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Preliminary communication

BASIC METALS

XXXIV*. SYNTHESIS AND REACTIVITY OF RuH(η^2-CH_2PMe_2)(PMe_3)$_3$

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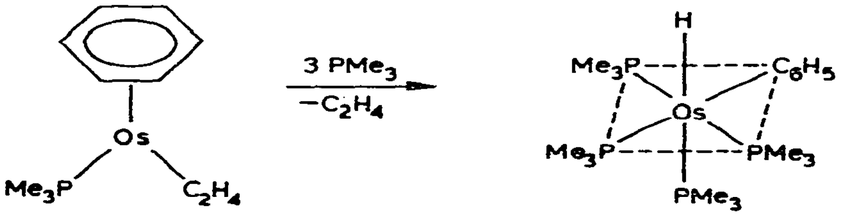
Summary

The complex RuH(η^2-CH_2PMe_2)(PMe_3)$_3$ is obtained by reduction of *trans*-$RuCl_2(PMe_3)_4$ with Na/Hg in benzene. In contrast to the iron analogue, this complex is configurationally stable on the NMR time scale and does not react with CO or $P(OMe)_3$ under normal conditions, but it does react with the electrophiles MeI, CS_2 and NH_4PF_6 to form RuI(η^2-CH_2PMe_2)(PMe_3)$_3$, Ru(η^3-$S_2CHPMe_2CH_2$)(PMe_3)$_3$ and $[RuH(PMe_3)_5]PF_6$, respectively.

The formation of the hydrido(phenyl)osmium complex *cis*-$OsH(C_6H_5)$-$(PMe_3)_4$ (II) by reaction of the benzeneosmium complex $C_6H_6Os(PMe_3)C_2H_4$ (I) [2] with an excess of PMe_3 represents an unusual example of an intramolecular insertion of a transition metal into an sp^2-C—H bond [3].



(I) (II)

To find out whether a reaction of this type represents a general method of forming aryl(hydrido)metal complexes we have now studied the reactivity of

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*For Part XXXIII see ref. 1.

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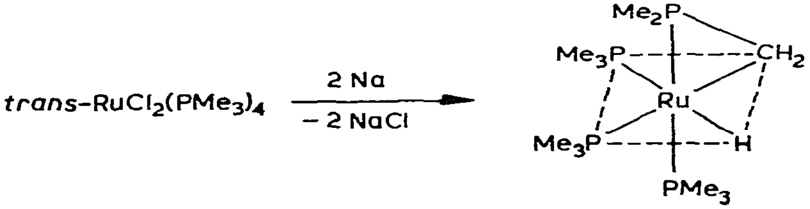
$C_6H_6Ru(PMe_3)C_2H_4$ [4], the ruthenium analogue of I, towards trimethylphosphine.

Although the Lewis-base properties of I and $C_6H_6Ru(PMe_3)C_2H_4$ (III) are very similar, the reactions of I and III with PMe_3 are completely different. Complex III reacts with PMe_3 by elimination of benzene rather than of ethylene to yield a rather labile compound, the spectroscopic data of which correspond to the composition $Ru(PMe_3)_4C_2H_4$ (^1H NMR (C_6D_6): δ = 1.47 vt, J' = 4.4 Hz and 1.19 vt, J' = 4.6 Hz (both signals corresponding to four PMe_3 groups); 0.95 m (C_2H_4)*. This finding led us to seek other routes to the aryl(hydrido) complex $RuH(C_6H_5)(PMe_3)_4$.

It is known from Chatt's work on low-valent transition metal complexes containing chelating diphosphines as ligands that the reduction of *trans*-$RuCl_2$-(dmpe)$_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) with sodium or potassium in the presence of benzene or naphthalene produces the compounds RuH(R)(dmpe)$_2$-(R = C_6H_5, $C_{10}H_7$) [5]. The corresponding iron complex $FeH(C_{10}H_7)$(dmpe)$_2$ [6] readily eliminates naphthalene to form the 16-electron species Fe(dmpe)$_2$, which is an excellent substrate for the activation of carbon—hydrogen bonds [7].

Expecting that $Ru(PMe_3)_4$ would oxidatively add to benzene, we tried to generate *cis*-$RuH(C_6H_5)(PMe_3)_4$ by reduction of *trans*-$RuCl_2(PMe_3)_4$ [8] with sodium amalgam in benzene. However, the ruthenium(II) complex is rather inert, and was consumed only after prolonged stirring for 7 days at 70°C. The elemental analysis and mass spectrum of the resulting orange, air-sensitive solid showed that its composition does not correspond to $RuH(C_6H_5)(PMe_3)_4$ but to $Ru(PMe_3)_4$. The ^1H and ^{31}P NMR data confirmed that the product is the ruthenium hydride complex $RuH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$ (IV), analogous to the well-known iron compound $FeH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$ (V) [9].



(IV)

The coordinatively unsaturated species $Ru(PMe_3)_4$ which is presumably an intermediate in the reduction of *trans*-$RuCl_2(PMe_3)_4$, evidently does not react with benzene by oxidative addition but is stabilised by an insertion of the metal into one of the $H—CH_2PMe_2$ bonds of the phosphine ligands.

Although they have wholly analogous structures complexes IV and V differ remarkably in their dynamic behaviour and also in their reactivity towards nucleophiles. Whereas complex V is fluxional at room temperature [9], the ruthenium analogue IV is configurationally stable on the NMR time scale. The equilibrium between the two isomers, $M(PMe_3)_4$ and $MH(CH_2PMe_2)$-

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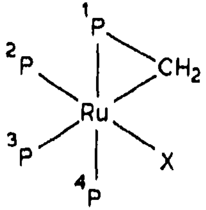
*Abbreviations used: vt, virtual triplet; vqui, virtual quintet; dqu, doublet of quartets; dqui, doublets of quintets

TABLE 1

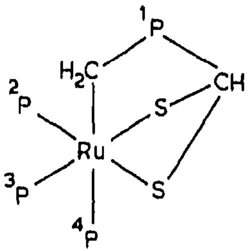
^{1}H NMR AND ^{31}P NMR SPECTRA OF IV, VI AND VIII, IN C_6D_6 (δ IN PPM, TMS INT. (^{1}H) AND 85% H_3PO_4 EXT. (^{31}P); J IN Hz) ASSIGNMENT ACCORDING TO STRUCTURES:

For IV,VI :



(X = H,I)

For VIII :

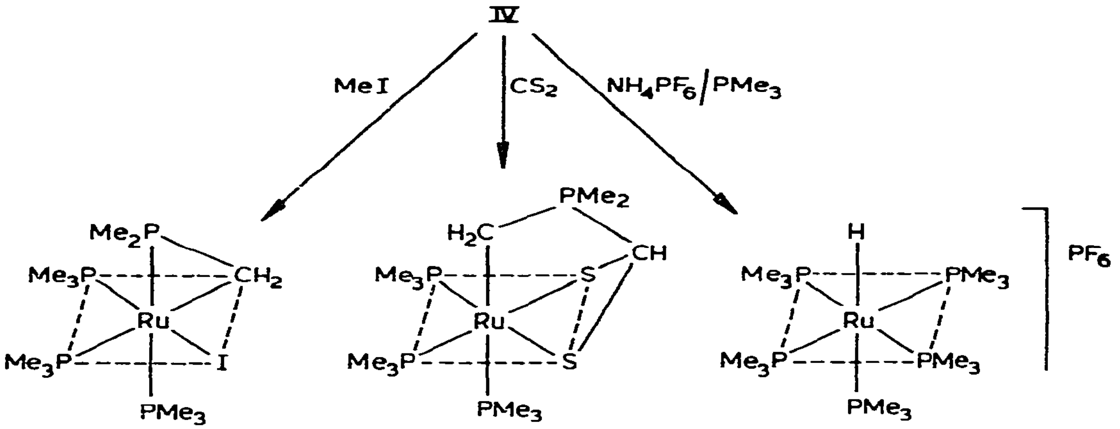


Complex	$^1PMe_2CH_2$	$^2PMe_3$	$^3PMe_3$	$^4PMe_3$	$^1PMe_2CH_2$	$^2PMe_3$	$^3PMe_3$	$^4PMe_3$
IV [a]	Me: 1.55dd $^2J(PH) = 7.0$, $^4J(PH) = 2.6$ Me: 1.26d $^2J(PH) = 5.0$ CH_2: −0.06, −0.59 [c]	1.34 m [b]	1.38 m [b]	1.12d $^2J(PH) = 5.2$	−30.72ddd $J(^1P^2P) = 25.3$ $J(^1P^3P) = 36.5$ $J(^1P^4P) = 191.3$	−9.23qu $J(^1P^2P) = J(^2P^3P)$ $= J(^2P^4P) = 25.3$	2.17ddd $J(^1P^3P) = 36.5$ $J(^2P^3P) = 25.3$ $J(^3P^4P) = 5.3$	6.25ddd $J(^1P^4P) = 191.3$ $J(^2P^4P) = 25.3$ $J(^3P^4P) = 5.3$
VI	Me: 2.12dd $^2J(PH) = 9.5$, $^4J(PH) = 2.2$ Me: 1.14dd $^2J(PH) = 9.5$, $^4J(PH) = 2.4$ CH_2: [d]	1.60 m [b]	1.64 m [b]	1.06d $^2J(PH) = 7.5$	−48.51ddd $J(^1P^2P) = 37.2$ $J(^1P^3P) = 34.2$ $J(^1P^4P) = 232.7$	−14.50dd $J(^1P^2P) = 37.2$ $J(^2P^3P) = 34.2$ $J(^2P^4P) < 3$	−9.31qu $J(^1P^3P) = J(^2P^3P)$ $= J(^3P^4P) = 34.2$	19.91dd $J(^1P^4P) = 232.7$ $J(^2P^4P) < 3$ $J(^3P^4P) = 34.2$
VIII [e]	Me: 1.43dd $^2J(PH) = 11.6$, $^4J(PH) = 0.9$ CH_2: [d]	1.22 vt $J' = 7.1$	(= $^2PMe_3$)	1.67d $^2J(PH) = 9.6$	27.08dt $J(^1P^4P) = 5.9$ $J(^1P^{2,3}P) = 13.4$	8.15dd $J(^{2,3}P^4P) = 26.8$ $J(^1P^{2,3}P) = 13.4$	(= $^2PMe_3$)	−0.88dt $J(^{2,3}P^4P) = 26.8$ $J(^1P^4P) = 5.9$

[a] Signal for RuH at $\delta = -10.20$ dqu, $J(^{1,2,3}PH) = 26$, $J(^4PH) = 82$ Hz. [b] Assignment of the two signals to the two PMe_3 groups in position 2 and 3 not possible; the ^{31}P-decoupled spectra show singlets. [c] Multiplets; the ^{31}P-decoupled spectrum shows two doublets of doublets with $J(HH) = 7.0$ and 3.5 Hz. [d] Signal not observed. [e] Signal for CH of the tripod ligand $CH_2Me_2P\,CHS_2$ at $\delta = 5.10$ dt, $^3J(PH) = 15.0$, $^4J(PH) = 4.0$ Hz.

$(PMe_3)_3$, which is well established for M = Fe [10], is largely shifted to the hydride side for M = Ru. Accordingly, complex IV does not react under normal conditions with CO or $P(OMe)_3$, whereas in the presence of the same ligands compound V readily forms the pentacoordinated iron(0) complexes $Fe(PMe_3)_{5-n}L_n$ (L = CO, $P(OMe)_3$; $n = 2$ and 3) [10].

In contrast to its inertness towards nucleophiles, the ruthenium compound IV readily reacts with electrophilic substrates such as methyl iodide, carbon disulfide and protonic acids. Thus treatment of IV with MeI in benzene gives the neutral iodoruthenium(II) complex $RuI(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$ (VI) as the main product (Scheme 1). Small amounts of *cis*-$RuI_2(PMe_3)_4$ (VII) are also obtained (^1H NMR (CH_2Cl_2): $\delta = 1.88$ vt. $J' = 6.0$ (two axial PMe_3 groups); 1.70 vt, $J' = 7.8$ Hz (two equatorial PMe_3 groups)). Complex VI is probably formed by nucleophilic attack of the ruthenium hydride on the carbon atom of the methyl iodide. The complex *cis*-$RuI_2(PMe_3)_4$ is possibly formed via $RuMe(I)(PMe_3)_4$ which would be expected as the primary product from the reaction of the isomer $Ru(PMe_3)_4$ and MeI, and which could react with methyl iodide to yield VII and ethane. Similar behaviour is known for $FeMe(I)(PMe_3)_4$, which gives $FeI_2(PMe_3)_2$ by further reaction with MeI [11].



(VI) (VIII) (IX)

+ *cis*-$RuI_2(PMe_3)_4$

(VII)

The reaction of IV with CS_2 in benzene leads (in 71% isolated yield) to a compound of empirical formula "$Ru(PMe_3)_4CS_2$". Although iron complexes of general composition $FeL_2L'_2(\eta^2\text{-}CS_2)$ are known [12], the NMR spectra of the product from IV and CS_2 clearly confirm the structure proposed in Scheme 1. The formation of the tripod ligand $CH_2PMe_2CHS_2$ in complex VIII presumably occurs by initial insertion of CS_2 into the Ru—P bond of the $Ru(\eta^2\text{-}CH_2PMe_2)$ unit and subsequent migration of the hydride ligand to the S_2C carbon atom.

Complex IV is inert towards PMe_3 in benzene, but in methanolic NH_4PF_6 the salt $[RuH(PMe_3)_5]PF_6$ (IX) is formed. In this case, the ruthenium complex behaves like the iron analogue V, which after treatment with PMe_3/NH_4PF_6 in THF yields $[FeH(PMe_3)_5]PF_6$ [13]. The formation of the cation $[RuH(PMe_3)_5]^+$ was observed previously during the replacement of cycloocta-1,5-diene in $[RuH(C_8H_{12})(PMe_3)_3]^+$ by PMe_3 but attempts to isolate the PF_6 salt led only to mixtures of IX and $[RuH(C_8H_{12})(PMe_3)_3]PF_6$ [14]. The ^1H NMR spectrum of IX shows in CD_3NO_2 three signals at δ = 1.57 vqui, J' = 4.8 Hz (four equatorial PMe_3 groups); 1.39 d, $J(PH)$ = 6.0 Hz (one axial PMe_3 group) and — 11.31 dqui, $J(P_{cis}H)$ = 25, $J(P_{trans}H)$ = 74 Hz (Ru—H).

There is clear evidence that in compounds of stoichiometric composition $M(PMe_3)_4$ ruthenium stabilises even more strongly than iron the hydride isomer $MH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$. For M = Ru, in contrast to M = Fe, this isomer determines the reactivity of the complex. Whereas nucleophilic attack is largely inhibited (probably due to the octahedral coordination and the 18-electron configuration of the metal atom), reactions with electrophiles readily occur to yield six-coordinate products. There is no indication that the coordinatively unsaturated isomer $Ru(PMe_3)_4$, which may be present in very small concentrations in solutions of IV, behaves like $Ru(dmpe)_2$ in activating sp^2-carbon—hydrogen bonds.

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References

1 H. Werner and B. Klingert, J. Organometal. Chem., in press.
2 H. Werner and R. Werner, J. Organometal. Chem., 194 (1980) C7.
3 R. Werner and H. Werner, Angew. Chem., in press.
4 H. Werner and R. Werner, J. Organometal. Chem., 174 (1979) C63.
5 J. Chatt and J.M. Davidson, J. Chem. Soc., (1965) 843.
6 S.D. Ittel, C.A. Tolman, A.D. English and J.P. Jesson, J. Amer. Chem. Soc., 98 (1976) 6073.
7 C.A. Tolman, S.D. Ittel, A.D. English and J.P. Jesson, J. Amer. Chem. Soc., 101 (1979) 1742.
8 R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse and K.M.A. Malik, J. Chem. Soc. Dalton, (1980) 511.
9 H.H. Karsch, H.F. Klein and H. Schmidbaur, Angew. Chem., 87 (1975) 630; Angew. Chem. Int. Ed. Engl., 14 (1975) 637; J.W. Rathke and E.L. Muetterties, J. Amer. Chem. Soc., 97 (1975) 3272.
10 H.H. Karsch, H.F. Klein and H. Schmidbaur, Chem. Ber., 110 (1977) 2200.
11 H.H. Karsch, Chem. Ber., 110 (1977) 2699.
12 H. Le Bozec, F.H. Dixneuf, A.J. Carty and N.J. Taylor, Inorg. Chem., 17 (1978) 2568; P. Conway, S.M. Grant and A.R. Manning, J. Chem. Soc. Dalton, (1979) 1920.
13 H.H. Karsch, Chem. Ber., 110 (1977) 2222.
14 T.V. Ashworth, E. Singleton, M. Laing and L. Pope, J. Chem. Soc. Dalton, (1978) 1032.