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Preliminary communication

Dimerisation of an olefinic tertiary phosphine on a rhodium centre

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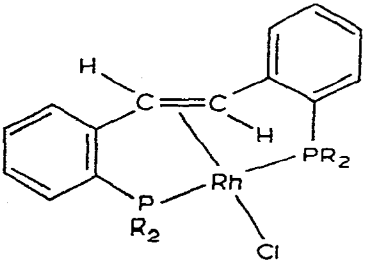
SUMMARY

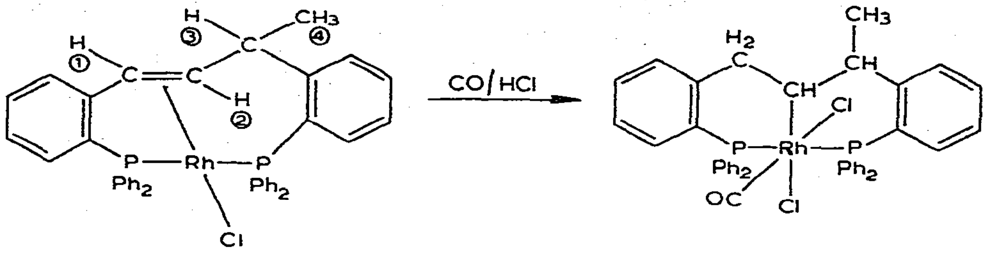
o-Styryldiphenylphosphine (Sp), *o*-$CH_2=CHC_6H_4PPh_2$, is dimerised by rhodium(III) chloride in refluxing 2-methoxyethanol to give a rhodium(I) complex of the tridentate olefinic ligand bis-1,3-[*o*-(diphenylphosphino)phenyl]-*trans*-1-butene, *o*-$Ph_2PC_6H_4CH=CHCH(CH_3)C_6H_4PPh_2$-*o*; the complex reacts reversibly with CO to give a five-coordinate adduct, and with HCl to give rhodium–carbon σ-bonded complexes.

It has been shown[1] that tri-*o*-tolylphosphine undergoes dehydrogenation and coupling at the methyl carbon atoms in the presence of rhodium(III) chloride in high-boiling alcohols to give a rhodium(I) complex (Ia) containing the tridentate ligand 2,2′-*o*-(di-*o*-tolylphosphino)-*trans*-stilbene. It is also well known[2] that ethanolic rhodium(III) chloride catalyses the dimerisation and codimerisation of olefinic hydrocarbons *e.g.* of ethylene to 1-butene, and of styrene and ethylene to 2-phenyl-2-butene. We now report the first example of dimerisation of an olefinic tertiary phosphine, *o*-styryldiphenylphosphine-[(*o*-vinylphenyl)diphenylphosphine], *o*-$CH_2=CHC_6H_4PPh_2$ (Sp) in the presence of



(Ia) $R = o\text{-}CH_3C_6H_4$
(Ib) $R = C_6H_5$

rhodium(III) chloride. Reaction of an excess of Sp with hydrated rhodium(III) chloride in refluxing 2-methoxyethanol gives, in ~70% yield based on Rh, a yellow, crystalline complex, of apparent formula "$RhCl(Sp)_2$", which is in fact a rhodium(I) complex (II) containing the tridentate ligand bis-1,3-[*o*-diphenylphosphino)phenyl]-*trans*-1-butene, 1-Bdpb, o-$Ph_2PC_6H_4CH\overset{t}{=}CHCH(CH_3)C_6H_4PPh_2$-$o$ (III). The free ligand (III) is readily

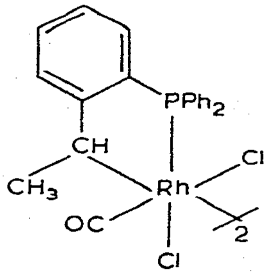


(II) (VII)

isolated as a white, crystalline solid, m.p. 122°, by heating (II) with sodium cyanide in aqueous 2-methoxyethanol [mass spectrum: *m/e* 576 (parent ion); mol. wt. ($CHCl_3$, 25°, vapour phase osmometry) 572; NMR ($CDCl_3$, 100 MHz): δ 1.11 (doublet, 3 protons, H_4), 4.36 (complex multiplet, 1 proton, H_3), δ5.97 (doublet of doublets, 1 proton, H_2), J_{34} 7.0 Hz, J_{12} 16.5 Hz, J_{23} 5.0 Hz, protons numbered as in (II), $\delta(H_1)$ is beneath aromatic resonances]. NMR spectra show that the rhodium(I) complex (II) contains two isomers in solution in a ratio of approximately 3/2. The ^1H NMR spectrum of (II) shows an overlapping pair of doublets arising from the methyl protons of the two isomers (δ 1.24, 1.28 in CD_2Cl_2, J_{34} 6.5Hz), and the ^1H-decoupled ^{31}P NMR spectrum contains 16 lines *i.e.* two AB quartets arising from the inequivalent phosphorus atoms in each isomer, split into doublets by coupling with ^{103}Rh [J(P–P) 398±4 Hz; J(Rh–P) 127±3 Hz for both phosphorus atoms]. The magnitude of J(P–P) indicates that the phosphorus atoms are mutually *trans*. The isomerism is unlikely to arise from *exo*- and *endo*-orientations of the methyl group with respect to the rhodium atom, since molecular models suggest that the *endo*-orientation would cause unacceptable steric hindrance in the coordination sphere. A more probable source of isomerism is the orientation of the double bond, which can be approximately at right angles to or approximately in the coordination plane; in both cases the methyl group is assumed to be *exo* to the metal atom. The first alternative has been observed in the solid state for the stilbene complex (Ib)[3], the second alternative presumably being disfavoured in this system by steric strain in the chelate rings.

Complex (II) is reversibly carbonylated at 25°/1 atm to give a five-coordinate adduct RhCl(CO)(1-Bdpb) (IV) which, in the presence of CO and $AgBF_4$, gives a five-coordinate dicarbonyl cation $[Rh(CO)_2(1\text{-Bdpb})]^+$ (V). On heating in dichloromethane, (V) gives a planar monocarbonyl cation $[Rh(CO)(1\text{-Bdpb})]^+$ (VI). The ^1H and ^{31}P NMR spectra of (VI) show that it, like (II), contains two isomers in a 3/2 ratio, ($\delta(CH_3)$ 1.40, 1.43; J_{34} 6.5Hz for both isomers), but the spectra of the five-coordinate complexes show only one methyl doublet [for (IV) in CD_2Cl_2, δ 1.28; for (V) in $CDCl_3$, δ 1.37; J_{34} 6.5 Hz for both complexes] and a single ^{31}P AB quartet split by ^{103}Rh-coupling [for (IV), J(P–P) 382±4 Hz, J(Rh–P) ~100 Hz for both phosphorus atoms; for (V), J(P–P) 296±4 Hz, J(Rh–P) 82 Hz for both phosphorus atoms]. It is not known whether (IV) and (V) consist only of one isomer, or of two rapidly interconverting isomers, but the magnitude of J(P–P) indicates that a *trans*-configuration of phosphorus atoms is maintained.

Complex (IV) is attacked by hydrogen chloride to give a monomeric, metal–carbon σ-bonded complex (VII), which contains two six-membered metallocycles; the process is reversed by heating (VII) in ethanol. (VII) may be involved in the coupling of Sp moieties on rhodium to give (II). The five-coordinate complex $RhCl(Sp)_2$[4,5] is unaffected by refluxing 2-methoxyethanol, and cannot therefore be an intermediate in the coupling, but the chelate σ-bonded complex (VIII)[8], obtained from the reaction of Sp (2 moles) with $[RhCl(CO)_2]_2$ (1 mole) in ethanolic HCl, reacts with an excess of Sp in refluxing 2-methoxyethanol to give (II) in good yield. Coupling can obviously occur by the insertion of either monodentate P-bonded or bidentate Sp into the Rh–C bond of (VIII) to give (VII). Since rhodium(III) halides readily abstract CO from alcohols in the presence of tertiary phosphines[7], complex (VIII) could easily be generated under the original reaction conditions. Apart from the CO abstraction step, the mechanism is similar to that proposed for the rhodium-catalysed dimerisation of ethylene to 1-butene[8].



(VIII)

Full details of this work, together with results on the coupling of olefinic tertiary phosphines on ruthenium centres, will be reported elsewhere.

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