cl$ or $ClO_4)$ made it clear that the ethene had been attacked by $PMe_2Ph$, not $AsMe_2Ph$, and the observation of only two methyl proton resonances for the $AsMe_2Ph$ ligands indicated that these ligands were mutually *trans* (four resonances would have resulted for any ligand arrangement including mutually *cis* $AsMe_2Ph$ ligands). The $^{13}C$ spectra of the perchlorate salts established that the carbonyl ligand was *cis* and the $-CH_2CH_2PMe_2Ph^+$ ligand *trans* to the one $PMe_2Ph$ ligand. The small long-range doublet splitting of the carbonyl resonance by the phosphorus nucleus in the $-CH_2CH_2PMe_2Ph^+$ ligand, mentioned above for $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3][ClO_4]$, was clearly visible for each of these complexes $[^4J(P-C) = ca.$ 2 Hz$]$. We concluded that these complexes also possessed structure (IV), where $L = AsMe_2Ph$ and $L' = PMe_2Ph$.

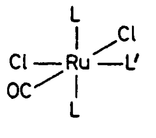
Studies by $^1H$ n.m.r. spectroscopy (see Table 1) of the reaction between $[Ru(CO)(\eta-C_2H_4)Cl_2(PMe_2Ph)_2]$ and $PMePh_2$ in $CDCl_3$ solution at 279 K, using a 1 : 2 molar ratio of the reactants, strongly suggested the formation of the cation $[Ru(CO)(CH_2CH_2PMePh_2)Cl(PMe_2Ph)_2(PMePh_2)]^+$ in the solution. The expected two triplets for the methyl protons in the mutually *trans* pair of $PMe_2Ph$ ligands were clearly visible, as were the narrow $[^2J(P-C) = 8.0$ Hz$]$ and wide $[^2J(P-C) = 14.0$ Hz$]$ doublets for the methyl protons in the $PMePh_2$ and $-CH_2CH_2PMePh_2^+$ ligands respectively, and the two broad resonances for the methylene protons in the $-CH_2CH_2PMePh_2^+$ ligand. Unfortunately all attempts to isolate either the chloride or the perchlorate salt of the cation were unsuccessful.

Even at 279 K, the product formed by reaction of $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(AsMe_2Ph)_2]$ with $PMePh_2$ in $CDCl_3$ solution was unstable, and it was only when the reaction was carried out at 253 K that its decomposition was completely suppressed. At this temperature, resonances of the type expected for $[Ru(CO)(CH_2CH_2PMePh_2)Cl(AsMe_2Ph)_2(PMePh_2)]^+$ very slowly increased in area. Unfortunately, after 7 months, a fire in the Department put an end to the experiment while the reaction was still incomplete.

*Mechanism of Formation of the Cations* $[Ru(CO)(CH_2CH_2L')XL_2L']^+$.—As a result of the experiments we had carried out with varying combinations of ligand L in the starting materials and added nucleophile L′, it seemed clear that the ligands L were not directly involved in the reaction and that it *was* the incoming nucleophile L′ which attacked the ethene and displaced the halide ion $X^-$.

We were interested to discover which of the two processes, displacement of halide ion or attack on the ethene, occurred first. Initial displacement of halide ion would involve the formation of the intermediate $[Ru(CO)(\eta\text{-}C_2H_4)XL_2L']^+$, whereas attack on the ethene would yield $[Ru(CO)(CH_2CH_2L')X_2L_2]$. We could find no evidence for the presence of either species in the reaction mixtures, and presumed at the time that this meant that the first step was rate-determining and the second much faster. In this context, both routes had their attractions: on the one hand, the positive charge on $[Ru(CO)(\eta\text{-}C_2H_4)XL_2L']^+$ would be expected to enhance the susceptibility of the ethene to nucleophilic attack; on the other, the large *trans* effect associated with alkyl ligands in ruthenium(II) complexes [9] would encourage displacement of the appropriate halide ligand from $[Ru(CO)(CH_2CH_2L')X_2L_2]$.

In an attempt to discover which was the correct pathway, we tried to synthesize one of the possible intermediates, $[Ru(CO)(\eta\text{-}C_2H_4)Cl(PMe_2Ph)_3]^+$, by an independent route so as to determine whether it reacted with $PMe_2Ph$ to form the correct product and at a sufficient rate to explain our failure to observe it in the reaction of $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ with $PMe_2Ph$. The first route tried involved removal of a chloride ligand from $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ with $Ag[ClO_4]$ and reaction of the resulting cation with $PMe_2Ph$. Unfortunately the attempt to remove a chloride ligand also resulted in loss of ethene from the complex. The second method involved removal of a chloride ligand from $[Ru(CO)Cl_2(PMe_2Ph)_3]$ [structure (V), where L = L′ = $PMe_2Ph$] [1] and reaction of the cation $[Ru(CO)Cl(PMe_2Ph)_3]^+$ with ethene. The white crystals obtained from the reaction of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ with $Ag[ClO_4]$ persistently gave analysis figures for carbon which were a little low for $[Ru(CO)Cl(PMe_2Ph)_3][ClO_4]$, but their i.r., $^1H$, and $^{13}C$ n.m.r. spectra were as expected for such a complex, and they rapidly reacted with $PMe_2Ph$ to yield *trans*-$[Ru(CO)Cl(PMe_2Ph)_4][ClO_4]$, for which acceptable analysis figures *were* obtained. We treated the crystals with ethene in propanone solution at three different temperatures, 273, 288, and 317 K, but i.r. spectra of the solutions provided no evidence of any reaction. In case a reaction had occurred, $PMe_2Ph$ was added at each temperature in the hope of obtaining $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3][ClO_4]$, but the only product obtained was *trans*-$[Ru(CO)Cl(PMe_2Ph)_4][ClO_4]$.



(V)

Although this negative evidence on its own could not be regarded as conclusively ruling out a mechanism involving initial substitution of halide ion, there were other reasons for favouring the alternative of initial attack on the ethene ligand. As mentioned above, there was a complete change-over from substitution of the ethene ligand to formation of $[Ru(CO)(CH_2CH_2L')ClL_2L']^+$ as the temperature was lowered. We have found that substitution (and isomerization) reactions in ruthenium(II) complexes have a dissociative first step.[1,10] If the first step of the low-temperature reaction to form $[Ru(CO)(CH_2CH_2L')ClL_2L']^+$ involved attack on the ethene ligand, it would be expected to have a very much more negative entropy of activation than that of a dissociative substitution reaction, and probably also a smaller enthalpy of activation. These factors would readily explain the change in reaction pathway with temperature. A change-over from high-temperature substitution of ethene to low-temperature substitution of chloride ion would be rather less easy to explain.

In addition, the crystal structure of $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ indicated that the Ru–Cl bond *trans* to CO was significantly longer than that *trans* to ethene.[2] We have found [1] that *trans*-labilizing and *trans*-directing effects run parallel with one another in ruthenium(II) complexes, and hence one would expect substitution of a halide ligand in the complexes $[Ru(CO)(\eta\text{-}C_2H_4)X_2L_2]$ to involve both loss of halide and pick-up of the nucleophile L′ *trans* to CO. This would lead to the wrong stereochemistry for the final product, $[Ru(CO)(CH_2CH_2L')ClL_2L']^+$. In contrast, as explained earlier, the assumption that attack on the ethene ligand is *followed* by substitution of halide ion leads automatically to a product of the correct stereochemistry.

*Reactions with Other Nucleophiles.*—Studies were made by $^1H$ n.m.r. spectroscopy of the reactions of $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ with the uncharged nucleophiles $AsMe_2Ph$, $NH_2CH_2Ph$, 4-methylpyridine, $P(OMe)_2Ph$, and $SMe_2$ in $CDCl_3$ solution. Since it was expected that attack on the ethene and substitution of the ethene would again compete with one another, the reactions were started at 268 K. After 1 week, there was no evidence in any instance of attack on the ethene, and the temperature was raised to 273 K. After a similar period the temperature was again raised, and so on until reaction was complete. With the successive increases in temperature, substitution of the ethene ligand occurred at an increasing rate, apparently without any competition from nucleophilic attack on the ethene. The substitution products from the reactions with L′ = $AsMe_2Ph$, $NH_2CH_2Ph$, and 4-methylpyridine were shown by elemental analysis and spectroscopic evidence to be complexes $[Ru(CO)Cl_2L'(PMe_2Ph)_2]$ of structure (II), where L = $PMe_2Ph$. Studies by $^1H$ n.m.r. spectroscopy showed that they, like other complexes of this general formula and structure,[10] isomerized at higher temperatures to structure (V), where L = $PMe_2Ph$, but we did not attempt isolation of these final products. The reaction with $P(OMe)_2Ph$ was complicated by a side reaction (probably of the Arbusov type [11]) between $P(OMe)_2Ph$ and the solvent $CDCl_3$, and was repeated in chlorobenzene. The product isolated from the latter solvent was the previously characterized [1] isomer (II) of $[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_2Ph\}]$, and its $^1H$ n.m.r. spectrum in $CDCl_3$ solution tallied with that of the ruthenium-containing product formed in $CDCl_3$ solution. Again isomerization to structure (V) occurred at higher temperatures.

In the case of the reaction with $SMe_2$, formation of a species believed on the basis of n.m.r. evidence to be isomer (II) of $[Ru(CO)Cl_2(PMe_2Ph)_2(SMe_2)]$ was first noticed at 273 K, at which temperature it was extremely slow. In order to speed the reaction up, we raised the temperature to 278 K, but even at this low temperature, rearrangement to the more stable and previously characterized isomer (V) of the complex occurred, and this was the isomer actually isolated. In their study of the isomerization of complexes $[Ru(CO)Cl_2L'(PMe_2Ph)_2]$ from structure (II) to (V), Barnard *et al.*[10] proposed a mechanism involving dissociation of the ligand L′, and the very ready rearrangement of isomer (II) of $[Ru(CO)Cl_2(PMe_2Ph)_2(SMe_2)]$ must reflect the weakness of the $Ru{-}SMe_2$ bond.

Of other nucleophiles studied, $NMe_2Ph$ and methoxide ion gave no evidence of attack either on the metal or on the alkene. Reactions of some kind did occur with hydride ion and with cyanide ion, but we were unable to isolate products from the reaction mixtures.

*Conclusions.*—It is interesting to speculate why only two of the various nucleophiles tried provided clear evidence of attack on the co-ordinated ethene. Since there are other known instances of readily reversible addition of phosphorus nucleophiles to organic ligands,[12] it may be that the reaction (1) is an equilibrium process,

$$[Ru(CO)(\eta\text{-}C_2H_4)X_2L_2] + L' \rightleftharpoons [Ru(CO)(CH_2CH_2L')X_2L_2] \qquad (1)$$

with the equilibrium position in all cases well to the left, and that the ability of the same nucleophile L′ then to displace halide ion and generate the relatively stable final product $[Ru(CO)(CH_2CH_2L')XL_2L']^+$ is crucial. Thus the successful nucleophile must be able to attack both organic ligand and metal. Such a kinetic scheme would also be compatible with our failure to observe the intermediates $[Ru(CO)(CH_2CH_2L')X_2L_2]$ in any of the reactions. There has been a recent report [13] in the literature of another system where a nucleophile fulfils this dual role, the reaction being that between pyridine (py) and $[Pt(\eta\text{-}C_2H_4)Cl_2(py)]$ to yield $[Pt(CH_2CH_2py)Cl(py)_2]^+$.

The switch from attack at the metal to attack on the ethene with lowering of the temperature is in accord with the findings of other authors. A fairly general claim has been made that, in cases where there is more than one possible site for attack, phosphorus nucleophiles have a *kinetic* preference for attack on η-hydrocarbon ligands.[14,15] An elegant recent example of this as applied specifically to an ethene complex is provided by the work of Cooper and Green [16] on the cation $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)Me]^+$.

## EXPERIMENTAL

*Preparation of Complexes.*—All preparative work was carried out under an atmosphere of dry nitrogen. Except where otherwise stated, the boiling range of the light petroleum used was 313—333 K. Analytical data for all new complexes are given in Table 3. Details of the preparation of $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ have been given elsewhere.[1,2]

$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$. The *cis* isomer of this complex was prepared from $RuCl_3{\cdot}3H_2O$ (2.00 g) and $AsMe_2Ph$ (2.80 g) (yield 70%) and then converted into the *trans* isomer (yield 60%) using the same techniques as those described [1,6] for $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$.

$[Ru(CO)_2Br_2(AsMe_2Ph)_2]$. The *cis* isomer was prepared from the same reactants as its chloro-analogue with the addition of NaBr (5.00 g) prior to carbonylation. After the reaction the solution was filtered and the filtrate evaporated to dryness under reduced pressure. The product was obtained as an oil by extraction with $CHCl_3$ and removal of the $CHCl_3$ under reduced pressure, and then crystallized from propanone (yield 88%). Conversion into the *trans* isomer (yield 60%) was carried out as described for $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$.[1]

$[Ru(CO)_2I_2(AsMe_2Ph)_2]$. The *trans* isomer was obtained directly by u.v. irradiation [1] of a propanone (10 $cm^3$) solution of *cis*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$ (0.50 g) and NaI (1.25 g). After 48 h the solvent was removed under reduced pressure and the product obtained by extraction with $CHCl_3$ and crystallization from propanone (yield 43%).

$[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(AsMe_2Ph)_2]$. This complex (yield 88%) and its bromo-analogue (yield 73%) were prepared in the same way as $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$.[1,2]

$[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3]Cl$. To a solution of $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ (0.20 g) in propanone (5 $cm^3$) at 263 K was added $PMe_2Ph$ (0.11 g). After 24 h at 273 K, the product, obtained as a white powder, was filtered off, washed with light petroleum, and dried *in vacuo* (yield 70%). The same method was used to prepare $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(AsMe_2Ph)_2(PMe_2Ph)]Cl$ from $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(AsMe_2Ph)_2]$ (0.20 g) and $PMe_2Ph$ (0.09 g) (yield 71%), and $[Ru(CO)(CH_2CH_2PMe_2Ph)Br(AsMe_2Ph)_2(PMe_2Ph)]Br$ from $[Ru(CO)(\eta\text{-}C_2H_4)Br_2(AsMe_2Ph)_2]$ (0.20 g) and $PMe_2Ph$ (0.08 g) (yield 34%).

$[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3][ClO_4]$. The preparation was carried out in the same way as that of the

TABLE 3

Analytical data

| Complex | Colour | Analysis (%) | | | |
|---|---|---|---|---|---|
| | | Found | | Calc. | |
| | | C | H | C | H |
| *cis*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$ | White | 36.3 | 3.65 | 36.5 | 3.75 |
| *cis*-$[Ru(CO)_2Br_2(AsMe_2Ph)_2]$ | Cream | 31.8 | 3.35 | 31.75 | 3.25 |
| *trans*-$[Ru(CO)_2Cl_2(AsMe_2Ph)_2]$ | Yellow | 36.7 | 3.80 | 36.5 | 3.75 |
| *trans*-$[Ru(CO)_2Br_2(AsMe_2Ph)_2]$ | Orange | 31.8 | 3.20 | 31.75 | 3.25 |
| *trans*-$[Ru(CO)_2I_2(AsMe_2Ph)_2]$ | Red | 27.7 | 2.90 | 27.9 | 2.85 |
| $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(AsMe_2Ph)_2]$ | Cream | 38.45 | 4.45 | 38.55 | 4.45 |
| $[Ru(CO)(\eta\text{-}C_2H_4)Br_2(AsMe_2Ph)_2]$ | Yellow | 33.65 | 4.05 | 33.5 | 3.85 |
| $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3]Cl$ | White | 53.65 | 6.20 | 53.85 | 6.20 |
| $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(PMe_2Ph)_3][ClO_4]$ | White | 49.8 | 6.05 | 49.75 | 5.75 |
| $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(AsMe_2Ph)_2(PMe_2Ph)]Cl$ | White | 48.45 | 5.55 | 48.4 | 5.55 |
| $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(AsMe_2Ph)_2(PMe_2Ph)][ClO_4]$ | White | 45.35 | 5.40 | 45.1 | 5.20 |
| $[Ru(CO)(CH_2CH_2PMe_2Ph)Br(AsMe_2Ph)_2(PMe_2Ph)]Br$ | White | 43.85 | 5.25 | 43.9 | 5.05 |
| $[Ru(CO)(CH_2CH_2PMe_2Ph)Br(AsMe_2Ph)_2(PMe_2Ph)][ClO_4]$ | White | 43.05 | 5.15 | 43.05 | 4.95 |
| $[Ru(CO)Cl(PMe_2Ph)_3][ClO_4]$ | White | 43.3 | 5.15 | 44.25 | 4.90 |
| $[Ru(CO)Cl(PMe_2Ph)_4][ClO_4]$ | White | 48.55 | 5.60 | 48.55 | 5.45 |
| $[Ru(CO)Cl_2(AsMe_2Ph)(PMe_2Ph)_2]$ | Yellow | 45.4 | 4.95 | 45.6 | 5.05 |
| $[Ru(CO)Cl_2(NH_2CH_2Ph)(PMe_2Ph)_2]$ [a] | Yellow | 49.5 | 5.30 | 49.4 | 5.35 |
| $[Ru(CO)Cl_2(4\text{-}MeC_5H_4N)(PMe_2Ph)_2]$ [b] | Yellow | 48.5 | 5.10 | 48.5 | 5.15 |

[a] Found: N, 2.30. Required: N, 2.40%. [b] Found: N, 2.40. Required: N, 2.45%.

chloride salt except that $Na[ClO_4]\cdot H_2O$ (0.06 g) was added at the start of the reaction. After 24 h the precipitate of NaCl was filtered off and light petroleum was added to the filtrate until the first signs of cloudiness appeared. Slow evaporation of the solution under a stream of nitrogen yielded white crystals. These were filtered off and washed with light petroleum (yield 92%). The same technique was used to obtain $[Ru(CO)(CH_2CH_2PMe_2Ph)Cl(AsMe_2Ph)_2(PMe_2Ph)][ClO_4]$ (yield 90%) and $[Ru(CO)(CH_2CH_2PMe_2Ph)Br(AsMe_2Ph)_2(PMe_2Ph)][ClO_4]$ (yield 45%), using the quantities listed for the halide salts with the addition of $Na[ClO_4]\cdot H_2O$ (0.05 g and 0.04 g respectively).

$[Ru(CO)Cl(PMe_2Ph)_3][ClO_4]$. A propanone (30 $cm^3$) solution of isomer (V) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ [1] (0.20 g) and $Ag[ClO_4]$ (0.07 g) was stirred, in the dark, for 2 h. The precipitate of AgCl was filtered off and the solvent removed from the filtrate under reduced pressure. The residual oil was crystallized from a mixture of benzene and light petroleum (b.p. 353—373 K) (yield 64%).

$[Ru(CO)Cl(PMe_2Ph)_4][ClO_4]$. A solution of $[Ru(CO)Cl(PMe_2Ph)_3][ClO_4]$ (0.20 g) in the minimum volume of propanone was stirred with $PMe_2Ph$ (0.04 g) for 0.1 h. The solution was then dripped into ethoxyethane (30 $cm^3$). The product, obtained as a white solid, was filtered off, washed with light petroleum, and dried *in vacuo* (yield 82%).

*Reactions of* $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ *with Other Nucleophiles* L′.—In each case where a product was obtained, the procedure used involved treating a $CDCl_3$ (0.5 $cm^3$) solution [except for L′ = $P(OMe)_2Ph$, where PhCl was used as solvent] of $[Ru(CO)(\eta\text{-}C_2H_4)Cl_2(PMe_2Ph)_2]$ (0.06 g) in an n.m.r. tube at 268 K with enough nucleophile [$AsMe_2Ph$, $NH_2CH_2Ph$, $4\text{-}MeC_5H_4N$, $P(OMe)_2Ph$, or $SMe_2$] to give a 2 : 1 molar ratio of nucleophile to complex. In each case the solution was allowed to stand for 1 week at 268 K, 1 week at 273 K, and 1 week at 278 K. The solvent was then removed under reduced pressure, and the oily residue was crystallized from ethanol. The product was washed with light petroleum and dried *in vacuo* (yields 50—70%). The products were complexes $[Ru(CO)Cl_2L'(PMe_2Ph)_2]$ of structure (II), except for L′ = $SMe_2$, where the structure was (V).

Details of the instrumentation used have been given elsewhere.[8] Except where otherwise specified, spectra were recorded at the ambient temperatures of the instruments.

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