Journal of Organometallic Chemistry, 156 (1978) C43—C46
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PHOSPHINE INDUCED REDUCTIVE ELIMINATION REACTIONS : SYNTHESIS OF RUTHENIUM(0) FLUOROPHOSPHINE COMPLEXES FROM RUTHENIUM(II) HYDRIDE PRECURSORS

ABDUL-RAZZAK AL-OHALY, ROBERT A. HEAD and JOHN F. NIXON,*

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ
(Great Britain)

(Received June 23rd, 1978)

Summary

The zerovalent ruthenium complexes $Ru(PF_2NMe_2)_5$, $Ru(PF_2NC_4H_8)_5$, $Ru(PF_3)_3(PPh_3)_2$, and $Ru(PF_3)_4(PPh_3)$ are readily obtained by reductive elimination of acetic acid from $RuH(CO_2Me)(PPh_3)_3$ by treatment with the appropriate fluorophosphine

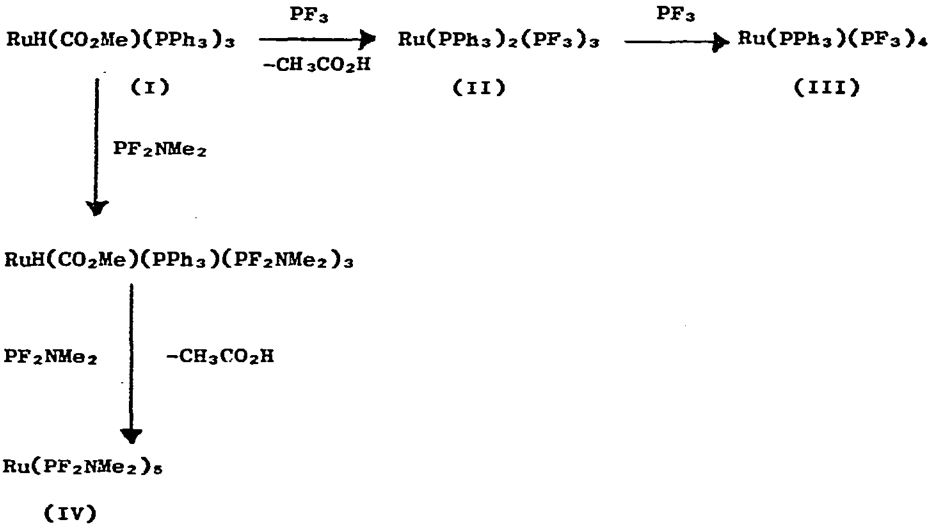
---

Oxidative addition and reductive elimination reactions are key steps in a number of homogeneous catalytic processes [1-6]. Recently Cole-Hamilton and Wilkinson [7] showed that alkane elimination from alkyl hydridotriphenylphosphine complexes of ruthenium(II) involves abstraction of an *ortho*-hydrogen of a phenyl ring on phosphorus by the alkyl group. In contrast to earlier reports [8,9], the reaction of $RuH_2(PPh_3)_4$ with ethylene does not give the zerovalent $Ru(PPh_3)_3(C_2H_4)$ complex. Instead a hydrido *ortho*-metallated phosphine complex of ruthenium(II) is formed, although with butadiene and pent-1-ene the zerovalent $Ru(PPh_3)_3$(diene) (diene = butadiene, penta-1,3-diene) complexes are formed [10].

In view of the report that $Ru(CO)_3(PPh_3)_2$ is obtained by prolonged treatment of $RuH(CO_2Me)(PPh_3)_3$ (I) with carbon monoxide [11].

we have studied the phosphine induced acetic acid elimination from (I) as a synthetic route to zerovalent ruthenium phosphine complexes.

A rapid reaction occurs when (I) and PF_3 (1:3) are warmed from -196° C to room temperature and an almost quantitative yield of the zerovalent complex $Ru(PPh_3)_2(PF_3)_3$, (II), is formed. When the reaction is carried out in benzene at 95° C, the product is $Ru(PPh_3)(PF_3)_4$, (III). Both complexes are fluxional in solution, exhibiting the typically complex ^{19}F and ^{31}P NMR spectra expected for these types of $[AX_3]_3$ and $[AX_3]_4$ spin systems (A = phosphorus, X = fluorine) with further coupling to the PPh_3 ligands [for (III) Φ_F = 4.3 p.p.m.; δ_{PF_3} (rel. TMP) = 3.9 p.p.m., δ_{PPh_3} = 96.4 p.p.m., $^2J(PP')$ = 65.9 Hz; $J(PF') + 2J(PF')$ = 1228 Hz, $J(\underline{P}Ph_3\underline{F})$ = 2.5 Hz. For (IV) Φ_F = -1.2 p.p.m., δ_{PF_3} = -6.3 p.p.m., δ_{PPh_3} = 10.2 p.p.m., $J(PF) + 3J(PF')$ = 1235 Hz.



Treatment of (I) with PF_2NMe_2 under mild conditions shows that the first step in these reactions is phosphine ligand exchange and $RuH(CO_2Me)(PPh_3)(PF_2NMe_2)_3$ is formed in which the acetate group is mono-dentate. At higher temperatures acetic acid elimination occurs and the white, air stable zerovalent complex $Ru(PF_2NMe_2)_5$. (IV), is formed. The ^1H NMR spectrum of (IV) shows the expected broad resonance at τ . 7.3, while the ^{19}F and ^{31}P NMR spectra show the expected complexity for an $[AX_2]_5$ spin system showing that the molecule is stereochemically non rigid [Q_F = 24.9 p.p.m., $J(PF) + 4J(PF')$ = 1014 Hz, δ_P = -39.5 p.p.m.]. The mass spectra of (IV) shows a parent ion at m/e = 667 and ions corresponding to the stepwise loss of PF_2NMe_2. The pentakis(piperidinodifluorophosphine)ruthenium(0) complex $Ru(PF_2NC_4H_8)_5$, (V), was made by a similar route [Φ_F = 24.0 p.p.m., $J(PF) + 4J(PF')$ = 1018 Hz, δ_P = -34.5 p.p.m.].

The syntheses of $Ru(PF_2NMe_2)_5$ and $Ru(PF_2NC_4H_8)_5$ are of interest in view of the very recent report [12] of the isolation of $Fe(PF_2NMe_2)_5$ in 14% yield by co-condensation of iron vapour with PF_2NMe_2.

We find evidence for acetic acid elimination from (I) on treatment with $P(OMe)_3$ in methanol. However, the resulting zerovalent complex appears to undergo protonation rather readily and this has been noted by other workers on related systems [13,14]. The cage phosphite $P(OCH_2)_3CMe$, on the other hand, reacts with (I) to give $RuH(CO_2Me)$-$[P(OCH_2)_3CMe]_3(PPh_3)$ while $Ph_2PCH_2CH_2PPh_2$ (dppe) gives $RuH(CO_2Me)$-$(dppe)_2$, (VI). Complex (VI) readily reacts with chlorinated solvents to give $RuHCl(dppe)_2$ and with carbon monoxide and phosphine ligands to give complexes of the type $RuH(CO_2Me)(dppe)_2L$ [L = CO, PF_3, PF_2NMe_2, $P(OMe)_3$, $P(OCH_2)_3CMe$] rather than *via* elimination of acetic acid and formation of $Ru(dppe)_2L$, related to the known complexes $M(dmpe)_2P'$ (M = Fe, Ru) reported recently [15].

Acknowledgement

We thank S.R.C. and the Saudi Arabian Governemt for financial support.

References

1 L. Vaska, Accounts of Chem. Research, 1 (1968) 335; J. Amer. Chem. Soc., 93 (1971) 6671.

2 J. Halpern, Accounts Chem. Research, 3 (1970) 386.

3 J.P. Collman, Accounts Chem. Research, 1 (1968) 136.

4 J.P. Collman and W.R. Roper, Advan. Organometal. Chem., 7 (1968) 54.

5 B.L. Shaw and R.E. Stainbank, J. Chem. Soc. (A), 3716 (1971).

6 E.L. Muetterties and P.L. Watson, J. Amer. Chem. Soc., 98 (1976) 4665; J. Chem. Soc. (Dalton), 1995 (1976).

7 D.J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc. (Dalton), 1995 (1976).

8 S. Komiya, A. Yamamoto, and S. Ikeda, J. Organometal. Chem., 42 (1972 C65.

9 S.Komiya and A. Yamamoto, Bull. Chem. Soc. Japan, 69 (1976) 2553.

11 G. Wilkinson, J.D. Rose, J.O. Gilbert and R.P. Richardson, J. Chem. Soc. (A), 2610 (1969).

10 D.J. Cole-Hamilton and G. Wilkinson, Nouveau J. de Chimie, 1 (1977) 141.

12 M. Chang, R.B. King, and M.G. Newton, J. Amer. Chem. Soc., 100 (1978) 998.

13 A.D. English, S.D. Ittel, C.A. Tolman, P. Meakin, and J.P.Jesson, J. Amer. Chem. Soc., 99 (1977) 117.

14 S.D. Ittel, personal communication.

15 S.D. Ittel, C.A. Tolman, A.D. English, and J.P.Jesson, J. Amer. Chem. Soc., 98 (1976) 6073; J. Amer. Chem. Soc., in the press.