

Preliminary communication

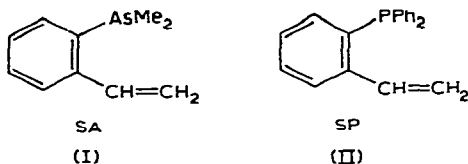
Addition of hydrogen chloride to rhodium(I)-olefin complexes formed by olefinic tertiary phosphines

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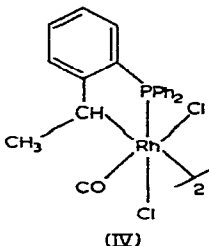
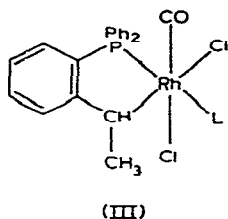
Ligands such as *o*-styryldimethylarsine, $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{AsMe}_2$ (SA) (I) and *o*-styryldiphenylphosphine, $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$ (SP) (II) form planar chelate mono-olefin



complexes of general formula PtBr_2 ligand which undergo addition with bromine to give octahedral $\text{Pt}^{\text{IV}}\text{-C}$ σ -bonded chelate complexes^{1,2}. The platinum(II) complexes do not react with other electrophiles such as the hydrogen halides, and the corresponding palladium(II) complexes fail to give $\text{Pd}^{\text{IV}}\text{-C}$ σ -bonded species on treatment with either halogens or hydrogen halides. We now report that electrophilic addition of hydrogen chloride to the coordinated double bond occurs very readily with rhodium(I) complexes of SP.

A boiling ethanolic or methanolic solution of hydrated rhodium(III) chloride is treated with carbon monoxide (1 atm) and is then heated under reflux with SP (1 mole per g-atom of Rh) for 5 h to give a yellow complex (A) of apparent formula $\text{RhCl}_2(\text{CO})(\text{SP})$ (83% yield), which is insoluble in most organic solvents, and has one band due to $\nu(\text{CO})$ at 2077 cm^{-1} in its infrared spectrum (Nujol mull). (A) reacts with monodentate tertiary phosphines in refluxing benzene to give yellow, monomeric complexes of apparent formula $\text{RhCl}_2(\text{CO})(\text{SP})\text{L}$ (L = Ph_3P , MePh_2P or Me_2PhP) which are assigned structure (III) on the basis of elemental analyses and infrared and proton NMR spectra. Thus, for the diphenylmethylphosphine complex $\text{RhCl}_2(\text{CO})(\text{PMePh}_2)(\text{CHMeC}_6\text{H}_4\text{PPh}_2\text{-}o)$: IR $\nu(\text{CO})$ 2052 cm^{-1} (Nujol), NMR (CDCl_3 , 100 MHz): δ 1.26 (doublet, $J = 7\text{ Hz}$, 3 protons, CH_3 of CHCH_3); 3.81 (triplet further split by coupling with ^{31}P and ^{103}Rh , 1 proton, CH of

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CHCH₃); 2.42 (doublet of doublets, main separation 11 Hz, smaller separation 2.5 Hz, 3 protons, CH₃ of (C₆H₅)₂CH₃P). The methyl resonance pattern of the coordinated diphenylmethylphosphine can be regarded as the X-portion of an ABX spectrum, the appearance of which indicates that the non-equivalent phosphorus atoms are strongly coupled* and hence mutually *trans*. Consequently (A) can be formulated as a chlorine-bridged dimer (IV) containing the Rh-CH(Me)C₆H₄PPh₂-*o* chelate ring formed by addition of HCl to the double bond of coordinated SP. The far infrared spectrum of (A) shows bands at ~230 cm⁻¹ and 265 cm⁻¹ [ν (RhCl) *trans* to C and P respectively]³⁻⁵ and at 239 cm⁻¹, which is tentatively assigned to ν (RhCl) (bridging) *trans* to CO. These data are consistent with the stereochemistry shown in (IV), although other possibilities cannot be excluded. The properties of A are very similar to the insoluble chelate σ -bonded complex RhCl₂(CO)[*o*-CH₂C₆H₄P(*o*-tol)₂] obtained from reactions involving hydrated RhCl₃ and tri-*o*-tolylphosphine⁶.

Addition of HCl to rhodium(I)-ethylene complexes has been reported to give unstable ethylrhodium(III) complexes.^{7,8} The initial product of reaction between [RhCl(CO)₂]₂ and SP is probably a rhodium(I)-olefin complex, which subsequently reacts with HCl; the latter is undoubtedly formed both when hydrated RhCl₃ is dissolved in ethanol and also when this solution is carbonylated. (A) is also obtained in good yield if the original preparation is carried out in the presence of added HCl. The addition does not appear to be reversible, since we have been unable to form rhodium(I) complexes by treatment of (A) or its phosphine derivatives with bases such as sodium carbonate or triethylamine.

If the reaction between the carbonylated rhodium chloride solution and SP is carried out for 30 min, and the resulting solid (which appears to contain [Rh(CO)(SP)₂]⁺Cl⁻ among other products) is treated with triphenylphosphine, a yellow complex of formula RhCl(CO)(PPh₃)(SP) can be isolated. The proton NMR spectrum of this compound indicates that SP is present as a bidentate ligand, since the vinyl proton resonances are upfield of those of the free ligand [δ ~3.1, 2 protons, =CH₂; ~4.2, 1 proton, =CH]. The broadness of the olefinic signals is probably due to coupling with mutually *trans*, strongly coupled phosphorus atoms. The complex is therefore five-coordinate, and is analogous to RhCl(SP)₂ and [Rh(CO)(SP)₂]⁺Cl⁻⁹. Consequently, the intermediate rhodium(I) complex to which HCl adds is probably either RhCl(CO)(SP) (4-coordinate monomer or 5-coordinate Cl-bridged dimer), or, more likely, RhCl(CO)₂(SP) (5-coordinate monomer).

*Spin tickling experiments by Dr. R. Bramley show that $|^2J_{PP}| = 450$ Hz.

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