Journal of Organometallic Chemistry, 51 (1973) C27–C29

Preliminary communication

π-Allylic complexes of cobalt(I) containing trifluorophosphine

M.A. CAIRNS and J.F. NIXON
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received February 14th, 1973)

SUMMARY

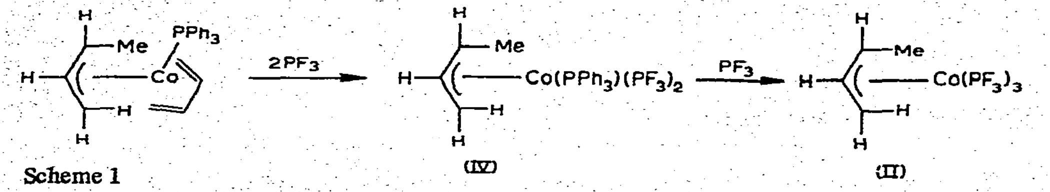
Several π-allylic complexes of cobalt(I) containing trifluorophosphine have been synthesised; they are much less reactive than their rhodium analogues and do not undergo phosphine exchange at room temperature.

Recently we reported low pressure syntheses of several π-allylic tris(trifluorophosphine)-rhodium(I) complexes which readily undergo phosphine exchange at room temperature[1] and oxidative addition with hydrogen chloride[2]. We now describe different routes to analogous complexes of cobalt(I) which show interesting differences in their chemical behaviour.

The parent complex π-allyltris(trifluorophosphine)cobalt(I), π-$C_3H_5Co(PF_3)_3$, (I), was obtained by reacting tri-π-allylcobalt with an excess of PF_3 at room temperature. (I) is a volatile, air sensitive orange liquid (m.p. 22°) exhibiting strong P—F stretching bands in the IR spectrum at 944m, 920s, 882vs, and 851 vs cm^{-1} (gas phase)★.

Specific routes for the synthesis of both *syn* and *anti* 1-methyl-π-allyltris(trifluorophosphine)cobalt(I) complexes (II) and (III) utilise the recently reported *syn*-$(\pi$-$C_4H_7)(C_4H_6)Co(PPh_3)$[3,4] and *anti*-$(\pi$-$C_4H_7)(C_4H_6)Co(PPh_3)$[4] complexes as precursors. Thus *anti*-1-methyl-π-allyltris(trifluorophosphine)cobalt(I) was obtained in 65% yield as a volatile yellow solid (m.p. 45°) by complete displacement of PPh_3 and butadiene from *anti*-$(\pi$-$C_4H_7)(C_4H_6)Co(PPh_3)$ using a large excess of PF_3 in pentane solution (see Scheme 1). The intermediate *anti*-π-$C_4H_7Co(PPh_3)(PF_3)_2$ complex (IV) was also isolated. In a similar fashion were prepared *syn*-π-$C_4H_7Co(PF_3)_3$ (III), (dark orange liquid, m.p. 0°) and *syn*-π-$C_4H_7Co(PPh_3)(PF_3)_2$.

★ A similar approach has been used by Dr. M.A. Bennett (personal communication)



Scheme 1

1,1-Dimethyl-π-allyltris(trifluorophosphine)cobalt(I), (V), (volatile orange solid m.p. 56°), *syn,syn*-1,3-dimethyl-π-allyltris(trifluorophosphine)cobalt(I), (VI), (volatile orange liquid m.p. −12°), π-cyclooctenyltris(trifluorophosphine)cobalt(I), (VII), (volatile orange solid m.p. 31°) were obtained from the reaction between PF_3 and $(\pi\text{-}C_5H_9)(C_5H_8)Co(PPh_3)$[4], $(\pi\text{-}C_5H_9)(C_5H_8)Co(PPh_3)$ (made by substituting 1,3-pentadiene for isoprene in ref. 4), and $(\pi\text{-}C_8H_{13})(C_8H_{12})Co$[5] respectively. The mixed triphenylphosphinebis(trifluorophosphine) compounds of (V) and (VI) were also isolated and characterised.

The ^1H NMR spectrum of $\pi\text{-}C_3H_5Co(PF_3)_3$ shows interesting differences from the analogous rhodium compound. The room temperature spectrum exhibits resonances typical of a π-allyl complex showing three resonances for the unique proton H_C, and the *syn* H_B and *anti* H_A pairs of protons. Both the resonances of H_A and H_B occur as two overlapping 1-3-3-1 quartets from coupling with H_C and the three equivalent phosphorus nuclei ($J(H_CH_A)$ 10.5 Hz; $J(H_AP)$ 7.3 Hz; $J(H_CH_B)$ 6.0 Hz; and $J(H_BP)$ 3.0 Hz). The observation of coupling with the three phosphorus nuclei indicates that unlike the related rhodium complex there is no exchange between free and coordinated PF_3 at room temperature and this conclusion is supported by the ^{19}F NMR spectrum which shows the typical complex pattern of lines expected for an $[X_3A]_3$ spin system (X = fluorine; A = phosphorus)[6,7] which was only evident in the rhodium complex at −30°. The ^1H and ^{19}F NMR of (I) appear to be temperature independent.

Unlike $\pi\text{-}C_3H_5Rh(PF_3)_3$ which is readily converted to $HRh(PF_3)_4$ on treatment with PF_3 and hydrogen at room temperature and atmospheric pressure[8], the cobalt compounds are unreactive. However, (IV) does catalyse the isomerisation of 1-octene to 2-octene in the presence of hydrogen, although no hydrogenation of the olefin is observed. Unlike related π-allylic tricarbonylcobalt complexes[9] tetrafluoroethylene does not insert into the metal carbon bond of (III) under mild conditions. The reactions of (I), (II), (III), (V), and (VI) with hydrogen chloride are very much slower than those of the corresponding rhodium compounds[2], and lead to breakdown to $CoCl_2$ and PF_3, but the distribution of olefin products is similar. An unusual thermal isomerisation of the 1,1-dimethyl-π-allyltris(trifluorophosphine)cobalt to the 1,2-dimethylallyl complex (a volatile orange solid, m.p. 98°) has been discussed recently in another paper[10].

The observation of parent ions in the mass spectra of all the π-allylic–$Co(PF_3)_3$ complexes contrasts with the behaviour of the rhodium analogues where the highest mass peak observed corresponded to the π-allylic–$Rh(PF_3)_2^+$ ions, and this is compatible with the difference in the ease of phosphine exchange established by the NMR studies.

Heck[11] has proposed a dissociative mechanism for the ready substitution reaction which $\pi\text{-}C_3H_5Co(CO)_3$ undergoes with triphenylphosphine. Preliminary results indicate that the corresponding π-$C_3H_5Co(PF_3)_3$ complex is much less reactive towards Ph_3P (at ambient temperature) as expected, in view of the absence of phosphine dissociation.

The above results illustrate the considerable decrease in reactivity of π-allyl complexes of cobalt(I) compared with their rhodium analogues.

ACKNOWLEDGEMENT

We thank the Cobalt Development Institute for financial support for this work.

REFERENCES

1 D.A. Clement, J.F. Nixon and B. Wilkins, *J. Organometal. Chem.*, 37 (1972) C43.
2 J.F. Nixon and B. Wilkins, *J. Organometal. Chem.*, 44 (1972) C25.
3 P.V. Rinze and H. Nöth, *J. Organometal. Chem.*, 30 (1971) 115.
4 G. Vitulli, L. Porri and A.L. Segre, *J. Chem. Soc. (A)*, (1971) 3246.
5 S. Otsuka and M. Rossi, *J. Chem. Soc. (A)*, (1968) 2630.
6 R.K. Harris, R. Schmutzler and J.R. Woplin, *Ber. Bunsengesellschaft. Phys. Chem.*, 75 (1971) 134.
7 J.F. Nixon, *J. Fluorine Chem.*, in the press.
8 J.F. Nixon and B. Wilkins, unpublished results.
9 A. Greco, M. Green and F.G.A. Stone, *J. Chem. Soc. (A)*, (1971) 3476.
10 M.A. Cairns, J.F. Nixon and B. Wilkins, *Chem. Commun.*, (1973) 86.
11 R.F. Heck, *J. Amer. Chem. Soc.*, 85 (1963) 655.