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Preliminary communication

Steric effects in oxidative addition and reductive elimination reactions of rhodium pentafluorophenylthiolate complexes

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Abstract

The complexes [*cis*-Rh(SC_6F_5)(PPh_3)$_2$(L)] (L = py, 3-Mepy, isoquin, *N*-MeIm; py = pyridine, 3-Mepy = 3-methylpyridine, isoquin = isoquinoline, *N*-MeIm = *N*-methylimidazole) readily undergo oxidative addition of HR (R = H, SC_6F_5, C_2Ph) to give [RhH(R)(SC_6F_5)(PPh_3)$_n$(L)$_{3-n}$] ($n = 1, 2$) whereas the complexes [*cis*-Rh(SC_6F_5)(PPh_3)$_2$(L′)] (L′ = 2-Mepy, 2,6-Me_2py, quin; 2-Mepy = 2-methylpyridine; 2,6-Me_2py = 2,6-dimethylpyridine, quin = quinoline) react only when R = C_2Ph. Where conditions favour the formation of [RhH(R)(SC_6F_5)(PPh_3)$_n$(L′)$_{3-n}$] reductive elimination of H_2 (R = H) or C_6F_5SH (R = SC_6F_5, C_2Ph) occurs.

Many important processes in which rhodium acts as a homogeneous catalyst involve both oxidative addition and reductive elimination reactions [1], the former class of reaction being favoured by small electron-releasing ligands [2], the latter by bulky ligands, a relatively low electron density at the metal [3,4], a *cis* orientation of the two eliminating groups [5,6] and the presence of ligands that can stabilise the reduced metal fragment [7]. Although the influence of electronic effects has been the subject of numerous studies [2–4,7–10] the contribution of steric effects has received less attention.

In this study an attempt has been made to minimise the electronic changes at the metal as a result of replacing a ligand and to determine the influence of steric effects alone. Thus ligands having substituent groups directed towards the metal, viz. 2-Mepy and quin and their less sterically hindering isomers 3-Mepy and isoquin, were used in an investigation of the oxidative addition of HR (R = H, SC_6F_5, C_2Ph) to [*cis*-Rh(SC_6F_5)(PPh_3)$_2$(L)] and reductive elimination from [RhH(R)(SC_6F_5)(PPh_3)$_n$(L′)$_{3-n}$] ($n = 1, 2$). Products were identified by ^1H and ^{31}P NMR spectroscopy.

The complex [$Rh_2(\mu$-$SC_6F_5)_2(PPh_3)_4$], which is readily prepared in high yield by the reaction of [$RhH(PPh_3)_4$] [11] with C_6F_5SH, is converted quantitatively to [*cis*-Rh(SC_6F_5)(PPh_3)$_2$(L)] (Ia) or [*cis*-Rh(SC_6F_5)(PPh_3)$_2$(L′)] (Ib) by reaction with excess L or L′ in toluene at room temperature [12]. Addition of HR to solutions of Ia gives [RhH_2(SC_6F_5)(PPh_3)$_2$(L)] (II) (H_2 bound reversibly), [RhH(SC_6F_5)$_2$(PPh_3)-

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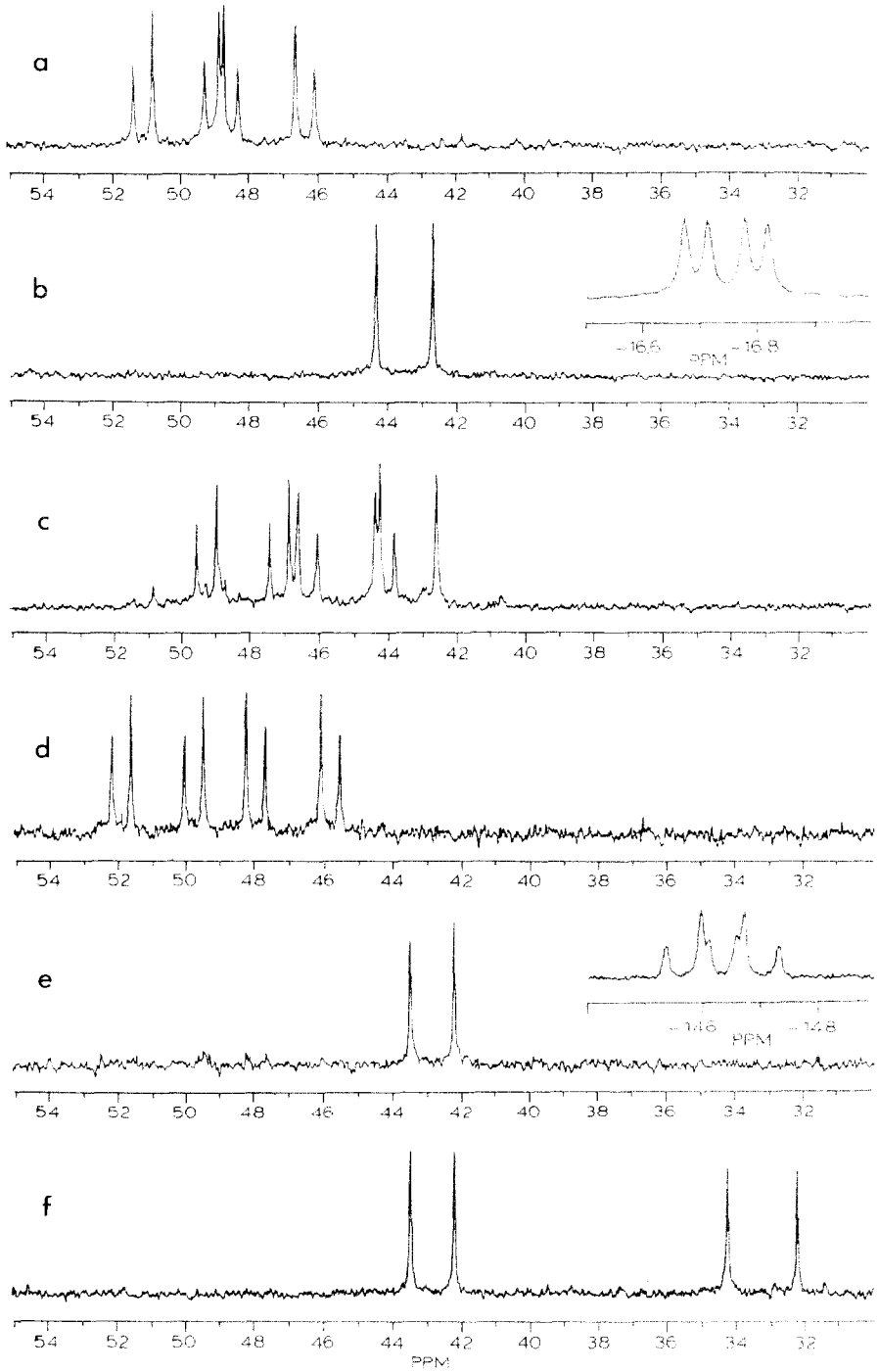
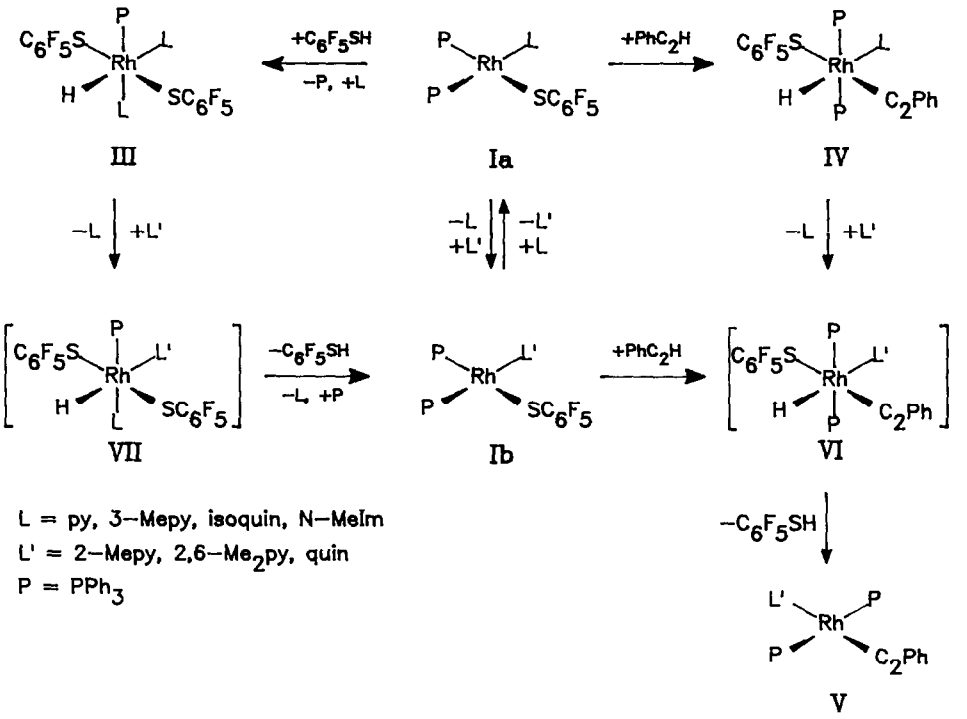


Fig. 1. a, $^{31}P\{^1H\}$ spectrum of Ia, L = py; b, $^{31}P\{^1H\}$ and high field ^1H spectra of III, L = py; c, $^{31}P\{^1H\}$ spectrum showing signals from Ib, L' = 2,6-Me_2py and III, L = py; d, $^{31}P\{^1H\}$ spectrum of Ia, L = *N*-MeIm; e, $^{31}P\{^1H\}$ and high field ^1H spectra of IV, L = *N*-MeIm; f, $^{31}P\{^1H\}$ spectrum showing signals from IV, L = *N*-MeIm and V, L' = 2,6-Me_2py.



Scheme 1.

$(L)_2]$ (III) and $[RhH(C_2Ph)(SC_6F_5)(PPh_3)_2(L)]$ (IV) (II and III at room temperature, IV on warming) with HR = H_2, C_6F_5SH and PhC_2H, respectively. With Ib a reaction occurs only with PhC_2H (75 °C, 1 min) to give [*trans*-$Rh(C_2Ph)(PPh_3)_2(L')$] (V), indicating that the oxidative addition product $[RhH(C_2Ph)(SC_6F_5)(PPh_3)_2(L')]$ (VI) is unstable.

Solutions in toluene of $[RhH(SC_6F_5)_2(PPh_3)(py)_2]$ or $[RhH(C_2Ph)(SC_6F_5)$-$(PPh_3)_2(N\text{-MeIm})]$ when treated with an excess (20–25% by volume) of L or L' (with warming to 75 °C for 2 min) give spectra showing that in the presence of L the only change is replacement of py and *N*-MeIm by L, while with L' a reductive elimination product is obtained:

$$[RhH(SC_6F_5)_2(PPh_3)(py)_2] \xrightarrow[-\text{py}, -C_6F_5SH]{+L', +PPh_3} \text{Ib}$$

$$[RhH(C_2Ph)(SC_6F_5)(PPh_3)_2(N\text{-MeIm})] \xrightarrow[-N\text{-MeIm}, -C_6F_5SH]{+L'} \text{V}$$

Spectral data for experiments with L' = 2,6-Me_2py are given in Fig. 1. Spectra a–c show the effects of treating Ia (L = py) with C_6F_5SH followed by L'; spectra d–f show the effects of treating Ia (L = *N*-MeIm) with PhC_2H followed by L'. The identity of V is confirmed by comparison of its $^{31}P\{H\}$ spectrum with that obtained from a mixture of $[RhH(PPh_3)_4]$ and PhC_2H in toluene/2,6-Me_2py.

These findings are consistent with the steps shown in Scheme 1 where VI and VII are unstable intermediates.

In a majority of cases in which the mechanism of reductive elimination has been

examined an initial dissociation of a σ-donor ligand is required before reductive elimination occurs [7,13–15]. This step would appear to be ruled out for VI and VII since here the ligand most likely to be lost is L′ and in the absence of L′ there is no reductive elimination. Ligands L′ clearly cause severe steric strain at the metal in VI and VII and it is perhaps surprising that they bind at all. That the consequence of their binding is a reductive elimination indicates that an almost entirely steric change in a relatively weakly bound σ-donor ligand can outweigh other factors in determining the stability of a complex.

Further investigation of these effects is now in progress.

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References

1 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711; J.P. Collman, Acc. Chem. Res., 1 (1968) 136; R. Cramer, Acc. Chem. Res., 1 (1968) 186; J.P. Collman and W.R. Roper, Adv. Organomet. Chem., 7 (1968) 53; J. Halpern, Acc. Chem. Res., 3 (1970) 386; J. Halpern and C.S. Wong, J. Chem. Soc., Chem. Commun., (1973) 629; J.K. Stille and K.S.Y. Lau, Acc. Chem. Res., 10 (1977) 434; D. Forster, Adv. Organomet. Chem., 17 (1979) 255; A.C.L. Su, Adv. Organomet. Chem., 17 (1979) 269; A.S.C. Chan and J. Halpern, J. Am. Chem. Soc., 102 (1980) 838; A. Mayanza, J.-J. Bonnet, J. Galy, P. Kalck and R. Poilblanc, J. Chem. Res. (S), (1980) 146; J. Halpern, Inorg. Chim. Acta, 50 (1981) 11; J. Halpern, Science, 217 (1982) 401; D. Milstein, J. Am. Chem. Soc., 104 (1982) 5227; D. Milstein, W.C. Fultz and J.C. Calabrese, J. Am. Chem. Soc., 108 (1986) 1336; J.K. Stille, in F.R. Hartley and S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, Vol. 2, J. Wiley, Chichester, UK, 1985, pp. 625–787.
2 A.J. Deeming and B.L. Shaw, J. Chem. Soc. A, (1969) 1802.
3 A.-R. Al-Ohaly, R.A. Head and J.F. Nixon, J. Organomet. Chem., 205 (1981) 99.
4 H. Kurosawa, M. Emoto and Y. Kawasaki, J. Organomet. Chem., 346 (1988) 137.
5 A. Gillie and J.K. Stille, J. Am. Chem. Soc., 102 (1980) 4933.
6 F. Ozawa, T. Ito, Y. Nakamura and A. Yamamoto, Bull. Chem. Soc. Jpn., 54 (1981) 1868.
7 J.W. Suggs, M.J. Wovkulich and S.D. Cox, Organometallics, 4 (1985) 1101.
8 P.W. Hall, R.J. Puddephatt and C.F.H. Tipper, J. Organomet. Chem., 84 (1975) 407.
9 P.S. Braterman, R.J. Cross and G.B. Young, J. Chem. Soc., Dalton Trans., (1977) 1892.
10 K. Tatsumi, R. Hoffmann, A. Yamamoto and J.K. Stille, Bull. Chem. Soc. Jpn., 54 (1981) 1857.
11 J.J. Levison and S.D. Robinson, J. Chem. Soc. A, (1970) 2947.
12 L. Carlton, to be published.
13 L. Carlton and Z. Bulbulia, J. Organomet. Chem., 389 (1990) 139.
14 D. Milstein, Acc. Chem. Res., 17 (1984) 221;
15 D.A. Wink and P.C. Ford, J. Am. Chem. Soc., 108 (1986) 4838.