Preparation of Hydridotetrakis(triphenylphosphine)ruthenium(II) Hexafluorophosphate and Related Complexes

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The reaction of $[RuH_2(PPh_3)_4]$ with trityl hexafluorophosphate leads to $[RuH(PPh_3)_4]^+PF_6^-$ by abstraction of a hydride ligand as H^-. This salt reacts with other phosphines and with nitriles to give salts of six-co-ordinate cations, and dissociates on standing to give $[RuH(PPh_3)_3]^+PF_6^-$, for which a structure containing a phosphine ligand co-ordinated to ruthenium *via* a π-bonded interaction is proposed.

CATIONIC transition metal species containing phosphorus ligands have recently been prepared by the general method of abstraction of a halide ligand X as X^- using sodium or silver salts of non-co-ordinating anions.[1-6] Many transition metal hydride complexes containing phosphorus ligands are now more readily available than the corresponding halides using techniques such as the treatment of metal salts with an excess of phosphorus

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[1] G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 2146.

[2] D. A. Couch and S. D. Robinson, *Chem. Comm.*, 1971, 1508.

[3] J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

[4] J. R. Sanders, *J. Chem. Soc.* (*A*), 1971, 2991.

[5] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 3089.

[6] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1685.

ligand and sodium borohydride.[7] This paper deals with the conversion of some Group VIII metal hydride complexes to cationic species by abstraction of a hydride ligand as H^- using the triphenylmethyl (trityl) cation.

This reagent has been used to prepare cationic organometallic species by abstraction of H^- from a hydrocarbon ligand [8] or by displacement of an acetylacetonate ligand.[9,10] There is a report of its reactions with some iridium and platinum hydrides in which no organometallic products were characterized,[11] and its reaction with the complex $[FeH_2(HPPh_2)_4]$ has been briefly mentioned; [12] a preliminary account of the present work has also appeared.[13] Boron trifluoride has also been used in one case to abstract a hydride ion as H^-.[14]

In the following account reference will only be made to hexafluorophosphate salts; the corresponding tetrafluoroborates have been made in some cases and are listed in the Table.

Analytical and spectroscopic data

Compound	% Found (required) C	H	P	M.p./°C	$\Lambda_{\cdot 001}$ [a]	ν(Ru-H) [b]	$\tau_{Ru\text{-}H}$ [c]	J_{PH}/Hz
$[Ph_3PCPh_3]^+PF_6^-$	68·4 (68·3)	4·6 (4·6)		215—219	140			
$[Ph_3PCPh_3]^+BF_4^-$	75·5 (75·0)	5·3 (5·1)		196—197	53			
$[(MeC_6H_4)_3PCPh_3]^+BF_4^-$	76·5 (75·8)	6·1 (5·7)		192—195	75			
$[(EtO)_3PCPh_3]^+PF_6^-$	54·0 (54·2)	5·4 (5·4)		178—180	141			
$[HPh_2PCPh_3]^+PF_6^-$	65·3 (64·9)	4·5 (4·6)		200—205	136			
$[(EtO)_2PhPCPh_3]^+PF_6^-$	59·0 (59·4)	5·1 (5·1)		140—144	141			
$[EtPh_2PCPh_3]^+PF_6^-$	65·1 (65·7)	5·0 (5·0)		162—165	139			
$[Bu_3PCPh_3]^+PF_6^-$	63·3 (63·0)	7·2 (7·1)		211—214	131			
$[Ph_2PCH_2CH_2(Ph)_2PCPh_3]^+PF_6^-$	68·9 (68·8)	5·0 (5·0)		74—76	124			
$[RuH(PPh_3)_4]^+PF_6^-$	66·2 (66·7)	4·8 (4·7)	12·2 (12·0)	136—138	138	2020	18·02	20
$[RuH\{P(OEt)_2Ph\}_5]^+PF_6^-$	49·0 (48·5)	6·0 (6·1)	15·5 (15·0)	227—229	123	1900	18·90	19 [d] : 85 [e]
$[RuH\{P(OMe)_2Ph\}_5]^+PF_6^-$	43·5 (43·7)	5·0 (5·1)		221—224	122	1908	18·85	19 [d] : 88 [e]
$[RuH(HPPh_2)_5]^+BF_4^-$	64·9 (64·3)	4·9 (5·0)		251—255	116	1972	17·95	19 [d] : 73 [e]
$[RuH(MeCN)_2(PPh_3)_3]^+PF_6^-$	61·9 (62·4)	4·9 (4·7)	11·1 (11·1)	195—200	121 : 61 [g]	1964	23·70	19 [h]
$[RuH(MeCN)_2(PPh_3)_3]^+BF_4^-$	65·3 (65·8)	5·6 (4·9)	10·0 (8·8)	207—209	112 : 64 [g]	1960	23·64	19 [i]
$[RuH(Pr^nCN)_2(PPh_3)_3]^+PF_6^-$	63·1 (63·5)	5·1 (5·1)		205—207	123	1964	23·74	21
$[RuH(Pr^iCN)_2(PPh_3)_3]^+PF_6^-$	64·0 (63·5)	5·1 (5·1)		205—208	122	1968	23·62	21
$[RuH(PhCN)_2(PPh_3)_3]^+PF_6^-$	65·2 (65·8)	4·5 (4·5)		200—202	118	1972	22·55	21
$[RuH(MeC_6H_4CN)_2(PPh_3)_3]^+PF_6^-$	66·3 (66·3)	4·7 (4·7)		201—205	131	1968	22·66	21
$[RuH(MeOC_6H_4CN)_2(PPh_3)_3]^+PF_6^-$	64·7 (64·6)	4·6 (4·6)		205—207	131	1959	22·78	22
$[RuH(ClC_6H_4CN)_2(PPh_3)_3]^+PF_6^-$	61·9 (62·3)	4·1 (4·1)		199—201	127	1970	22·43	21
$[RuH(PPh_3)_3]^+PF_6^-$	63·2 (62·8)	4·8 (4·5)	12·3 (12·0)	200—201	116 : 59 [g]	2020	18·75	See text
$[RuH(PPh_3)_3]^+BF_4^-$	64·9 (66·5)	4·8 (4·7)		120—121	113 : 62 [g]	2020	18·75	See text

[a] In acetone at 20°. [b] In cm^{-1}, as Nujol mulls. [c] In dichloromethane. [d] H *cis* to P. [e] H *trans* to P. [f] Nitrogen analysis, 2·5 (2·6%). [g] In $MeNO_2$. [h] Two distinct singlet absorptions assigned to Me groups found at τ 8·19 and 8·89. [i] Two similar absorptions found at τ 8·15 and 8·86.

Phosphonium Salts.—During the course of this work trityl hexafluorophosphate was treated with various trivalent phosphorus compounds Z_3P (Z = H or various alkyl, alkoxy, or aryl groups) to form trityl-substituted phosphonium salts; some similar compounds formed from phosphites have been reported,[15] as have the compounds Bu_3PCPh_3Cl and Ph_3PCPh_3Cl.[16] The n.m.r. spectra of these salts indicate that they have the simple structure $[Z_3PCPh_3]^+PF_6^-$; in several of the spectra an absorption at τ 4·7 appeared to support the less sterically hindered structure $[Z_3P\text{-}C_6H_4\text{-}CHPh_2]^+PF_6^-$ but this absorption disappeared after intensive drying *in vacuo* and was probably due to CH_2Cl_2 which was tightly held by the salts. These compounds are white, air-stable solids which are reasonably soluble in halogenated solvents. $[Ph_3PCPh_3]^+PF_6^-$ did not dissociate or isomerize to another structure on prolonged heating in 1,2-dichloroethane but on standing in presence of methanol it was cleaved to triphenylphosphine and methyl trityl ether. As in some cases these salts undergo the same reactions as do trityl salts with metal hydrides, they may be used instead of the trityl salts for greater experimental convenience.

Attempts to Prepare Iron Complexes.—The compounds $[FeH_2(Ph_2PCH_2CH_2PPh_2)_2]$,[17] $[FeH_2\{P(OEt)_2Ph\}_4]$,[18] and $[FeH_2N_2(PEtPh_2)_3]$ [17] were treated with trityl hexafluorophosphate or with the phosphonium salt made from the same phosphine that was present as a ligand. This was done to try to extend the scope of the reaction of $[FeH_2(HPPh_2)_4]$ with $[HPh_2PCPh_3]^+PF_6^-$ which gives $[FeH(HPPh_2)_5]^+PF_6^-$; [13] however, no iron-containing cationic species could be characterized from any of these reactions.

Ruthenium–Triphenylphosphine Complexes.—$[RuH_2(PPh_3)_4]$[7] reacts with a stoicheiometric quantity of $[Ph_3C]^+PF_6^-$ or $[Ph_3PCPh_3]^+PF_6^-$ to give $[RuH(PPh_3)_4]^+PF_6^-$, a red solid which is moderately air-stable and soluble in halogenated solvents, in which it slowly dis-

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[7] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 2947.

[8] For a review see E. W. Abel and S. P. Tyfield, *Adv. Organometallic Chem.*, 1970, **8**, 126.

[9] M. Green, T. A. Kuc, and S. H. Taylor, *J. Chem. Soc.* (*A*), 1971, 2334.

[10] B. F. G. Johnson, J. Lewis, and D. A. White, *J. Chem. Soc.* (*A*), 1971, 2699.

[11] N. C. Deno, N. Friedman, J. D. Hodge, F. P. MacKay, and G. Saines, *J. Amer. Chem. Soc.*, 1962, **84**, 4713.

[12] J. R. Sanders, *J.C.S. Dalton*, 1972, 1333.

[13] J. R. Sanders, Abstracts, Annual Meeting of the Chemical Society, Manchester, 1972, 4.10b.

[14] E. O. Fischer and K. Ulm, *Z. Naturforsch.*, 1961, **16b**, 757.

[15] K. Dimroth and A. Nürrenbach, *Chem. Ber.*, 1960, **93**, 1649.

[16] F.P. 1,535,554; *Chem. Abs.*, 1970, **72**, 55650d.

[17] M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 1971, **5**, 115, 203.

[18] D. Titus, A. A. Orio, and H. B. Gray, *Inorg. Synth.*, 1972, **13**, 117.

sociates. Its i.r. spectrum shows bands due to ν(M–H) and ν(P–F) as well as those due to triphenylphosphine ligands and its n.m.r. spectrum, measured in CH_2Cl_2 with an excess of triphenylphosphine added to suppress dissociation, shows an absorption due to the hydrogen on ruthenium consisting of five sharp lines in a 1 : 4 : 6 : 4 : 1 quintet at room temperature. As the solution is cooled to —40° (where precipitation occurs) the lines become broader. This suggests that the $[RuH(PPh_3)_4]^+$ cation is a nearly tetrahedral species in which the hydrogen on ruthenium traverses between tetrahedral faces quickly enough to make all the phosphorus atoms equivalent on the n.m.r. time scale at room temperature. This behaviour has been postulated for several MHP_4 species [19] (M = various Group VIII metals; P = various phosphorus ligands), and *X*-ray studies on some of these have shown them to have nearly tetrahedral structures.

The formation of the ' unsaturated ' 16-electron cation $[RuH(PPh_3)_4]^+$ rather than an 18-electron cation $[RuH(PPh_3)_5]^+$ in this reaction is probably due to the large size of the triphenylphosphine molecule which stops more than four of them acting as ligands on the same metal atom.

$[RuH(PPh_3)_4]^+PF_6^-$ reacts with sodium borohydride or sodium ethoxide at 20° to regenerate $[RuH_2(PPh_3)_4]$. It reacts with formaldehyde and with hydrogen chloride at 20° to give $[RuH_2(CO)(PPh_3)_3]$ [20] and $[RuCl_2(PPh_3)_3]$ [21] respectively, and with lithium chloride and with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide at 80° to give $[RuHCl(PPh_3)_3]$ [20] and $[Ru(NO)_2(PPh_3)_2]$.[7] These products are obtained in high yields and pure, but may be made by shorter routes starting from ruthenium trichloride.

When $[RuH(PPh_3)_4]^+PF_6^-$ is treated with the relatively small phosphines $P(OEt)_2Ph$, $P(OMe)_2Ph$, and $HPPh_2$, all the PPh_3 ligands are replaced and an extra ligand is added, giving salts of the six-co-ordinate cations $[RuH\{P(OEt)_2Ph\}_5]^+$, $[RuH\{P(OMe)_2Ph\}_5]^+$, and $[RuH(HPPh_2)_5]^+$.[4] These can also be made from $[RuHCl(PPh_3)_3]$ by treatment with the appropriate phosphine and KPF_6. They show double quintets in the hydride region of their n.m.r. spectra, as expected. The similarity of the stoicheiometries of the three salts is also to be expected in view of the similar steric requirements of $P(OEt)_2Ph$, $P(OMe)_2Ph$, and $HPPh_2$ which are much less than those of PPh_3.

$[RuH(PPh_3)_4]^+PF_6^-$ reacts with acetonitrile to give $[RuH(MeCN)_2(PPh_3)_3]^+PF_6^-$ whose n.m.r. spectrum shows a 1 : 3 : 3 : 1 quartet absorption assigned to the hydrogen on ruthenium and two distinct absorptions of the right intensity relative to those of phenyl hydrogens which may be assigned to the hydrogens of the methyl groups of the two nitrile ligands. On this basis the cation may be assigned an octahedral structure with a nitrile ligand *trans* to the hydride. This compound may also be made by treatment of $[RuH_2(PPh_3)_4]$ with $[Ph_3PCPh_3]^+PF_6^-$ in presence of acetonitrile, or by the reaction of $[RuHCl(PPh_3)_3]$ with acetonitrile and KPF_6. Similar compounds may be made using other nitriles. They are light yellow air-stable compounds, soluble in halogenated solvents.

On treatment of $[RuH(PPh_3)_4]^+PF_6^-$ with dienes such as norbornadiene or cyclo-octa-1,5-diene, materials whose spectra suggested the structure $[RuH(diene)(PPh_3)_3]^+PF_6^-$ were obtained, but could not be properly characterized.

A solution of $[RuH(PPh_3)_4]^+PF_6^-$ in dichloromethane at 20° changes colour from red to green in a few hours and a light yellow compound which analyses as $[RuH(PPh_3)_3]^+PF_6^-$ may then be obtained by adding ether or methanol. The reaction is accelerated by heating in polar or non-polar solvents (methanol, ethanol, hexane, and 1,2-dichloroethane) and is retarded by addition of triphenylphosphine. The molar conductivity of the yellow complex in acetone and in nitromethane is nearly the same as that of $[RuH(MeCN)_2(PPh_3)_3]PF_6$ suggesting that it is a 1 : 1 electrolyte. Its i.r. spectrum is the same as that of $[RuH(PPh_3)_4]^+PF_6^-$ except for the addition of a medium-intensity band at 1390, a shoulder at 1450, and some changes in the 600—500 cm^{-1} region. Its n.m.r. spectrum shows the following features: (a) an absorption band at τ 2·5—3 of intensity *ca.* 40 due to aromatic protons; (b) a broadened triplet (splitting 6 Hz) at τ 4·72 of intensity *ca.* 2; (c) a sharper triplet at τ 5·72 (splitting 6 Hz) again of intensity 2; (d) a 1 : 2 : 1 triplet (splitting 39 Hz) of doublets (splitting 9 Hz) at τ 18·75 of intensity 1. This spectrum is temperature independent over the range +70 to —70°, it is independent of the solvent used to record the spectrum in and of the solvent used to make the compound, and it is the same for the analogous tetrafluoroborate salt.

The yellow compound reacts with lithium chloride, with diphenylphosphine and with acetonitrile in the same way that $[RuH(PPh_3)_4]^+PF_6^-$ does. It reacts with sodium borohydride at 20° to give $[RuH_4(PPh_3)_3]$ [22] but if it is treated overnight with a concentrated solution of sodium ethoxide in ethanol half of it may be recovered unchanged.

The hydrogen atom attached to ruthenium does not exchange with deuterium on standing in presence of MeOD for a week. The compound also does not react with triphenylphosphine to regenerate $[RuH(PPh_3)_4]^+PF_6^-$ even on prolonged heating in various solvents.

There are several reasons why this compound cannot have the simple structure $[RuH(PPh_3)_3]^+PF_6^-$. First, the observed n.m.r. spectrum in the hydride region is incompatible with this structure. A tetrahedral $RuHP_3$ system will give a 1 : 3 : 3 : 1 quartet absorption in this region and this will also occur if the cation is non-rigid so that the hydride ligand is seeing all the phosphorus

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[19] P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 1797, and references therein.

[20] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3143.

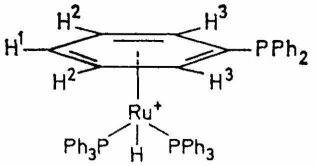
[21] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1945.

[22] W. H. Knoth, *J. Amer. Chem. Soc.*, 1972, **94**, 104.

atoms equally on the n.m.r. time scale. A square planar $RuHP_3$ system would give a doublet of triplets as $J_{HMP}(trans)$ is much larger than $J_{HMP}(cis)$ in ruthenium hydrides containing phosphorus ligands. Second, this structure provides no explanation for the absorptions at τ 4·72 and 5·72. Third, this structure would be expected to add PPh_3 reversibly, as does $[RhH(PPh_3)_3]$.[23] Fourth, this structure implies a '14-electron' cation which seems very unlikely.

Many four-co-ordinate complexes containing triphenylphosphine ligands change into six-co-ordinate complexes by the oxidative addition to the metal of a phenyl C–H bond *ortho* to a phosphorus atom.[24] In this case the resulting structure would be $[RuH_2(o\text{-}C_6H_4PPh_2)(PPh_3)_2]^+PF_6^-$ which could have several isomers. There are however, several reasons why this structure must also be rejected. First, complexes containing this structural feature show a characteristic i.r. absorption at 730 cm^{-1}, which is absent. Second, the structure does not explain the n.m.r. absorptions at τ 4·72 and 5·72. Third, the absorption due to the protons on ruthenium on this structure should have intensity 2 and not 1 as observed. Fourth, the observed shape of this absorption cannot be reconciled with any of the possible isomers, assuming first-order treatment is possible. There are no known MH_2 complexes of the formula $[MH_2(o\text{-}C_6H_4PPh_2)(PPh_3)_2]$ (M = any metal) but the spectra of complexes such as $[RuH_2(CO)(PMePh_2)_3]$ [23] which also contain two hydride ligands, one carbon ligand, and three phosphorus ligands, have been interpreted on a first-order basis.

An *X*-ray study is probably needed to find out the structure of this compound but a tentative structure can be put forward. The colour and stability of the complex suggest that the cation has 18 electrons rather than 16 where a red colour would be expected. The conductivity data suggest that the cation is monomeric and the n.m.r. data suggest that there is one hydrogen atom on ruthenium. This is coupled to two phosphorus atoms equally, with coupling constants (39 Hz) about what would be expected from H–M–P angles of 90°, and to one other phosphorus atom quite weakly (9 Hz). This phosphorus atom therefore cannot be directly attached to the metal atom and the structure shown in the Figure is proposed.



Proposed structure of $[RuH(PPh_3)_3]^+$

Two phosphine ligands are bound to the metal through the phosphorus atom, and the other is bound *via* a π-bonded interaction of one of its phenyl rings. This ligand therefore contributes six electrons to the metal atom giving it 18 in all. The hydride absorption at τ 18·75 is split into a triplet by coupling with the two equivalent phosphorus atoms and further split by the unique phosphorus atom. The absorptions at τ 5·72 and 4·72 are due to the H^2 and H^3 protons in the Figure respectively. They are split into triplets, the H^2 absorption by coupling with H^1 and H^3 protons ($J_{12} \sim J_{23} \sim 6$ Hz) and the H^3 absorption by coupling with the H^2 protons ($J_{12} \sim 6$ Hz) and the phosphorus atom ($J_{HP} \sim 6$ Hz). The H^1 absorption is hidden under the other phenyl group absorptions.

Complexes containing BPh_4 ligands in which one phenyl group is bonded to the metal in a way similar to that postulated here for $[RuH(PPh_3)_3]^+PF_6^-$ are known.[3,25] The i.r. spectra of these complexes contain characteristic absorptions at 1460 and 1390 cm^{-1} which are absent in the spectra of complexes where BPh_4 is acting as a non-co-ordinating anion. These extra absorptions occur in the same place as the extra absorptions found in the spectrum of $[RuH(PPh_3)_3]^+PF_6^-$. The n.m.r. spectrum of $[Ru(norbornadiene)BPh_4]$ [25] shows a triplet due to H^2 protons at τ 3·9 ($J_{12} = J_{13} = 6·5$ Hz) and a doublet due to H^3 protons at τ 3·6 ($J_{23} = 6·5$ Hz) and a triplet due to the H^1 proton at τ 3·3. The absorptions observed in the spectrum of $[RuH(PPh_3)_3]^+PF_6^-$ are also shifted upfield from the absorptions due to other phenyl groups, the H^1 absorption being shifted least, and the coupling constants are similar to those observed for the rhodium compound, suggesting that these absorptions are indeed due to protons on a phenyl ring co-ordinated to a metal atom.

An *X*-ray study of the complex $[Rh\{P(OMe)_3\}_2BPh_4]$ [26] shows that it contains a phenyl group co-ordinated to the metal *via* a π-interaction, but this group is puckered into a boat shape with H^2 and H^3 much nearer the metal than H^1. This explains why the n.m.r. absorption due to H^1 is shifted upfield to a smaller extent.

If this tentative structure is correct, the lone pair of electrons on the unique phosphorus atom should still be able to take part in bonding and it might be expected that the compound could be protonated further. However, triphenylphosphine is a weak base even among phosphines [27] and would be expected to become even weaker when co-ordinated to a metal atom bearing a positive charge. $[RuH(PPh_3)_3]^+PF_6^-$ was treated with HPF_6 in methanol and in acetone but no organometallic products containing a P–H bond were obtained.

It must be postulated that the unique triphenylphosphine ligand is able to revert to a ligand bound through phosphorus when the compound is treated with reagents such as hydride or chloride ion or acetonitrile.

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[23] K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, **7**, 546.

[24] For a review see G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[25] R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, 1970, **9**, 2339.

[26] M. J. Nolte, G. Gafner, and L. M. Haines, *Chem. Comm.*, 1969, 1406.

[27] W. A. Henderson, jun., and C. A. Streuli, *J. Amer. Chem. Soc.*, 1960, **82**, 5791.

DISCUSSION

The abstraction of a hydride ligand as H^- using the trityl cation appears to be a feasible alternative method to the abstraction of a halide ligand as X^- using sodium or silver salts for the preparation of cationic complexes of ruthenium containing triphenylphosphine ligands. There seems no reason why it should not be a general method for the preparation of cationic transition metal complexes. It would be particularly useful in cases where the hydride starting materials are more easily accessible than the corresponding halides. The hydride abstraction method is also useful in that the by-product from it is the fairly inert compound triphenylmethane which is moreover readily soluble in all organic solvents. In contrast, the by-product from a halide abstraction reaction is an ionic metal halide, which will probably have to be filtered off before the product is purified. It is also possible that the halide ion will reverse the reaction.

If the phosphonium salts $[Z_3PCPh_3]^+PF_6^-$ are heated in 1,2-dichloroethane, a red colour appears at high temperatures suggesting that reversible dissociation to Z_3P and the trityl salt is taking place. This process may be expected to take place to a small extent even at room temperature especially in the case of the sterically crowded $[Ph_3PCPh_3]^+PF_6^-$. It seems likely that when $[RuH_2(PPh_3)_4]$ is treated with $[Ph_3PCPh_3]^+PF_6^-$ the phosphonium salt dissociates and it is the trityl salt itself which reacts with the ruthenium–hydrogen bond.

Olah has shown that the trityl cation is able to react with carbon–hydrogen σ bonds at more than one site. On steric grounds it is unlikely that the central carbon atom of the trityl cation can get very near to the ruthenium–hydrogen bond in $[RuH_2(PPh_3)_4]$; the reaction possibly takes place at a carbon atom in a position *para* to the central carbon atom and involves a species such as $[C_6H_5{=}CPh_2]^+$. The transition state in the reaction probably contains either a linear Ru–H–C system or a triangular, two-electron, three centre bond between Ru, H, and C as postulated for the reactions between carbenium ions and C–H bonds of saturated hydrocarbons.[28]

EXPERIMENTAL

Preparations were carried out in dried solvents under dinitrogen or argon. Trityl hexafluorophosphate was made by the reaction of triphenylmethanol with HPF_6 in propionic anhydride.[29] Compounds were dried and m.p.s determined *in vacuo*; conductivities were measured at 20° in acetone and nitromethane.

Mass spectra were recorded on an A.E.I. MS 902 instrument and i.r. and n.m.r. spectra as in ref. 4. Microanalyses were carried out by Yarsley Testing Laboratories, Ashtead, Surrey, by Dr. G. Strauss, 10 Carlton Road, Oxford, and by the Division of Chemical Standards at the National Physical Laboratory. The Table gives analytical, m.p., and conductivity data for all new compounds and ν(M–H), τ_{M-H}, and J_{MPH} for metal hydrides.

Phosphonium Salts.—The phosphine or phosphite, either neat or in dichloromethane, was added to the trityl salt in dichloromethane until the red colour was discharged. The hexafluorophosphates formed from PPh_3 and $HPPh_2$ precipitated and were recrystallized from 1,2-dichloroethane. The other salts were precipitated by adding hexane and recrystallized from dichloromethane–methanol [salts from $PEtPh_2$, PBu_3, and $P(C_6H_4Me)_3$] or dichloromethane–ether in 60—80% yield. The salts were dried at 100°.

Hydridotetrakis(triphenylphosphine)ruthenium(II) *Hexafluorophosphate.*—$[RuH_2(PPh_3)_4]$ (1·15 g) was added to a stirred suspension of $[Ph_3PCPh_3]^+PF_6^-$ (0·65 g) and PPh_3 (0·8 g) in dichloromethane (10 ml) at 20°. A red solution quickly formed, which was filtered after 10 min and red crystals precipitated in 50% yield by adding methanol. They were dried at 20°. A higher yield of less crystalline material could be obtained by using ether instead of methanol.

Hydridopentakis(diethoxyphenylphosphine)ruthenium(II) *Hexafluorophosphate.*—(a) $[RuH(PPh_3)_4]^+PF_6^-$ (0·8 g) and diethoxyphenylphosphine (1·5 ml) were heated to reflux in methanol (15 ml) for 5 min and then cooled. The white solid resulting was recrystallized from dichloromethane–methanol in 70% yield, and dried at 100°.

(b) $[RuHCl(PPh_3)_3]$ (0·5 g) and diethoxyphenylphosphine (1·5 ml) were heated to reflux in methanol (15 ml) giving a colourless solution. Potassium hexafluorophosphate (0·2 g) was added giving a white precipitate which was recrystallized from dichloromethane–methanol and identified by its i.r. spectrum as the same compound as that prepared by method (a).

Similar compounds were made by both methods using dimethoxyphenylphosphine and diphenylphosphine instead of diethoxyphenylphosphine.

Hydridobis(acetonitrile)tris(triphenylphosphine)ruthenium(II) *Hexafluorophosphate.*—(a) $[RuHCl(PPh_3)_3]$ (0·86 g) and acetonitrile (1 ml) were heated to reflux in methanol (5 ml) for 5 min giving a light green solution. KPF_6 (0·3 g) was added giving a yellow precipitate which was recrystallized from dichloromethane–methanol in 70% yield and dried at 100°.

(b) $[RuH(PPh_3)_4]^+PF_6^-$ (0·5 g) and acetonitrile (0·2 ml) were heated to reflux in methanol (5 ml) and ether (5 ml) for 5 min giving a yellow precipitate with identical i.r. and n.m.r. spectra to the compound formed by method (a). (c) $[RuH_2(PPh_3)_4]$ (0·575 g) was added to a stirred suspension of $[Ph_3PCPh_3]^+PF_6^-$ (0·325 g) in dichloromethane (10 ml) and acetonitrile (1 ml) at 20°. A vigorous reaction took place giving a light green solution which was filtered. Methanol was added to precipitate the product which was identified by its i.r. spectrum.

Similar compounds, listed in the Table, were made by method (a) using other nitriles instead of acetonitrile.

Hydridotris(triphenylphosphine)ruthenium(II) *Hexafluorophosphate.*—A suspension of $[RuH(PPh_3)_4]^+PF_6^-$ (1·0 g) in ethanol (10 ml) was heated to reflux for 30 min. The suspension became an off-white colour. The mixture was cooled and the solid recrystallized from dichloromethane–methanol in 70% yield and dried at 100°.

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[28] G. A. Olah, J. J. Svoboda, and J. A. Olah, Abstracts, Annual Meeting of the Chemical Society, Manchester, 1972, 2.13b.

[29] H. J. Dauben, jun., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, 1960, **25**, 1442.