ortho-Metallated Triphenylphosphine(2-diphenylphosphinophenyl) and Related Complexes of Ruthenium(II): Interaction of Chlorohydridotris-(triphenylphosphine)ruthenium(II) with Methyl and Trimethylsilylmethyl Alkylating Agents (Li, Mg, Zn); Hydrido Methyl and Trimethylsilylmethyl Complexes †

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The interaction of chlorohydridotris(triphenylphosphine)ruthenium(II), $RuHCl(PPh_3)_3$, with lithium, magnesium, and zinc alkyls has been studied.

With trimethylsilylmethyl-lithium and methyl-lithium in diethyl ether and tetrahydrofuran, unstable, very reactive hydridoalkyls, $RuH(R)(PPh_3)_2(S)_2$ ($R = CH_2SiMe_3$ or Me, and $S = Et_2O$ or C_4H_8O) are formed. When warmed these compounds readily lose Me_4Si or CH_4 via an ortho-metallation reaction of PPh_3 to give the hydrido-(η^3-2-diphenylphosphinophenyl) species, $RuH(C_6H_4PPh_2)(PPh_3)_2(S)$. With an excess of methyl-lithium in diethyl ether and with magnesium and zinc dimethyls, lithium-, magnesium-, and zinc-containing methyl complexes are obtained. The reaction of $RuHCl(PPh_3)_3$ with lithium alkyls has been monitored by n.m.r. spectroscopy of the intermediates, and the isolated complexes have been characterised and their stereochemistries derived from i.r. and ^1H and ^{31}P n.m.r. spectroscopy.

The isolated and chemically analysed new complexes are: $RuHMe(PPh_3)_2(Et_2O)_2$, $RuHMe(PPh_3)_2(MeLiOEt_2)_2$, $RuMe(C_6H_4PPh_2)(PPh_3)_2(Et_2O)$, $RuMe(C_6H_4PPh_2)(PPh_3)(MeLiOEt_2)_2$, $RuH(C_6H_4PPh_2)(PPh_3)_2(Et_2O)$, $RuH-(C_6H_4PPh_2)(PPh_3)_2(thf)$, $\{RuH(C_6H_4PPh_2)(PPh_3)_2\}_2(Zn_2Me_3Cl)$, $\{RuH(C_6H_4PPh_2)(PPh_3)_2\}_2[Mg_2Me_3Cl(Et_2O)_2]$.

ALKYL or aryl hydrido-complexes have been reported for Mo,[1,2] W,[1,2] Co,[3] Ni,[4] Pt,[5] Ru,[6-8] and Co.[9] Some of these complexes decompose readily to give unidentified products. For $RuH(C_{10}H_7)(dmpe)_2$[7] (dmpe = bisdimethylphosphinoethane) and the postulated complex $W(\pi-C_5H_5)_2(CH_2CH=CMe_2)H$, obtained [2] by insertion of isoprene into one W–H bond of $WH_2(\pi-C_5H_5)_2$, reductive elimination of alkane or alkene occurs. The tungsten complex gives $W(\pi-C_5H_5)_2$ which immediately oxidatively adds solvents (e.g. C_6H_6) to give $WH(\pi-C_5H_5)_2(C_6H_5)$. The ruthenium complex gives a compound which was initially thought to be a tautomeric mixture of the ruthenium(0) species $Ru(dmpe)_2$ and $RuH\{CH_2P(Me)-CH_2CH_2PMe_2\}(dmpe)$,[7] but which has subsequently been shown, at least in the solid state, to be a dimeric species $[RuH\{CH_2P(Me)CH_2CH_2PMe_2\}(dmpe)]_2$.[10] A similar complex, $FeH\{C_6H_4P(Ph)CH_2CH_2PPh_2\}(dppe)$,[11] (dppe = bisdiphenylphosphinoethane) has also been reported, as arising from the reduction of $Fe(acac)_3$ in

the presence of dppe, but this reaction is thought to proceed via $Fe(C_2H_4)(dppe)_2$ as an intermediate.

These ready reductive eliminations of alkane from metal complexes have led us to study the formation of alkylhydrido-complexes of ruthenium that contain triphenylphosphine, in the hope that these complexes might generate ruthenium(0) species or, more likely, hydrido-complexes of ruthenium(II) containing an ortho-metallated phosphine ligand.

Reports of ruthenium(0) species that do not contain either carbon monoxide or phosphorus trifluoride as ligands are confined to $Ru(PPh_3)_3(olefin)$ (olefin = C_2H_4,[12] styrene,[12] and pentene[13]), $Ru(PPh_3)_3N_2$,[13] $Ru(PPh_3)_4(MeCN)_2$[14] and the postulated $Ru(PPh_3)_3$,[15] which is thought to be the active species in the transfer of hydrogen from isopropyl alcohol to cyclohexene,

† No reprints available.

[1] A. Nakamura and S. Otsuka, J. Amer. Chem. Soc., 1973, 95, 5091 and references therein.

[2] M. L. H. Green and P. J. Knowles, J. Chem. Soc. (A), 1971, 1508 and references therein.

[3] J. Ellermann and W. H. Gruber, Angew. Chem. Internat. Edn., 1968, 7, 129.

[4] K. Jonas and G. Wilke, Angew. Chem. Internat. Edn., 1969, 8, 519.

[5] B. Wozniak, J. D. Ruddick, and G. Wilkinson, J. Chem. Soc. (A), 1971, 3116.

[6] J. Chatt and R. G. Hayter, J. Chem. Soc., 1963, 6017.

[7] J. Chatt and J. M. Davidson, J. Chem. Soc., 1965, 843.

[8] S. Centini, A. Mantovani, A. Fusi, and M. Keubler, Gazzetta, 1975, 105, 255.

[9] F. L'Eplattenier, Inorg. Chem., 1969, 8, 965.

[10] F. A. Cotton, B. A. Frenz, and D. L. Hunter, J.C.S. Chem. Comm., 1974, 755.

[11] G. Hata, H. Kondo, and A. Miyake, J. Amer. Chem. Soc., 1968, 90, 2278.

[12] S. Komiya, A. Yamamoto, and S. Ikeda, J. Organometallic Chem., 1972, 42, C65.

[13] F. Panella, Co-ordination Chem. Rev., 1975, 16, 51.

[14] E. O. Sherman and P. R. Schreiner, J.C.S. Chem. Comm., 1976, 3.

[15] H. Imai, T. Nishiguchi, M. Kobayashi, and K. Fukuzumi, Bull. Chem. Soc. Japan, 1975, 48, 1585.

using $RuH_2(PPh_3)_4$ as catalyst. Other attempts to prepare complexes of this kind have been unsuccessful,[8,16] but it seems likely that if such complexes exist they should be extremely active towards oxidative addition of both common and unusual molecules and may even be capable of activating alkyl and aryl C–H bonds.

Complexes of ruthenium(II) containing *ortho*-metallated phosphines and hydrides, on the other hand, are also of interest, firstly since the only isolated ruthenium complexes containing an *ortho*-metallated triphenyl-phosphine group are $\{Ru(C_6H_4PPh_2)(PPh_3)Cl\}_n$ and $Ru(\pi-C_5H_5)(C_6H_4PPh_2)(PPh_3),$[17] and secondly, since the hydrides have often been postulated as intermediates in the deuteriation of the *ortho*-hydrogen atoms of the phenyl rings of the phosphine when hydridoruthenium species interact with deuterium.[18]

We now show that the reaction of alkylating agents with $RuHCl(PPh_3)_3$ gives unstable alkylhydrido-complexes that readily eliminate alkane with concomitant *ortho*-metallation of the phenyl ring of the PPh_3 ligand to give the often postulated, but not previously isolated, $RuH(C_6H_4PPh_2)(PPh_3)_2S$ (S = Et_2O or thf) (thf = tetrahydrofuran).

Alkylation Reactions of $RuHCl(PPh_3)_3$

Lithium Reagents.—The interaction of $RuHCl(PPh_3)_3$ with an excess of alkyl-lithium reagents, RLi (R = Me or Me_3SiCH_2), in ethers (S = Et_2O or thf), at room temperature leads to the formation of yellow solutions from which yellow, air- and moisture-sensitive, crystalline complexes may be isolated. For R = Me_3SiCH_2 and S = Et_2O or thf or for R = Me, S = thf, the products have stoicheiometry $Ru(PPh_3)_3S$ but are correctly formulated $RuH(C_6H_4PPh_2)(PPh_3)_2S$ on the basis of spectroscopic data (see below).

Molecular-weight measurements on $RuH(C_6H_4PPh_2)$-$(PPh_3)_2(Et_2O)$ (cryoscopically in benzene) give a value (710) rather less than that expected (961) and, although this could arise from partial dissociation in solution, no such dissociation is observed by [31]P n.m.r. spectroscopy (see later); the low value is more likely due to the ready reaction of the complex with traces of water to form $RuH(OH)(PPh_3)_2(H_2O)$ [19] and triphenylphosphine. Attempts to recrystallise $RuH(C_6H_4PPh_2)(PPh_3)_2S$ from benzene–light petroleum mixtures lead to formation of $RuH_2(PPh_3)_4$ in low yield, a phenomenon that has also been observed in the recrystallisation of $Ru(PPh_3)_3$-(styrene) from toluene.[12] The extra phosphine may be assumed to arise, once again, from interaction of $RuH(C_6H_4PPh_2)(PPh_3)_2S$ with traces of moisture. Slow recrystallisation of $RuH(C_6H_4PPh_2)(PPh_3)_2(Et_2O)$ from tetrahydrofuran–light petroleum produces $RuH_2(PPh_3)_3$-(thf) [20] in high yield.

From the reaction of $RuHCl(PPh_3)_3$ with methyl-lithium in ether, however, the nature of the yellow

crystals isolated depends upon the Li : Ru ratio. With 2.5—3 mol of MeLi per g atom of ruthenium, the product analyses as $RuMe(C_6H_4PPh_2)(PPh_3)_2(Et_2O)$ but with a larger excess of methyl-lithium a complex of formula $RuMe(C_6H_4PPh_2)PPh_3(MeLiOEt_2)_2$ is obtained. Both these complexes dissolve in tetrahydrofuran with evolution of 1 mole equiv. of methane to form, respectively $RuH(C_6H_4PPh_2)(PPh_3)_2(thf)$ ([1]H n.m.r. evidence) and $RuH(C_6H_4PPh_2)(PPh_3)(thf)_2$ ([31]P n.m.r. evidence). They also react with water releasing, respectively, 1 and 3 mole equiv. of methane and producing red solids.

For R = Me, the paths by which the different products are formed from $RuHCl(PPh_3)_3$ have been followed by [31]P n.m.r. spectroscopy (see below) and many of the reaction intermediates have been isolated and character-ised. These results are summarised in Scheme 1. Supporting spectroscopic data are given later.

Thus, if $RuHCl(PPh_3)_3$ is treated with a small excess (2.5—3 mole equiv.) of MeLi in Et_2O at 0 °C, a yellow compound, which we have been unable to obtain free from LiCl, but which appears to be the methylhydrido-complex, $RuH(Me)(PPh_3)_2(Et_2O)_2$, is formed. If, however, a large excess of MeLi is used, $RuH(Me)(PPh_3)_2$-$(MeLiOEt_2)_2$ may be crystallised from the filtered solution at low temperatures. Both these alkyl-hydrido-complexes are extremely reactive, being pyro-phoric in air and evolving methane immediately on contact with water (1 and 3 mole equiv. respectively) or organic solvents (1 mole equiv.). From their re-actions with water, a red solid of formula $RuH(OH)$-$(PPh_3)_2(H_2O)$, to be described in detail separately,[20] may be isolated.

Both these alkylhydrido-complexes dissolve in tetra-hydrofuran at low temperatures to give orange solutions. When warmed these evolve 1 mole equiv. of methane and the complex $RuH(C_6H_4PPh_2)(PPh_3)(thf)_2$ is formed. $RuHMe(PPh_3)_2(MeLiOEt_2)_2$ also decomposes slowly to give the ether-insoluble complex, $RuMe(C_6H_4PPh_2)$-$(PPh_3)(MeLiOEt_2)_2$, when stirred under an ethereal solution of methyl-lithium; hydrogen may be detected in the mass spectrum of the gaseous products. From the orange, ethereal solution, a few crystals, thought to be $RuH(C_6H_4PPh_2)(PPh_3)(Et_2O)_2$, may be isolated.

Other Alkylating Agents.—Since we were unable to prepare $RuH(Me)(PPh_3)_2(Et_2O)_2$ free from lithium chloride, we attempted to alkylate $RuHCl(PPh_3)_3$ with agents, the halogenated products from which are soluble in diethyl ether.

With an excess of trimethylaluminium in ether at 0 °C, the reaction was very slow and since the only identifiable product was $RuH_2(PPh_3)_4$ there is doubtless substantial decomposition.

With dimethylzinc or dimethylmagnesium, on the

16 J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, 1972, **11**, 2714.

17 B. R. James, L. D. Markham, and D. K. W. Wang, *J.C.S. Chem. Comm.*, 1974, 439; M. I. Bruce, R. C. F. Gardiner, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **40**, C39.

18 T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1970, **92**, 3011.

19 D. J. Cole-Hamilton and G. Wilkinson, *Nouveau J. Chem.*, 1977, in the press.

20 B. N. Chaudret, D. J. Cole-Hamilton, R. Nohr, and G. Wil-kinson, *J.C.S. Dalton*, in the press.

other hand, the reactions proceed smoothly to give yellow crystalline complexes that contain either zinc or
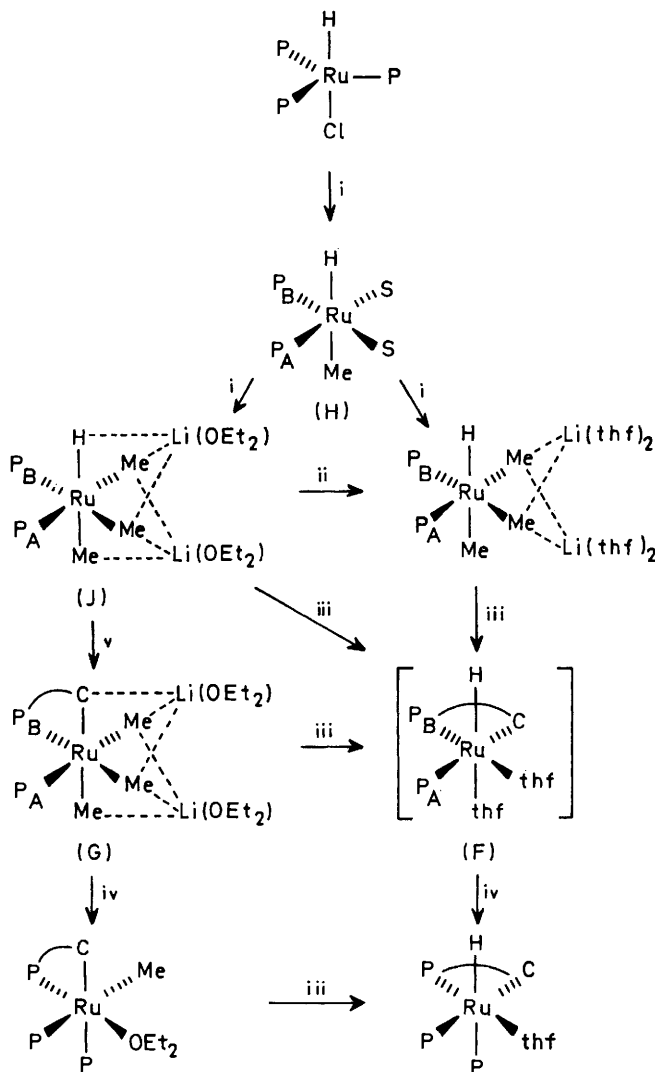
Scheme 1   Reaction of RuHCl(PPh$_3$)$_3$ with methyl-lithium: P = PPh$_3$, P–C = (C$_6$H$_4$PPh$_2$), S = ether solvent

magnesium. The zinc compound analyses approximately half way between that required for RuH-(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$(ZnMe$_2$) and for RuH(C$_6$H$_4$PPh$_2$)-(PPh$_3$)$_2$(ZnMeCl), which means either that these two complexes crystallise together from the solution, or more likely that the complex is a dimer, {RuH-(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$}$_2$(Zn$_2$Me$_3$Cl). The pale yellow complex dissolves in cold tetrahydrofuran or warm benzene to give magenta solutions but, on addition of light petroleum, the pale yellow complex is recovered

unchanged. The molecular weight in benzene (1 000) is close to that required for a monomer but since the colour of the solution is so different from that of the solid it seems likely that the dimer dissociates in solution to RuH(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$(ZnMeCl) and RuH(C$_6$H$_4$PPh$_2$)-(PPh$_3$)$_2$(ZnMe$_2$). The magnesium-containing product appears to be similar, except that it contains 1 mole equiv. of ether per mole equiv. of magnesium. N.m.r. data (see later) apparently suggest that it dissociates in solution, losing triphenylphosphine. The spectra are very complex and it is impossible to recrystallise the product.

Reactions of many of these complexes, together with the syntheses of other ortho-metallated triphenylphosphine complexes of ruthenium will be presented later.[19]

Spectroscopic Properties of the Complexes.—I.r. spectra (Table 1). All the complexes show peaks in their i.r. spectra characteristic of co-ordinated triphenylphosphine. Absorptions in the regions 1 500—1 600,[21] 1 400—1 450,[22] 1 100,[23] and 730[21] cm^{-1} have been assigned as arising from the ortho-disubstituted phenyl ring of an ortho-metallated phosphine and, although many of the complexes reported herein have extra peaks in all these regions, we find that the most characteristic absorptions are at ca. 1 550 and ca. 1 410 cm^{-1}. The assignment of peaks near 1 100 and 730 cm^{-1} is complicated by the presence of vibrations from the mono-substituted phenyl rings. Thus, for {RuH(C$_6$H$_4$PPh$_2$)-(PPh$_3$)$_2$}$_n$L ($n = 1$, L = OEt$_2$ or thf; $n = 2$, L = Zn$_2$Me$_3$Cl or Mg$_2$Me$_3$Cl(OEt$_2$)$_2$ as well as for RuMe-(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$(Et$_2$O),   RuMe(C$_6$H$_4$PPh$_2$)(PPh$_3$)-(MeLiOEt$_2$)$_2$, and RuH(C$_6$H$_4$PPh$_2$)(PPh$_3$)(Et$_2$O)$_2$ absorptions near 1 550 and 1 410 cm^{-1} indicate the presence of ortho-metallated phosphine moieties. The slightly lower frequency and stronger intensity of the peak near 1 530 cm^{-1} for RuMe(C$_6$H$_4$PPh$_2$)(PPh$_3$)(MeLiOEt$_2$)$_2$ compared with this peak for the other complexes may indicate some interaction between the metallated carbon atom of the phosphine and a lithium atom.

For RuMe(C$_6$H$_4$PPh$_2$)(PPh$_3$)(MeLiOEt$_2$)$_2$ and RuH-(Me)(PPh$_3$)$_2$(MeLiOEt$_2$)$_2$ vibrations near 2 700 cm^{-1} indicate the kind of interaction between co-ordinated methyl groups and lithium atoms that is found in many lithium salts of permethylated transition-metal complexes, e.g., Li$_2$MnMe$_4$[24] and in methyl-lithium itself.[25]

Apart from these absorptions, the i.r. spectra of those complexes for which hydrides are indicated by their ^{1}H n.m.r. spectra, with the exception of RuH(Me)(PPh$_3$)$_2$-(Et$_2$O)$_2$, show absorptions in the region 1 600—2 000 cm^{-1}. Most of these are in the region expected for v(M–H) in complexes of ruthenium(ii),[26] but the very low frequency for v(M–H) in RuH(Me)(PPh$_3$)$_2$(MeLiOEt$_2$)$_2$ and {RuH(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$}$_2$(Zn$_2$Me$_3$Cl) indicates some interaction between the hydride and the main group

[21] M. A. Bennett, D. L. Kilner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

[22] R. J. McKinney, R. Hoxmeier, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3059.

[23] L. W. Gosser, *Inorg. Chem.*, 1975, **14**, 1453.

[24] R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, and G. Wilkinson, *J.C.S. Dalton*, 1976, 2204.

[25] R. West and W. Glaze, *J. Amer. Chem. Soc.*, 1961, **83**, 3580.

[26] E. L. Muetterties, ed., 'Transition Metal Hydrides,' Marcel Dekker Inc., New York, 1971, p. 87.

metal as found in, e.g. Li_2BeH_4 [ν(M–H) = 1 600 cm^{-1}].[27] That these absorptions do, indeed arise from ν(M–H) is proven by their disappearance when RuDClP-$(C_6H_3D_2)_3$ is employed as starting material, and the appearance of an absorption near 1 150 cm^{-1} ($\nu\dfrac{M-H}{M-D} =$ 1.41 and 1.39 respectively). For {RuH($C_6H_4PPh_2$)-(PPh_3)$_2$}$_2$(Zn$_2$Me$_3$Cl), the interaction of the zinc atom with the metal hydride does not appear to be broken in

met by the addition of diethyl ether to its co-ordination sphere.

N.m.r. spectra. (i) ^{1}H n.m.r. (Table 2). The ^{1}H n.m.r. spectra of the complexes all show broad resonances between τ 2 and 4 which arise from the phenyl ring protons of the co-ordinated phosphines. On account of the number of phenyl rings present, it has not been possible to observe the ABCD pattern that should arise from the protons of the *ortho*-disubstituted rings, and the slight shift to higher field which is often re-

TABLE 1

I.r. spectra of ruthenium complexes [a]

Compound	o-C_6H_4 bands [b]	ν(M–H)	Other bands
RuH($C_6H_4PPh_2$)(PPh_3)$_2$(Et_2O)	1 550m, 1 530w, 1 410m	1 773m, vbr	1 060s [c]
RuH($C_6H_4PPh_2$)(PPh_3)$_2$(thf)	1 548m, 1 407m	1 748mvbr	1 045s [c]
RuMe($C_6H_4PPh_2$)(PPh_3)$_2$(Et_2O)	1 550m, 1 530w, 1 412m		1 060s [c]
RuH($C_6H_4PPh_2$)(PPh_3)(Et_2O)$_2$	1 550m, 1 410m	1 790mbr	1 060s [c]
RuMe($C_6H_4PPh_2$)(PPh_3)(MeLiOEt$_2$)$_2$	1 550w, 1 528m, 1 415m		2 755m,[d] 2 720m,[d] 1 060s [d]
RuHMe(PPh_3)$_2$(Et_2O)$_2$			1 065s [c]
RuHMe(PPh_3)$_2$(MeLiOEt$_2$)$_2$		1 610mbr (1 140m) [e]	2 740m,[d] 2 710m,[d] 2 695m,[d] 1 058s [e]
{RuH($C_6H_4PPh_2$)(PPh_3)$_2$}$_2$(Zn$_2$Me$_3$Cl)	1 553m, 1 540w, 1 417m	1 675sbr (1 180s) [e]	
{RuH($C_6H_4PPh_2$)(PPh_3)$_2$}$_2${Mg$_2$Me$_3$Cl(OEt$_2$)$_2$}	1 553m, 1 412m	1 757mbr	1 068sh [e]

[a] In Nujol mulls, CsI plates. [b] From *ortho*-metallated phosphine, ($C_6H_4PPh_2$). [c] ν(C–O) of co-ordinated ether. [d] ν(C–H). [e] ν(Ru–D).

TABLE 2

^{1}H N.m.r. spectra of complexes at 36 °C and 60 MHz

Compound	Structure type	Solvent	τ *	J_{HPA}	J_{HPB}	J_{HPC}	Methyl	Co-ordinated ether τ(J_{HH}) *	Phenyl
RuH($C_6H_4PPh_2$)(PPh_3)$_2$(Et_2O)	(B)	C_6D_6	18.6d [a]			80		7.05q (7), 9.30t (7)	2.0—3.5
RuH($C_6H_4PPh_2$)(PPh_3)$_2$(thf)	(B)	C_6D_6	18.8d			80		6.69,[b] 8.80 [b]	2.0—3.5
RuH($C_6H_4PPh_2$)(PPh_3)$_2$(thf)	(B)	thf	18.7	22	12	82			
RuMe($C_6H_4PPh_2$)(PPh_3)$_2$(Et_2O)	(B)	C_6D_6					10.2s [a]	6.98q (7), 9.23t (7)	2.0—3.3
RuH($C_6H_4PPh_2$)(PPh_3)(thf)$_2$	(F)	thf	18.8	15	20				
RuMe($C_6H_4PPh_2$)(PPh_3)(MeLiOEt$_2$)$_2$	(G)	C_6D_6					10.3s [a]	6.85q (7), 9.05t (7)	2.0—3.5
RuHMe(PPh_3)$_2$(MeLiOEt$_2$)$_2$	(J)	thf [c]	21.1s [a]				11.10s,[a] 11.35s [a]		
RuHMe(PPh_3)(MeLiOEt$_2$)$_2$	(J)	thf [d]	21.8	15	15		11.10s,[a] 11.35t (4) [e]		
{RuH($C_6H_4PPh_2$)(PPh_3)$_2$}$_2$(Zn$_2$Me$_3$Cl)	(D)	C_6D_6	18.5	21	12	51	10.3s		2.0—4.0
{RuH($C_6H_4PPh_2$)(PPh_3)$_2$}$_2$(Zn$_2$Me$_3$Cl)	(D)	thf	18.3	21	12	48	10.3s		1.5—3.5
{RuH($C_6H_4PPh_2$)(PPh_3)$_2$}$_2${Mg$_2$Me$_3$Cl(OEt$_2$)$_2$}	(E)	C_6D_6	19.9s [a]				11.3s	7.00q (7), 9.12t (7)	2.0—3.5

[a] Broad. [b] Second-order resonances from thf. [c] At −60 °C. [d] At 0 °C. [e] J_{PH}.

* s = singlet, d = doublet, t = triplet, and q = quartet.

tetrahydrofuran solution since, although the peak broadens, it does not shift to higher frequency. On some occasions, ν(M–H) for the zinc-containing complex occurs at 1 635 cm^{-1} and there is an extra peak at 290 cm^{-1}. We assume that this simply reflects a different bridging system and the complex is probably {RuH-($C_6H_4PPh_2$)(PPh_3)$_2$}$_2$(Zn$_2$Me$_2$Cl$_2$).

Finally, the position of ν(M–H) (at 1 757 cm^{-1}) for {RuH($C_6H_4PPh_2$)(PPh_3)$_2$}$_2${Mg$_2$Me$_3$Cl(OEt$_2$)$_2$} indicates that no interaction between hydride and magnesium atom is occurring, presumably because the co-ordination requirements of the magnesium atom are

ported [28] for this type of complex is not observed. Resonances from other ligands present, of the correct relative intensity with respect to the phenyl resonances, are observed but afford little structural information apart from the observation that their chemical shifts, being different from those of free ligand, indicate that they remain co-ordinated to the metal in solution.

For the methyl-containing complexes, the resonances arising from the methyl groups all occur between τ 10 and 11.5 and are unequivocally assigned since addition

[27] N. A. Bell and G. E. Coates, *J. Chem. Soc. (A)*, 1968, 628.
[28] W. Keim, *J. Organometallic Chem.*, 1968, **14**, 179.

of water to the n.m.r. solutions causes these peaks to disappear and a peak at τ 9.8 (methane) to appear. The observation of only a single methyl resonance for $\{RuH(C_6H_4PPh_2)(PPh_3)_2\}_2(Zn_2Me_3Cl)$ presumably indicates some kind of methyl-group exchange at room temperature.

For $RuH(Me)(PPh_3)_2(MeLiOEt_2)_2$ in tetrahydrofuran, two methyl resonances at τ 11.10 and 11.35, which do not exchange with added MeLi (τ 11.75), both broad and of relative intensity 2 : 1, are observed at low temperatures. At higher temperatures, the unique methyl group appears as a triplet ($J_{PH} = 4$ Hz), whilst the other remains broad. We suggest that this broadening may be explained by interaction of all the methyl groups with a lithium atom (which has a quadrupole moment) at low temperatures, and that the interaction with the unique methyl group is broken at higher temperatures, perhaps by co-ordination of tetrahydrofuran to the lithium atom.

From the hydride resonances, considerable structural information can be deduced since correlations of phosphorus–hydrogen coupling constants with stereochemistry are available. Thus, in ruthenium complexes, a value of $J_{PH} < 40$ Hz is assigned to cis couplings whereas for a hydride trans to phosphorus $J_{PH} > 40$ Hz.[6] From the number of lines in the hydride resonance, the equivalence of the various phosphines may be deduced.

Thus, for $\{RuH(C_6H_4PPh_2)(PPh_3)_2\}_nL$ ($n = 1$, L = Et_2O or thf; $n = 2$, L = Zn_2Me_3Cl) the presence of an eight-line hydride resonance indicates that all three phosphorus atoms are non-equivalent and hence split the hydride resonance into a doublet of doublets of doublets. The values of J_{PH} indicate that the hydride is trans to one of the phosphines and that the complex has stereochemistry (A), (B), or (C) (see Figure). For $RuH(C_6H_4PPh_2)(PPh_3)_2(thf)_2$ the observation of a doublet of doublets with both $J_{PH} \simeq 20$ Hz indicates non-equivalent phosphines to both of which the hydride is cis.

The broad hydride resonance arising from the magnesium-containing complex is insufficiently resolved to provide any stereochemical information.

Finally, the hydride resonance (triplet at τ 21.1, $J_{PH} = 14$ Hz) of $RuH(Me)(PPh_3)_2(MeLiOEt_2)_2$ at 0 °C, indicates that the hydride is cis to two equivalent phosphines but at lower temperatures it is broadened and we once again assign this to interaction of the hydride with a quadrupolar lithium atom at low temperature, and solvolysis of this interaction by tetrahydrofuran at higher temperatures.

(ii) ^{31}P N.m.r. spectra (Table 3). The ^{31}P n.m.r. spectrum of $RuH(C_6H_4PPh_2)(PPh_3)_2(C_2H_4)$ [isomer (A)], which we show unequivocably to be an ortho-metallated species,[19] indicates that the phosphorus atom of an ortho-metallated phosphine, or of any phosphine trans to a hydrido-ligand, resonates at lower frequencies than other phosphines. On this assumption, we can make unequivocal assignments of stereochemistry for the present complexes. Thus, for $RuH(C_6H_4PPh_2)(PPh_3)_2S$,

since all the values of J_{PP} are low (<30 Hz), the phosphines must all be mutually cis and occupy one face of the octahedron, thus ruling out structure (C). Since none of the phosphorus chemical shifts is as low in frequency as that of the metallated ligand in $RuH(C_6H_4PPh_2)(PPh_3)_2(C_2H_4)$ [isomer (A)] (−38.5), it seems unlikely that the phosphorus atom of the ortho-metallated phosphine group is trans to a hydride; thus the stereochemistry must be as in (B). The resonances may then be assigned such that in order of decreasing frequency they arise from P_A, P_B, and P_C since partial decoupling

(A)　　　　　(B)　　　　　(C)

(D)

(E)

(K)　　　　　　(L)
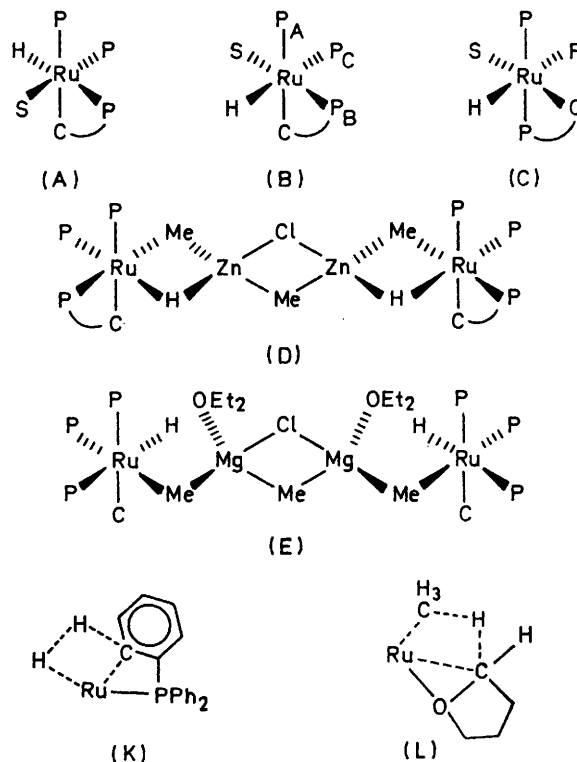
Stereochemistries of ruthenium complexes. For (F), (G), (H), and (J) see Scheme

studies indicate that P_C is the one trans to hydride. Also the very small P–H coupling constant (10—12 Hz) arises from coupling between the hydride and the cis-phosphorus atom of the metallated ligand and is presumably small because the H–Ru–P angle deviates significantly from 90° on account of the distortion caused by the formation of the four-membered ring. A very similar spectrum is observed for $\{RuH(C_6H_4PPh_2)(PPh_3)_2\}_2(Zn_2Me_3Cl)$ and this, together with the i.r. evidence, indicates structure (D). This type of structure has a precedent[29] in $\{(\pi-C_5H_5)Mo(CO)_3(ZnClOEt_2)\}_2$ where the zinc atom attains four co-ordination by two Zn–Cl–Zn bridges and co-ordination of an ether molecule. For $\{RuH(C_6H_4PPh_2)(PPh_3)_2\}_2\{MgMe_3Cl(OEt_2)_2\}$ the ^{31}P n.m.r. spectrum at room temperature shows only broad peaks, but on cooling, some sharp resonances arising from PPh_3 and a pattern similar to that observed for

[29] J. St. Denis, W. Butler, M. D. Glick, and J. P. Oliver, J. Amer. Chem. Soc., 1974, 96, 5427.

{RuH(C₆H₄PPh₂)(PPh₃)₂}₂(Zn₂Me₃Cl), together with broad resonances, indicate that, although substantial decomposition occurs in solution, the complex probably has stereochemistry (E). Presumably the phosphine dissociate occurs because of steric congestion caused by the bulky MgMeXOEt₂ group (X = Me or Cl).

For RuMe(C₆H₄PPh₂)(PPh₃)₂(Et₂O), the ³¹P n.m.r. spectrum is very similar to that for RuH(C₆H₄PPh₂)-(PPh₃)₂(Et₂O), except that the resonance in the latter arising from the phosphorus atom *trans* to hydride (at −26.1 p.p.m.) has been replaced by a similar resonance at 42.3 p.p.m., consistent with its being *trans* to the

The Course of the Reaction of RuHCl(PPh₃)₃ *with Alkyl-lithium Reagents.*—Monitoring of the reactions of RuHCl(PPh₃)₃ with alkyl-lithium reagents in diethyl ether or tetrahydrofuran by ¹H and ³¹P n.m.r. together with chemical studies confirm the sequences shown in Scheme 1. However, it appears that an additional reaction for the transformation of the alkyl hydride to the final *ortho*-metallated complex may occur in some cases. Thus, allowing the reaction mixture containing RuH(Me)(PPh₃)₂(thf)₂, LiMe, and PPh₃ to warm to room temperature for several hours, peaks arising from RuH(C₆H₄PPh₂)(PPh₃)(thf)₂ are seen in the ³¹P n.m.r.

TABLE 3

³¹P N.m.r. spectra of ruthenium complexes at 36 °C [a]

Compound	Structure type	Solvent	Chemical shifts [b]			Coupling constants (Hz)					
			P_A	P_B	P_C	P_AP_B	P_BP_C	P_CP_B	P_AH [c]	P_BH [c]	P_CH [c]
RuH(C₆H₄PPh₂)(PPh₃)₂(Et₂O)	(B)	C₆H₅CH₃	51.4	−20.0	−26.1	23.7	17.7	17.7	22	10	74
RuH(C₆H₄PPh₂)(PPh₃)₂(thf)	(B)	thf	52.6	−21.2	−25.8	21.5	17.5	17.1	22	12	83
RuMe(C₆H₄PPh₂)(PPh₃)₂(Et₂O)	(B)	Et₂O	50.6	−18.0	42.3	16.6	16.6	20.0			
RuH(C₆H₄PPh₂)(PPh₃)(thf)₂	(F)	thf	65.8	−10.7		21.5			15	20	
RuMe(C₆H₄PPh₂)(PPh₃)(MeLiOEt₂)₂	(G)	Et₂O	65.4	−10.6		23.0					
RuHMe(PPh₃)₂(Et₂O)₂	(H)	thf [d]		66.2					14	14	
RuHMe(PPh₃)₂(MeLiOEt₂)₂	(J)	thf [d]		66.0					15	15	
RuHMe(PPh₃)₂(MeLiOEt₂)₂	(J)	Et₂O [e]		67.4					15	15	
RuHMe(PPh₃)₃		thf		53.9					7.3	7.3	7.3
{RuH(C₆H₄PPh₂)(PPh₃)₂}₂(Zn₂Me₃Cl)	(D)	thf	45.9	−26.8	−31.2	22.5	22.5	22.5	21	12	46
{RhH(C₆H₄PPh₂)(PPh₃)₂}₂{Mg₂Me₃Cl(OEt₂)₂}	(E)	C₆H₅CH₃ [d]	36.6	−24.0	−29.3	17.5	17.5	17.5	Not determined		

[a] Measured at 40.505 MHz on Varian Associates XL100-12 n.m.r. spectrometer in the Fourier transform mode with total ¹H decoupling. [b] P.p.m. to high frequency of external 85% H₃PO₄. [c] ¹H decoupling in phenyl region. [d] −60 °C. [e] 0 °C.

methyl group. The complex thus has stereochemistry (B) but with the hydride replaced by a methyl group. The complexes RuH(C₆H₄PPh₂)(PPh₃)(thf)₂ and RuMe-(C₆H₄PPh₂)(PPh₃)(MeLiOEt₂)₂ both have ³¹P n.m.r. spectra consisting of two doublets ($J_{PH} ≃ 15$ Hz, indicative of *cis*-phosphorus atoms) whose chemical shifts confirm that one phosphine is *ortho*-metallated and the other is not. Partial decoupling in the phenyl region of the ¹H spectrum of RuH(C₆H₄PPh₂)(PPh₃)(thf)₂ indicates that the hydride is *cis* to the two phosphine groups (consistent with the ¹H n.m.r. data) and hence the complex probably has stereochemistry (F) (Scheme 1). The most likely structure for RuMe(C₆H₄PPh₂)-(PPh₃)(MeLiOEt₂)₂ taking into account i.r. and ³¹P n.m.r. evidence is (G) (Scheme 1) in which the lithium atoms both attain their normal co-ordination number of four.

The ³¹P n.m.r. spectra of the alkyl hydrido-complexes RuHMe(PPh₃)₂(thf)₂ and RuHMe(PPh₃)₂(MeLiOEt₂)₂ both consist of a single resonance which splits into a doublet $J_{PH} ≈ 20$ Hz when the hydride is coupled with the phosphorus atoms. This spectrum could be consistent with mutually *trans*-phosphines or with *cis*-phosphines that are both *trans* to the additional ligand and *cis* to the hydride. Since, when the metallation reaction occurs, the phosphines in the product are indubitably *cis*, it seems likely that the phosphines in the alkylhydrido-complexes are also *cis* and that they have the stereochemistries (H) and (J) (Scheme 1) respectively. The ³¹P chemical shifts are also inconsistent with mutually *trans* phosphines.[30]

spectrum, together with small peaks arising from un-decomposed RuHMe(PPh₃)₂(thf)₂ and PPh₃. A further resonance, at 53.9 p.p.m., which splits into a doublet ($J_{PH} = 7.3$ Hz) when allowed to couple with a hydride is also observed. This resonance, which does not appear on warming a solution of RuH(Me)(PPh₃)₂(MeLi-OEt₂)₂ and MeLi in tetrahydrofuran cannot arise from exchange of RuH(Me)(PPh₃)₂(thf)₂ with free phosphine since resonances from both these species are observed in the spectrum and since no P–H coupling would be expected in this case. Because only a small amount of free phosphine is observed, it seems likely that the resonance at 53.9 p.p.m. arises from a tris-phosphine species, RuHMe(PPh₃)₃, which would be fluxional, rendering the phosphines equivalent. This complex may then *ortho*-metallate to give the final product, RuH(C₆H₄PPh₂)(PPh₃)₂(thf) (see Scheme 2).

The formation of RuMe(C₆H₄PPh₂)(PPh₃)₂(Et₂O) from the reaction of RuHCl(PPh₃)₃ with methyl-lithium in diethyl ether is accompanied by elimination of hydrogen in the *ortho*-metallation step, whereas in tetrahydrofuran methane is evolved and the product is RuH(C₆H₄PPh₂)-(PPh₃)₂(thf). This marked difference in behaviour may be attributed to the weakening of the Ru–H bond [as evidenced by the very low ν(Ru–H)] by interaction with a lithium atom in RuHMe(PPh₃)₂(MeLiOEt₂)₂ to such an extent that expulsion of hydrogen rather than of methane is favoured. The actual mechanism of the *ortho*-metallation step is of interest since, there

³⁰ P. R. Hoffmann and R. G. Coulton, *J. Amer. Chem. Soc.*, 1975, 94, 4221.

being only one hydride, it cannot involve reductive elimination to give a ruthenium(0) species followed by oxidative addition of the *ortho* C–H bond of a phenyl ring. It is also unlikely that oxidative addition of the C–H bond of the phenyl ring precedes the reductive elimination of hydrogen since this would involve a formally eight-co-ordinate ruthenium(IV) intermediate. Hence, it seems likely that the elimination of hydrogen is a concerted process, occurring through a four-centre transition state (K).
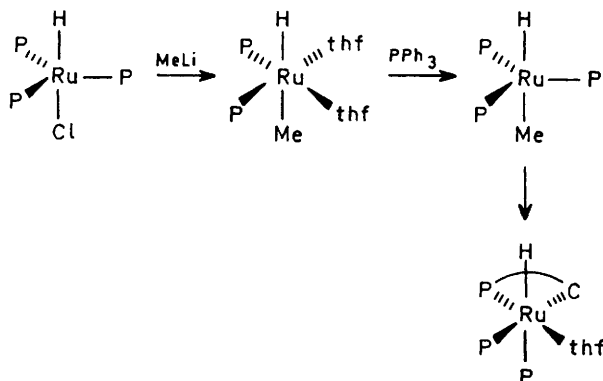
SCHEME 2 Alternative mechanism for formation of RuH(C₆H₄-PPh₂)(PPh₃)₂(thf) from RuHCl(PPh₃)₃ + MeLi in tetrahydrofuran

Presumably $RuH(C_6H_4PPh_2)(PPh_3)_2(Et_2O)$ is formed from the reaction of $RuHCl(PPh_3)_3$ with Me_3SiCH_2Li in diethyl ether because the ruthenium atom is unable to accommodate three bulky trimethylsilylmethyl groups

$(PPh_3)_2(thf)$ and $RuH(C_6H_4PPh_2)(PPh_3)(thf)_2$ respectively probably occur by elimination of methane from the methyl group and co-ordinated tetrahydrofuran *via* a transition state as in (L) followed by loss of dihydrofuran to give the hydride. A similar mechanism is implicated for the slow reaction of $RuH(C_6H_4PPh_2)$-$(PPh_3)_2(Et_2O)$ with tetrahydrofuran to give RuH_2-$(PPh_3)_3(thf)$.

EXPERIMENTAL

Microanalyses by Butterworth Microanalytical Consultancy Ltd. I.r. spectra were obtained using Perkin-Elmer 457 instrument, n.m.r. spectra using Perkin-Elmer R12 (60 MHz) and Varian XL 100 spectrometers, and mass spectra on V.G. Micromass model 770. M.p.s were determined in closed capillaries under argon using an Electrothermal melting point apparatus and are uncorrected. All solvents were thoroughly and carefully degassed and dried over sodium benzophenone ketyl (diethyl ether, tetrahydrofuran, or toluene) or sodium [benzene or light petroleum (b.p. 60—80 °C)] before use and all operations were carried out in an argon atmosphere using standard subaseal and catheter tubing techniques. Methane analyses were carried out by hydrolysis with water and measurement of gas evolved in a standard gas burette. Lithium analyses were carried out microanalytically or by destruction of a known weight of the complex with degassed water followed by titration with 0.01N-HCl.

All yields are *ca.* 70% or greater unless otherwise stated. Analytical data for the compounds are given in Table 4.

(*Diethyl ether*)(η³-2-*diphenylphosphinophenyl*)*hydridobis*-(*triphenylphosphineruthenium*(II).—RuHCl(PPh₃)₃ (2.1 g) was stirred with Me₃SiCH₂Li (7 ml, 0.68M in light petroleum)

TABLE 4

Analytical data for ruthenium complexes

Compound	Colour	M.p. (θc/°C)	Found (%)				Required (%)			
			C	H	P	Other	C	H	P	Other
RuH(C₆H₄PPh₂)(PPh₃)₂(Et₂O)	Yellow	90d	72.5	5.7	9.3		72.4	5.7	9.7	
RuH(C₆H₄PPh₂)(PPh₃)₂(thf)	Yellow	115—125d	72.6	5.8	10.4		72.5	5.5	9.7	
RuMe(C₆H₄PPh₂)(PPh₃)₂(Et₂O)	Yellow	160—170d	71.1	5.8	9.4	Me 1.7	72.7	5.9	9.5	Me 1.5
RuMe(C₆H₄PPh₂)(PPh₃)(MeLiOEt₂)₂	Yellow	220—240d	66.4	6.6	7.6	Me 4.7, Li 1.4, Ru 13.1	68.0	7.0	7.5	Me 5.4, Li 1.7, Ru 12.1
RuHMe(PPh₃)₃(Et₂O)₂ ᵃ	Yellow	175—180d	68.5	6.7	8.7	Me 1.93	67.6	6.8	7.9	Me 1.90
RuHMe(PPh₃)₃(MeLiOEt₂)₂	Yellow	165—170d	68.2	7.5	7.5	Me 5.6, Li 1.5	67.7	7.2	7.5	Me 5.4, Li 1.7
{RuH(C₆H₄PPh₂)(PPh₃)₂}₂(Zn₂Me₃Cl)	Light yellow	170—200d	67.2	4.8	9.9	Cl 1.1, Zn 6.3, Ru 9.2	67.1	5.0	9.4	Cl 1.8, Zn 6.6, Ru 10.2
{RuH(C₆H₄PPh₂)(PPh₃)₂}₂{Mg₂Me₃Cl(OEt₂)₂}	Yellow	190—210d	67.7	6.3	8.4	Cl 1.1	69.4	5.8	9.0	Cl 1.7

ᵃ Contaminated by *ca.* 5.5% LiCl according to Cl analysis.

on a face of the octahedron as in (J) and the weakening of the Ru–H bond of the alkylhydrido-complex does not occur. Similarly, $RuH(C_6H_4PPh_2)(PPh_3)_2(thf)$ forms in the reaction of $RuHCl(PPh_3)_3$ with methyl-lithium in tetrahydrofuran because the solvent, being a better base than diethyl ether, competes favourably with the metal hydride for the co-ordination sites on the lithium atom.

Finally, the reactions of $RuMe(C_6H_4PPh_2)LL'$ (L = PPh_3, L' = OEt_2; L = L' = $MeLiOEt_2$) with tetrahydrofuran to give methane and $RuH(C_6H_4PPh_2)$-

in degassed diethyl ether (100 ml) for 1 h. The yellow solution was filtered free from LiCl (after allowing it to settle) and evaporated to 25 ml. Yellow crystals of the *complex* separated overnight and were collected. Additional crops of the complex could be obtained by setting the filtrate aside after further evaporation.

(η³-2-*Diphenylphosphinophenyl*)*hydrido*(*tetrahydrofuran*)-*bis*(*triphenylphosphine*)*ruthenium*(II).—(*a*) RuHCl(PPh₃)₃ (0.4 g) and Me₃SiCH₂Li (1.5 ml, 1.01M in light petroleum) were stirred in degassed tetrahydrofuran (10 ml) for 10 min. The red-orange solution was evaporated to 3 ml and stored overnight at −17 °C. Yellow crystals of the

complex separated on addition of tetrahydrofuran (2 ml) and light petroleum (10 ml) and cooling to -17 °C. These were collected and dried *in vacuo*. Additional crops of the complex could be obtained by further addition of light petroleum and cooling.

(b) Similarly from $RuHCl(PPh_3)_3$ (0.6 g) and MeLi (5 ml; 0.57M in diethyl ether) at 0 °C for 30 min followed by warming to 36 °C. The product was identified by its ^{31}P and ^1H n.m.r. spectra.

(c) $RuMe(C_6H_4PPh_2)(PPh_3)_2(Et_2O)$ (*ca.* 0.1 g) was dissolved in tetrahydrofuran (0.5 ml); 1 mole equiv. of methane was evolved. On the evidence of the ^1H n.m.r. spectra only $RuH(C_6H_4PPh_2)(PPh_3)_2(thf)$ was present.

(*Diethyl ether*) (η^3-2-*diphenylphosphinophenyl*)*methylbis*(*triphenylphosphine*)*ruthenium*(II).—$RuHCl(PPh_3)_3$ (0.7 g, 0.075 mmol) and MeLi (2.1 ml; 0.9M in diethyl ether; 1.875 mmol) were stirred together at 0 °C in degassed diethyl ether for 30 min at 0 °C. After the LiCl had been allowed to settle at -12 °C the solution was filtered and evaporated to 4 ml. The *complex* separated as yellow crystals which were filtered off and dried *in vacuo*, during which time the yellow crystals decrepitated.

(η^3-2-*Diphenylphosphinophenyl*)*methylbis*(*methyl-lithium–diethyl ether*)*triphenylphosphineruthenate*(II). The reaction was carried out as described above with $RuHCl(PPh_3)_3$ (1 g) and MeLi (10 ml; 0.9M in diethyl ether) at room temperature.

$RuMe(C_6H_4PPh_2)(PPh_3)(MeLiOEt_2)_2$ was also prepared by stirring $RuH(Me)(PPh_3)_2(MeLiOEt_2)_2$ (0.2 g) under a solution of MeLi (2 ml; 0.9M) in diethyl ether (50 ml). After gas evolution had stopped (24 h), the yellow solid was filtered off and dried *in vacuo*. A few orange *crystals* of $RuH(C_6H_4PPh_2)(PPh_3)(OEt_2)_2$ were obtained by evaporation of the orange solution to 2 ml and cooling for several days at -15 °C.

Bis(*diethyl ether*)*hydridomethylbis*(*triphenylphosphine*)-*ruthenium*(II).—$RuHCl(PPh_3)_3$ 1.1 g (1.2 mmol) was stirred with MeLi (6 ml; 0.66M in diethyl ether, 3.6 mmol) at 0 °C in Et_2O (30 ml) for 1 h. The yellow crystalline *solid* which was contaminated with lithium chloride was filtered off and dried *in vacuo*.

Hydridomethylbis(*methyl-lithium–diethyl ether*)*bis*(*triphenylphosphine*)*ruthenate*(II). $RuHCl(PPh_3)_3$ (0.4 g) was stirred with MeLi (1.0 ml; 1.8M in diethyl ether) in degassed diethyl ether (30 ml) at 0 °C for 1 h. After the LiCl had been allowed to settle at 0 °C for several hours, the yellow solution was filtered, never being allowed to warm above 0 °C, and evaporated to 10 ml. Yellow crystals of the *complex* separated when the solution was cooled to -17 °C, and were collected and dried *in vacuo*. *Note:* It is essential to use methyl-lithium freshly prepared from lithium and methyl chloride for this reaction. If the MeLi has been stored at low temperatures, LiCl crystallises and lithium chloride does not then precipitate during the reaction being soluble in an excess of MeLi; it then co-precipitates with the product.

μ-*Chloro*-μ-*methyl-bis*[μ-*hydrido*-μ-*methyl*-(η^3-*diphenylphosphinophenyl*)*bis*(*triphenylphosphine*)*rutheniumzinc*] (Zn, Zn). $RuHCl(PPh_3)_3$ (0.4 g) and Me_2Zn (0.45 ml) were stirred together in diethyl ether (8 ml) at 0 °C for 3 h. The initially red solution precipitated a pale yellow solid which was filtered off and washed with diethyl ether (2 × 5 ml). The *complex* may be recrystallised unchanged from tetrahydrofuran–light petroleum as yellow crystals.

μ-*Chloro*-μ-*methyl-bis*{μ-*methyl*-(η^3-2-*diphenylphosphinophenyl*)*hydridobis*(*triphenylphosphine*)*ruthenium*[(*diethyl ether*)*magnesium*]}(Mg,Mg).—This complex was similarly prepared from $RuHCl(PPh_3)_3$ (0.44 g) and Me_2Mg (3.8 ml; 0.75M in diethyl ether) in diethyl ether (10 ml) at 0 °C. It could not be recrystallised.