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Preliminary communication

Ethylene displacement from π-cyclopentadienyldiethylenerhodium(I)

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In contrast to the ready displacement of ethylene from certain square planar rhodium(I) ethylene complexes[1–5] the related π-cyclopentadienyldiethylenerhodium(I) compound[6], π-$C_5H_5Rh(C_2H_4)_2$, is inert to substitution by ligands such as triphenylphosphine, carbon monoxide and cyanide ion[2]. This difference has been attributed to the fact that in π-$C_5H_5Rh(C_2H_4)_2$ the metal can be regarded as having an inert gas configuration whereas the 16*e* square-planar rhodium(I) complex has a vacant orbital available to the incoming ligand[2].

Ethylene is, however, readily displaced from π-$C_5H_5Rh(C_2H_4)_2$ by ligands such as SO_2 and tetracyanoethylene which have Lewis acid character and the metal is believed to act as the donor atom[2]. Recently the complex π-$C_5H_5Rh(C_2H_4)_2 \cdot HgCl_2$ has been reported[7], and the Lewis basicity of transition metals is well established[8,9].

We have found that fluorophosphines, L, which have acceptor properties[10,11] (*e.g.*, PF_3 forms a 1/1 complex with Me_3N at low temperature)[12], also readily displace ethylene from π-$C_5H_5Rh(C_2H_4)_2$ under mild conditions affording high yields of the yellow π-cyclopentadienylbis(fluorophosphine)rhodium(I) complexes, π-$C_5H_5RhL_2$ (I).

$$\pi\text{-}C_5H_5Rh(C_2H_4)_2 \xrightarrow{2L} \pi\text{-}C_5H_5RhL_2 + 2C_2H_4$$

(I)

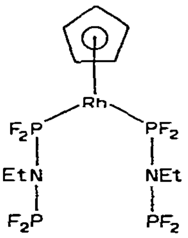
($L = PF_3, CF_3PF_2, CCl_3PF_2, CCl_2HPF_2, Me_2NPF_2, (CF_3)_2PF$)

(I) ($L = PF_3$) has recently been synthesised from $[RhCl(PF_3)_2]_2$ and NaC_5H_5[13]. The failure of carbon monoxide to displace ethylene from π-$C_5H_5Rh(C_2H_4)_2$[2] suggests that CO has weaker acceptor properties than fluorophosphines[10,11].

As in the case of the ethylene-π-$C_5H_5Rh(C_2H_4)_2$ system, no exchange is observed between free and coordinated PF_3 in π-$C_5H_5Rh(PF_3)_2$[13], whereas PF_3 and $[RhCl(PF_3)_2]_2$ readily undergo rapid intermolecular exchange[13,14]. Similarly no evidence was found for the intermediate π-$C_5H_5Rh(C_2H_4)(PF_3)$ when a solution of equimolar amounts of

π-$C_5H_5Rh(C_2H_4)_2$ and π-$C_5H_5Rh(PF_3)_2$ was heated at 60°, in sharp contrast to the immediate formation of $[RhCl(C_2H_4)(PF_3)]_2$ when solutions of $[RhCl(C_2H_4)_2]_2$ and $[RhCl(PF_3)_2]_2$ were mixed at room temperature[15]. π-Allylic trifluorophosphinerhodium(I) complexes, *e.g.*, π-all $Rh(PF_3)_3$, (all = C_3H_5; C_4H_7; C_6H_9) undergo phosphine exchange via a dissociative mechanism[16].

Ethylaminobis(difluorophosphine), $EtN(PF_2)_2$, which acts as a bidentate ligand towards Group VI metals[17] rapidly reacts with π-$C_5H_5Rh(C_2H_4)_2$ at room temperature to yield rather unexpectedly π-$C_5H_5Rh[EtN(PF_2)_2]_2$. ^{19}F NMR studies establish the presence of coordinated and uncoordinated PF_2 groups in this complex in accordance with structure (II).



(II)

The identity of the complexes of type (I) is confirmed by their characteristic ^{19}F NMR spectra which are typical of the X part of an $[X_nA]_2$ spin system, (X = fluorine, A = phosphorus)[17,18,19], each line being further split into a 1/1 doublet by the ^{103}Rh nucleus (I ½, 100% natural abundance). These NMR spectra will be discussed in detail in a later publication[20]

REFERENCES

1 R. Cramer, *J. Amer. Chem. Soc.*, 86 (1964) 217; *Accounts Chem. Res.*, 1 (1968) 186.
2 R. Cramer, *J. Amer. Chem. Soc.*, 89 (1967) 5377.
3 J.T. Mague and G. Wilkinson, *J. Chem. Soc. A*, (1966) 1736.
4 J. Powell and B.L. Shaw, *J. Chem. Soc. A*, (1968) 211.
5 S. Otsuka, A. Nakamura and H. Minamido, *Chem. Commun.*, (1969) 191.
6 R.B. King, *Inorg. Chem.* 2 (1963) 528.
7 R. Cramer and J.J. Mrowa, *Inorg. Chim. Acta*, 5 (1971) 528.
8 D.F. Shriver, *Accounts Chem. Res.*, 3 (1970) 231.
9 J.C. Kotz and D.G. Pedrotty, *Organometal. Chem. Rev. A*, (1969) 479.
10 J.F. Nixon, *Advan. Inorg. Chem. Radiochem.*, 13 (1970) 363.
11 Th. Kruck, *Angew. Chem. Int. Ed.*, 6 (1967) 53.
12 R.R. Holmes and R.P. Wagner, *Inorg. Chem.*, 2 (1963) 384.
13 M.A. Bennett and D.J. Patmore, *Inorg. Chem.*, 10 (1971) 2387.
14 J.F. Nixon and J.R. Swain, *J. Chem. Soc. (Dalton Transactions)*, in press.
15 D.A. Clement and J.F. Nixon, unpublished results.
16 D.A. Clement, J.F. Nixon and B. Wilkins, *J. Organometal. Chem.*, 37 (1972) C43.
17 T.R. Johnson and J.F. Nixon, *J. Chem. Soc. A*, (1969) 2518.
18 C.G. Barlow, J.F. Nixon and J.R. Swain, *J. Chem. Soc. A*, (1969) 1082.
19 J.F. Nixon, *J. Chem. Soc. A*, (1969) 1087.
20 J.F. Nixon and A.A. Pinkerton, in preparation.