Journal of Organometallic Chemistry, 210 (1981) C5—C8
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY. PREPARATION AND REACTIONS OF SOME TRIMETHYLPHOSPHINE COMPLEXES

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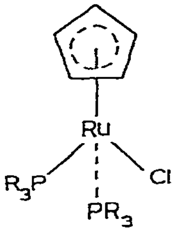
(Received February 2nd, 1981)

Summary

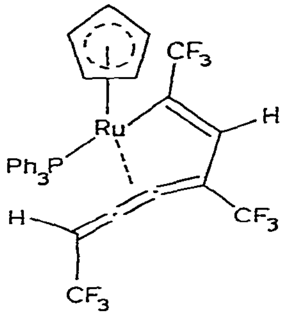
Cationic complexes $[Ru(L)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (L = olefin, allene, diene, alkyne, CS_2) have been prepared from $RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$ and L in the presence of NH_4PF_6. Oxidative addition of HCl or Cl_2 to the chloro complex affords the organoruthenium(IV) complexes $[RuXCl(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (X = H or Cl, respectively); related reactions have given $[HOsBr(PR_3)_2(\eta\text{-}C_5H_5)]^+$ (R = Me and Ph).

Our studies of the chemistry of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (I) and its derivatives have uncovered a wealth of unusual chemistry [1], resulting in the synthesis of such complexes as the 1,3,4,5-hexatetraenyl complex II [2], and the vinylidene derivative III [3]. Many reactions of I are facilitated by the ready loss of the bulky PPh_3 ligand. It was thus of interest to investigate the chemistry of the trimethylphosphine analogue IV; the smaller size of the PMe_3 ligand should result in its being attached more tightly, and its increased basicity should result in the reactivity of IV towards unsaturated molecules, for example, being considerably higher than that of I.

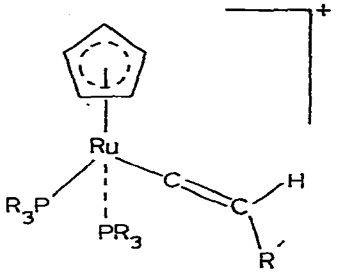
Complex IV is readily made by tertiary phosphine exchange with I in light petroleum at 100°C; the complex forms orange crystals, m.p. 130°C, and is accompanied by white $[Ru(PMe_3)_3(\eta\text{-}C_5H_5)]Cl$ (V), formed by displacement of chloride by a third molecule of the highly nucleophilic PMe_3. The tighter bonding of the PMe_3 ligand is demonstrated by the considerably shorter Ru—P distances: 2.273 Å in IV versus 2.335 Å in I [4].



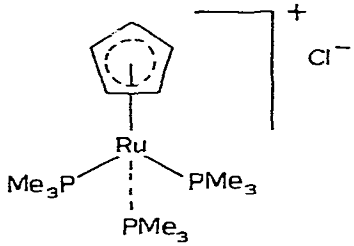
(I, R = Ph ;
IV, R = Me)



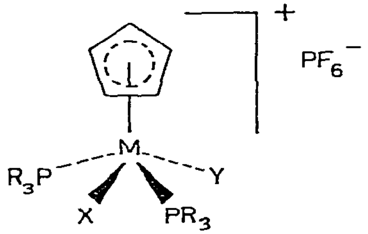
(II)



	R	R'
III	Ph	Ph
XV	Me	H
XVI	Me	Ph



(V)



	M	R	X	Y
XVIII	Ru	Me	H	Cl
XIX	Os	Me	H	Br
XX	Ru	Me	Cl	Cl
XXI	Os	Ph	H	Br

The increased reactivity of IV towards olefins and alkynes (un) is demonstrated by the ready formation of the cationic complexes $[Ru(un)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ in reactions carried out in the presence of NH_4PF_6 (Scheme 1). Thus complexes with ethylene (VI) [white; ^{1}H NMR* δ 2.48 t, *J*(HP) 3.8 Hz, C_2H_4], fumaronitrile (VII) [red; ν(CC) 1600w, ν(CN) 2209s cm^{-1}; ^{1}H NMR δ 6.78, 6.87, =C*H*], 1,3-butadiene (VIII) [white; ν(CC) 1619w cm^{-1}], allene (IX) [white; ν(CC) 1725w, 1685w cm^{-1}; ^{1}H NMR δ 5.50 m, =CH_2; 6.23 m, coordinated =CH_2], 1,1-dimethylallene (X) [white; ^{1}HNMR δ 1.83 s, C*Me*$_2$; 5.35 m, =CH_2], diphenylacetylene (XI) [yellow; ν(CC) 1900w cm^{-1}], ethyl phenylpropiolate (XII) [yellow; ν(CC) 1880w, 1852w; ν(CO) 1698vs cm^{-1}], dimethyl acetylenedicarboxylate (XIII) [yellow; ν(CC) 1865s; ν(CO) 1696vs cm^{-1}], and hexafluorobut-2-yne (XIV) [orange-yellow; ν(CC) 1863m cm^{-1}] have been prepared and suitably characterised**, whereas we have been unable

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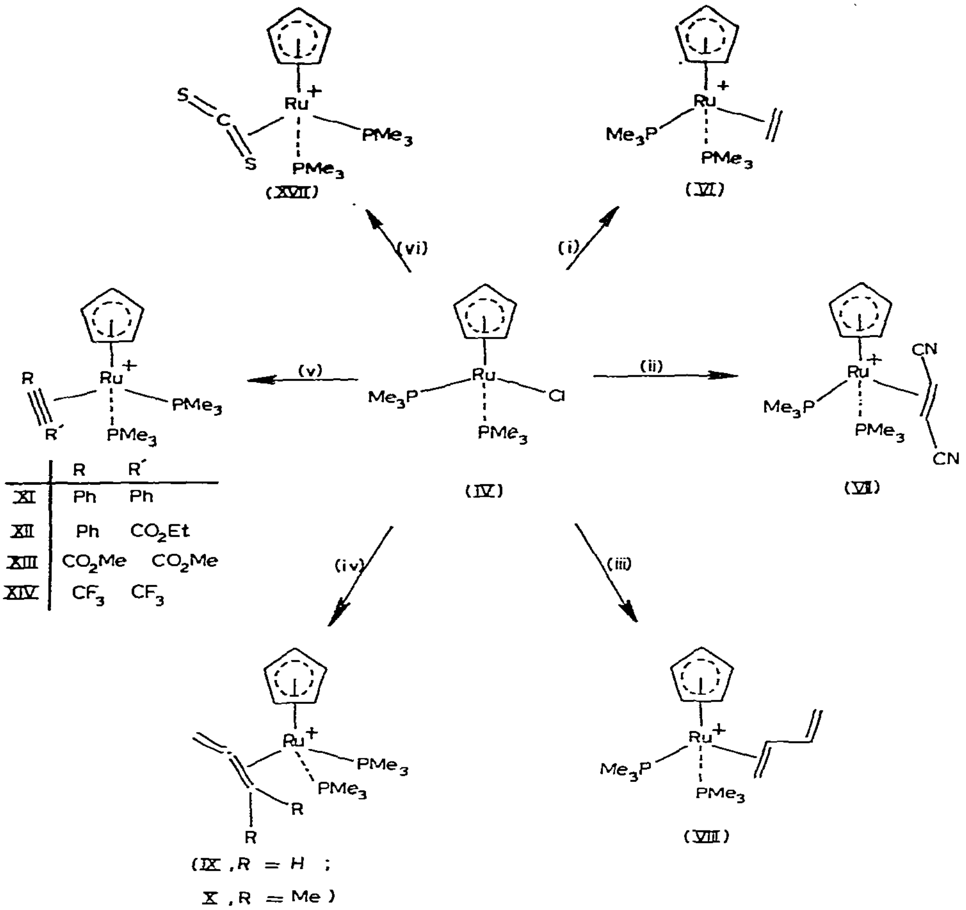
*In ppm.

** All new complexes have satisfactory elemental analyses, and characteristic resonances for the C_5H_5 and PMe_3 ligands in their ^{1}H and ^{13}C NMR spectra.



	R	R′
XI	Ph	Ph
XII	Ph	CO_2Et
XIII	CO_2Me	CO_2Me
XIV	CF_3	CF_3

SCHEME 1

Reagents (i) C_2H_4 ; (ii) *trans*-CH(CN)=CH(CN); (iii) $CH_2=CHCH=CH_2$; (iv) $CH_2=C=CR_2$; (v) $RC\equiv CR'$; (vi) CS_2 ; all reactions carried out in the presence of NH_4PF_6.

to prepare analogous complexes containing PPh_3 from I. We note that the complexes $[Ru(un)(dppe)(\eta\text{-}C_5H_5)]PF_6$ (un = C_2H_4, CH_2=CHMe, CH_2=CHPh, $CH_2=CHCO_2Me$ and $CH_2=CHCH=CH_2$, dppe = $Ph_2PCH_2CH_2PPh_2$) have been briefly reported [5]. As found with the PPh_3 series, however, 1-alkynes react with IV to give the vinylidene complexes, such as yellow $[Ru(\eta^1\text{-}C=CH_2)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (XV) [ν(CC) 1749m, 1632w cm^{-1}; ^1H NMR δ 5.35 t, J(HP) 7.2 Hz, $=CH_2$] and deep red $[Ru(\eta^1\text{-}C=CHPh)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (XVI). A further indication of the reactivity of IV is given by the reaction with CS_2, which affords orange $[Ru(\eta^2\text{-}S=C=S)(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (XVII) [ν(CS) 824s cm^{-1}].

This high reactivity suggested that IV and the related osmium complex should undergo oxidative addition reactions to form ruthenium(IV) or osmium(IV) derivatives. The reactions between these complexes and either HPF_6 or Cl_2 gave directly $[HMX(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ [M = Ru, X = Cl

(XVIII); M = Os, X = Br (XIX)] and $[RuCl_2(PMe_3)_2(\eta\text{-}C_5H_5)]PF_6$ (XX), respectively. Complexes XVIII and XIX are readily characterised on the basis of characteristic MH resonances at δ −9.7t and −14.9t, respectively, and weak ν(MH) bands around 2040 cm^{-1}. These metal(IV) complexes also have unusually low-field C_5H_5 resonances, at δ ca. 6.0. In the PPh_3 series, only $[HOsBr(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (XXI) has been obtained, and characterised by the OsH resonance at δ −12.5t [*J*(HP) 34 Hz]. Addition of dibromine to $RuBr(CO)_2(\eta\text{-}C_5Me_4Et)$ gives $RuBr_3(CO)(\eta\text{-}C_5Me_4Et)$ in an oxidative elimination reaction. In this case, it is interesting to note that a CO group is lost, the high electron density at the metal atom being supplied by the strongly electron-donating polyalkylcyclopentadienyl group [6].

Acknowledgement

We thank the Australian Research Grants Committee for support of this work.

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Note added in proof. Shortly after submission of this Communication, the paper by P.M. Treichel and D.A. Komar, "Syntheses of olefin and acetylene complexes $[Ru(C_5H_5)(PMe_3)_2(un)]PF_4$" (*Inorg. Chim. Acta*, 42 (1980) 277) was received in the authors' library. This describes the preparation of complexes XI, XIII and XVI, and of several related derivatives.