Journal of Organometallic Chemistry, 72 (1974) C15–C17

Preliminary communication

CATALYTIC HYDROGENATION AND ISOMERISATION OF TERMINAL OLEFINS BY TRIFLUOROPHOSPHINERHODIUM HYDRIDE COMPLEXES

JOHN F. NIXON and J. RICHARD SWAIN

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

(Received April 5th, 1974)

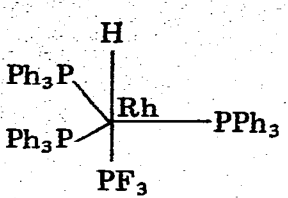
Summary

The trifluorophosphine complex $RhH(PF_3)(PPh_3)_3$, the analogue of the well-known homogeneous catalyst $RhH(CO)(PPh_3)_3$, has been synthesised and found to be a highly active catalyst for both the hydrogenation and isomerisation of terminal olefins, and the complex $RhH(PF_3)_2(PPh_3)_2$ has been found to bring about rapid isomerisation of terminal olefins.

The similarity of the chemical behaviour of transition metal complexes of carbon monoxide and that of analogous complexes of trifluorophosphine is well established [1, 2]. The ability of the carbonyl complex $RhH(CO)(PPh_3)_3$ to function as a homogeneous catalyst for hydrogenation, isomerisation and hydroformylation of terminal olefins [2–6] prompted us to study related trifluorophosphine complexes.

We have synthesised the yellow crystalline complex $RhH(PF_3)(PPh_3)_3$ (I) [ν(Rh–H) 2066 cm^{-1}] from the reaction of equimolar amounts of $RhH(PPh_3)_4$ and trifluorophosphine in benzene at room temperature. Similarly, the rather insoluble white solid complex $RhH(PF_3)_2(PPh_3)_2$ (II) [ν(Rh–H) 1986 cm^{-1}] was obtained in high yield when the molar ratio of $RhH(PPh_3)_4$ to PF_3 is 1/2.

In the ^1H NMR spectrum of (I) in CH_2Cl_2 solution the resonance for the hydride proton is centred at τ 19.8 ppm and consists of a widely spaced doublet [^2J(PH) 199 Hz] of quartets [^3J(HF) 37 Hz] further split into doublets [^1J(RhH) 3.6 Hz]. The large coupling constant to the phosphorus of the unique phosphorus ligand suggests that the PF_3 molecule is *trans* to the hydride in a trigonal bipyramidal structure. In the analogous complex $RhH(CO)(PPh_3)_3$ the CO and hydride ligands are known to occupy apical positions in a slightly distorted trigonal bipyramid [7]. The ^{31}P NMR spectrum of (I) shows two doublets of quartets for the coordinated PF_3 [^1J(PF) 1333, ^2J(PRh) 254, ^2J(PH) 200 Hz] and a doublet [^2J(PRh) 147 Hz] for the three equivalent triphenylphosphine ligands. The ^{19}F NMR spectrum of (I) is broad at room temperature but at 50°



(I)

consists of two well resolved widely spaced doublets of doublets [^1J(PF) 1331, ^2J(RhF) 11, ^3J(HF) 38 Hz].

It is interesting to note that whereas the hydride resonance in the ^{1}H NMR spectrum of $RhH(PF_3)(PPh_3)_3$ is well resolved at 30° and is little changed on cooling the sample to —70°, the corresponding resonance for $RhH(CO)(PPh_3)_3$ is broad at room temperature and is only resolved at —30° [3, 8]. This broadening has been ascribed to the ready dissociation of a triphenylphosphine molecule to produce $RhH(CO)(PPh_3)_2$, and the latter is suggested to be the reactive intermediate in hydrogenation and isomerisation reactions catalysed by $RhH(CO)(PPh_3)_3$ [5]. The observation of spin coupling between the rhodium and phosphorus nuclei in both $RhH(PF_3)(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ [^1J(PRh) 155 Hz] in the presence or absence of added PPh_3 at room temperature indicates that the lifetime of free and coordinated ligand is about 10^{-2}—10^{-3} sec in these complexes.

Complex (I) is a very highly active catalyst for the hydrogenation of terminal olefins. The initial rate of hydrogenation of 1-octene (10 ml in 90 ml benzene) with 0.1 mMol catalyst is found to be six times faster for (I) than for $RhH(CO)(PPh_3)_3$. The isomerisation of 1-octene to 2-octenes is also catalysed by (I) in the presence of hydrogen or nitrogen and again the rate of isomerisation is faster than for $RhH(CO)(PPh_3)_3$ [e.g., 10 ml 1-octene treated with 0.15 mMol (I) under 1 atm H_2 in benzene at 25° gives 47% octane and 53% 2-octenes after 30 min]. Interestingly the analogous cobalt complex $CoH(PF_3)(PPh_3)_3$ exhibits no catalytic hydrogenation properties, but does slowly isomerise 1-alkenes at 50° in benzene [9].

The ready isolation of (II) is noteworthy since the analogous carbonyl complex $RhH(CO)_2(PPh_3)_2$, which has been suggested to be the principal catalytically active intermediate in the hydroformylation reactions catalysed by $RhH(CO)(PPh_3)_3$ [4], exists only in solution under a pressure of H_2 and carbon monoxide. Complex (II) does not catalyse hydrogenation of terminal olefins, but does catalyse their isomerisation under hydrogenation conditions at an even faster rate than (I) [e.g., 5 ml 1-octene in benzene at 25° is 80% isomerised to 2-octenes by 0.08 mMol (II) after 8 min and the conversion is complete after 30 min].

Treatment of (I) with C_2F_4 results in absorption of an equimolar amount of the fluoro-olefin to afford $Rh(C_2F_4H)(PF_3)(PPh_3)_2$ while hexafluoro-2-butyne readily inserts into the metal—hydrogen bond to yield the vinyl complex $Rh(CF_3C{=}CCF_3H)(PF_3)(PPh_3)_2$ [10]. (I) also reacts with allyl chloride affording propene and the known complex *trans*-$RhCl(PF_3)(PPh_3)_2$ [11], but no reaction occurs with alkyl halides or triethylsilane.

We wish to thank the S.R.C. for a postdoctoral Fellowship (for J.R.S.).

References

1 J.F. Nixon, Advan. Inorg. Chem. Radiochem., 13 (1970) 363; Endeavour, (1973) 19.
2 Th. Kruck, Angew. Chem. Intern. Ed., 6 (1967) 53.
3 D. Evans, G. Yagupsky and G. Wilkinson, J. Chem. Soc. A, (1968) 2660.
4 D. Evans, J.A. Osborn and G. Wilkinson, J. Chem. Soc. A, (1968) 3133.
5 C. O'Connor and G. Wilkinson, J. Chem. Soc. A, (1968) 2665.
6 M. Yagupsky and G. Wilkinson, J. Chem. Soc. A, (1970) 941.
7 S.J. La Placa and J.A. Ibers, Acta Cryst., 18 (1965) 511.
8 K.C. Dewhirst, W. Keim and C.A. Reilly, Inorg. Chem., 7 (1968) 546.
9 M.A. Cairns and J.F. Nixon, J. Organometal. Chem., in press.
10 J.F. Nixon and J.S. Poland, unpublished results.
11 D.A. Clement and J.F. Nixon, J. Chem. Soc. Dalton, (1972) 2553.