

## Preliminary communication

### Five-coordinate olefin complexes of rhodium(I) formed by an olefinic tertiary phosphine

M.A. BENNETT\* and E.J. HANN

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600 (Australia)

(Received March 1st, 1971)

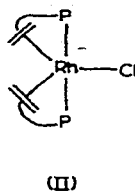
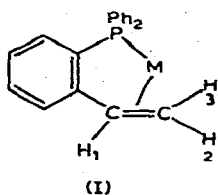
Current interest in the chemistry of rhodium with chelating olefinic tertiary phosphines<sup>1-4</sup> prompts us to give preliminary details of work with *o*-styryldiphenylphosphine,  $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$  (SP), which forms stable mono-olefin complexes with  $\text{Pt}^{\text{II}}$ <sup>5</sup>,  $\text{Fe}^0$ ,  $\text{Ru}^0$ <sup>6</sup>,  $\text{Cr}^0$ ,  $\text{Mo}^0$ ,  $\text{W}^0$ <sup>7</sup>,  $\text{Mn}^{\text{I}}$  and  $\text{Re}^{\text{I}}$ <sup>8</sup>.

Reaction of SP with the cyclooctene complex  $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_n$  gives a yellow complex of empirical formula  $\text{RhCl}(\text{SP})_2$ ★★. Higher yields (~85%) and purer product are obtained by reducing ethanolic hydrated rhodium(III) chloride (1 mole) with formaldehyde in the presence of > 2 moles of SP. Use of triphenylphosphine in this reaction provides a convenient synthesis of  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ <sup>9,10</sup>, and in our case a likely intermediate is  $[\text{Rh}(\text{CO})(\text{SP})_2]^+\text{Cl}^-$  (see below). The complex  $\text{RhCl}(\text{SP})_2$  is monomeric in chloroform and its 100 MHz proton NMR spectrum in  $\text{CD}_2\text{Cl}_2$  shows broad signals at  $\delta$  4.17 and 3.17 in an intensity ratio of 1/2 assignable to the  $\alpha$ - and  $\beta$ -vinylic protons respectively★★★. The upfield shift of these resonances compared with those of free SP<sup>7</sup> suggests that both double bonds are coordinated. The breadth of the signals is due to strong coupling with two <sup>31</sup>P nuclei which are themselves strongly coupled, and hence probably *trans*. The <sup>31</sup>P-decoupled NMR spectrum is very similar in appearance to those of  $\text{Cr}(\text{CO})_4(\text{SP})$ <sup>6,7</sup> and  $\text{Fe}(\text{CO})_3(\text{SP})$ <sup>6</sup> [ $\delta$  3.03 ppm (doublet, intensity 1, H<sub>3</sub>)  $\delta$  3.30 ppm (doublet, intensity 1, H<sub>2</sub>) and  $\delta$  4.17 ppm (doublet of doublets, intensity 1, H<sub>1</sub>), protons being numbered as in (I);  $J_{13}$  10 Hz,  $J_{12}$  8 Hz,  $J_{23}$  ~0]. The far infrared spectrum of  $\text{RhCl}(\text{SP})_2$  shows a band at 237  $\text{cm}^{-1}$  (Nujol mull) due to  $\nu(\text{RhCl})$ ; this is absent from the spectrum of  $\text{RhBr}(\text{SP})_2$ , for which  $\nu(\text{RhBr})$  appears at 143  $\text{cm}^{-1}$ . These observations suggest that  $\text{RhCl}(\text{SP})_2$  is a five-coordinate complex both in solution and in the solid state. The molar conductivity ( $\Lambda_m$ ) of the complex in nitromethane (17.6  $\text{ohm}^{-1} \cdot \text{cm}^2$  at 28°) and in nitrobenzene (1.4  $\text{ohm}^{-1} \cdot \text{cm}^2$  at 28°) is much less than expected for a 1/1

\*Author to whom enquiries may be addressed.

★★First prepared by this method by Dr. S.J. Gruber, University College London, 1967.

★★★A previous report (P.R. Brookes, cited in ref. 1) that the  $\beta$ -vinylic proton resonances of  $\text{RhCl}(\text{SP})_2$  appear at  $\delta$  4.2 and 3.2 is incorrect.



electrolyte, showing that ionisation to  $[\text{Rh}(\text{SP})_2(\text{solvent})]^+$  and  $\text{Cl}^-$  is incomplete. We suggest the trigonal bipyramidal structure (II) for  $\text{RhCl}(\text{SP})_2$ , analogous to  $\text{RhCl}[\text{P}(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\text{-}o)_3]^+$  and  $\text{RhCl}[\text{P}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_3]^+$ , though other possibilities (e.g. tetragonal pyramidal structures) cannot be excluded.

Treatment of  $[\text{RhCl}(\text{CO})_2]_2$  with SP (2 moles per g-atom of Rh) in benzene gives a five-coordinate cationic complex  $[\text{Rh}(\text{CO})(\text{SP})_2]\text{Cl}$  [ $\nu(\text{CO})$  2039  $\text{cm}^{-1}$  in  $\text{CHCl}_3$ ], which loses CO rapidly in solution, and more slowly in the solid state, to give  $\text{RhCl}(\text{SP})_2$ . The cation is reformed when  $\text{RhCl}(\text{SP})_2$  is treated with CO at 25°, 1 atm, and can be precipitated as its  $\text{PF}_6^-$  salt. This shows no tendency to lose CO, probably owing to the poor coordinating ability of  $\text{PF}_6^-$ . The presumably planar cation  $[\text{Rh}(\text{SP})_2]^+$  can be isolated as its tetraphenylborate salt by treating  $\text{RhCl}(\text{SP})_2$  with  $\text{NaBPh}_4$ ; this reacts reversibly with ethylene to give  $[\text{RhCl}(\text{C}_2\text{H}_4)(\text{SP})_2]^+$ , which is stable only in the presence of ethylene.  $[\text{Rh}(\text{SP})_2]^+$  also undergoes additions with CO,  $\text{PF}_3$ ,  $\text{PPh}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{AsPh}_3$ ,  $\text{H}_2$  and  $\text{C}_2(\text{CN})_4$ , which will be discussed in a later publication.

## REFERENCES

- 1 D.J. Hall and R.S. Nyholm, *Chem. Commun.*, (1970) 488.
- 2 P.W. Clark and G.E. Hartwell, *Inorg. Chem.*, 9 (1970) 1948.
- 3 G.E. Hartwell and P.W. Clark, *Chem. Commun.*, (1970) 1115.
- 4 M.A. Bennett, S.J. Gruber, E.J. Hann and R.S. Nyholm, *J. Organometal. Chem.*, 29 (1971) 12.
- 5 M.A. Bennett, W.R. Kneen and R.S. Nyholm, *J. Organometal. Chem.*, 26 (1971) 293.
- 6 M.A. Bennett, G.B. Robertson, I.B. Tomkins and P.O. Whimp, *Chem. Commun.*, (1971) 341.
- 7 M.A. Bennett, R.S. Nyholm and J.D. Saxby, *J. Organometal. Chem.*, 10 (1967) 301.
- 8 L.V. Interrante and G.V. Nelson, *Inorg. Chem.*, 7 (1968) 2059.
- 9 D. Evans, J.A. Osborn and G. Wilkinson, *Inorg. Synth.*, 11 (1968) 99.
- 10 J.J. Levison and S.D. Robinson, *J. Chem. Soc. A*, (1970) 2947.

*J. Organometal. Chem.*, 29 (1971) C15–C16