

FACILE CLEAVAGE OF THE P–H BOND OF SECONDARY PHOSPHINE SULPHIDES BY NUCLEOPHILIC RHODIUM(I) AND IRIDIUM(I) METAL COMPLEXES

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Summary

The secondary phosphine sulphide, Ph_2HPS , reacts with $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ under mild conditions to give $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_2(\text{SPPH}_2)\text{Cl}$ (I); the ^{31}P NMR spectrum indicates that the SPPH_2 group is S-bonded to metal. The same reaction with $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ gives $\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{SPPH}_2)$, probably by reductive elimination of HCl from a transient intermediate rhodium(III) complex analogous to I. A possible mechanism for these reactions is proposed. The complex I reacts with MeI or EtI to give $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_2\text{ClI}$.

Introduction

The reactions of secondary phosphine sulphides with transition metal complexes have been little studied. Recent reports concern the reactions of secondary phosphine sulphides R_2HPS ($\text{R} = \text{Me, Et, Ph}$) with metal-carbonyl derivatives of Cr, Mo and Mn [1–3]. The results indicate that the ligand initially coordinates through sulphur to carbonylmetal system although, in some cases, ambivalent behaviour has been observed. Thus, the S-bonded complexes $\text{Mn}(\text{CO})_4\text{-X}(\text{SPHMe}_2)$ ($\text{X} = \text{Cl, Br}$) isomerize to the P-bonded complexes $\text{Mn}(\text{CO})_4\text{-[PMe}_2(\text{SH})]$ on raising the temperature [3]. Moreover, spectral data have shown that in S-bonded complexes such as $\text{Cr}(\text{CO})_5(\text{SPHMe}_2)$ the proton is tautomericly linked either to sulphur or phosphorus [1].

We have studied the reaction of diphenylphosphine sulphide with coordinatively unsaturated rhodium(I) and iridium(I) metal complexes with the aim of obtaining complexes in which phosphorus(V) is bonded to a transition metal [4]. The results show this route not to be valid; complexes containing the SPPH_2 group S-bonded to metal are, in fact, obtained.

Experimental

The starting materials $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ [5], $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ [6] and Ph_2HPS [7] were prepared by published methods. Other chemicals were reagent grade

and were used without purification. IR spectra were recorded as Nujol mulls (CsI discs) on a Perkin—Elmer 457 spectrophotometer, using a polystyrene film for calibration. ^1H NMR spectra were recorded on a Perkin—Elmer R24/B spectrometer. ^{31}P NMR spectra were recorded at ca. 40.4 MHz on a JEOL PS-100 spectrometer equipped with Fourier Transform accessories; the shifts were quoted with respect to 85% H_3PO_4 (external reference).

Elemental analyses were by Bernhardt Mikroanalytisches Laboratorium, Elbach uber Engelskirchen, Germany. All reactions were carried out under oxygen-free dinitrogen.

Preparation of $\text{IrClH}(\text{CO})(\text{PPh}_3)_2(\text{SPPH}_2)$ (I)

A benzene solution of Ph_2HPS (0.115 g, 0.53 mmol) was added dropwise to a solution of $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ (0.40 g, 0.51 mmol) in the same solvent; the colour of the solution changed from yellow to pale yellow. The progress of the reaction was followed by IR spectra. The solvent was evaporated off to 5 ml under reduced pressure, and heptane was added to give a pale yellow solid. This was washed with a little ether and then with petroleum ether (40–70°C). (Yield 82%). (Found: C, 59.04; H, 4.19; Cl, 3.43; S, 3.15. $\text{C}_{49}\text{H}_{41}\text{ClIrOP}_3\text{S}$ calcd.: C, 58.94; H, 4.13; Cl, 3.55; S, 3.11%).

Preparation of $\text{IrCl}(\text{D})(\text{CO})(\text{PPh}_3)_2(\text{SPPH}_2)$

The deuteride was prepared by adding an excess of D_2O to I in benzene solution. The mixture was stirred for about 3 h, then the solvent was removed under reduced pressure and the residual oil was left overnight over P_4O_{10} . The crude product was crystallised from benzene/hexane.

Preparation of $\text{IrHI}(\text{CO})(\text{PPh}_3)_2(\text{SPPH}_2)$

A mixture of I (0.18 g; 0.18 mmol) and LiI (0.029 g; 0.22 mmol) in dichloromethane was left at room temperature, with stirring, for about 1 h. The solvent was evaporated off and the crude product extracted with benzene. The solvent was evaporated to small volume and hexane was added to give a yellow solid. (Found: C, 53.86; H, 3.72; I, 11.70; S, 2.97. $\text{C}_{49}\text{H}_{41}\text{IrOP}_3\text{S}$ calcd.: C, 53.99; H, 3.79; I, 11.64; S, 2.94%).

Alkylation reactions

CH_3I (4 ml) or $\text{C}_2\text{H}_5\text{I}$ (4 ml) and I (0.15 g; 0.15 mmol) were heated under reflux with stirring. The progress of the reaction was followed by IR spectra in dichloromethane. After ca. 2 h the reaction was complete. The solvent was evaporated off and the crude product washed with ether. The yellowish solid obtained was identified as $\text{Ir}(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ by comparison with an authentic sample.

Reaction of $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ with Ph_2HPS

To a solution of $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ (0.350 g; 0.50 mmol) in degassed benzene (100 ml) was added an excess of Ph_2HPS (0.11 g; 0.52 mmol). The mixture was left at room temperature for ca. 6 h then the yellow solution was concentrated to 5 ml. Addition of hexane gave a mixture of starting material and probably $\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{SPPH}_2)$. All attempts to obtain the latter were unsuccessful.

The same reaction was repeated using a large excess of diphenylphosphine sulphide and a long reaction time. Again the product was obtained mixed with the starting compound.

Results and discussion

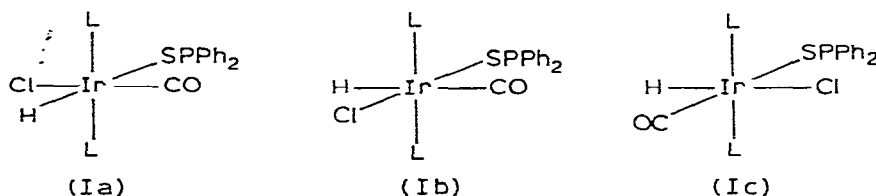
Spectral analysis indicates that secondary phosphine sulphides, R_2HPS , and thiophosphinic acids, $R_2P(SH)$, exist in a tautomeric equilibrium [8] which lies completely to the left at room temperature [9]:



Furthermore, the P—H bond in secondary phosphine sulphides is cleaved only at elevated temperatures [3].

On adding diphenylphosphine sulphide to $Ir(CO)(PPh_3)_2Cl$ in benzene at room temperature the solution turns from yellow to pale yellow and the pale yellow iridium(III) complex $Ir(CO)H(PPh_3)_2(SPPH_2)Cl$ I is obtained. Monitoring the reaction by IR spectra in the carbonyl stretching region revealed only formation of the bands of the product and thus the formation of the product involves a single spectroscopically observable step.

The ^{31}P NMR results indicate for the compound (I) a configuration in which the Ph_2PS group is bonded to metal atom through sulphur. The PPh_3 groups exhibit an AA' spectrum with $\delta + 34.0$ ppm ($^2J(P-P)$ 406 Hz) as expected for triphenylphosphine ligands in *trans* positions if a plane of symmetry along the $Ph_3P-Ir-PPh_3$ axis is not present; the lack of coupling between phosphorus atoms in *cis* positions indicates that the Ph_2PS is S-bonded. The Ph_2PS group shows a singlet at $\delta +55.1$ ppm. On this basis, the possible configurations for the compound are shown in the diagram (Ia–c); their analysis is necessary owing to the lack of knowledge of the *trans*-influence of the S-bonded Ph_2PS group.



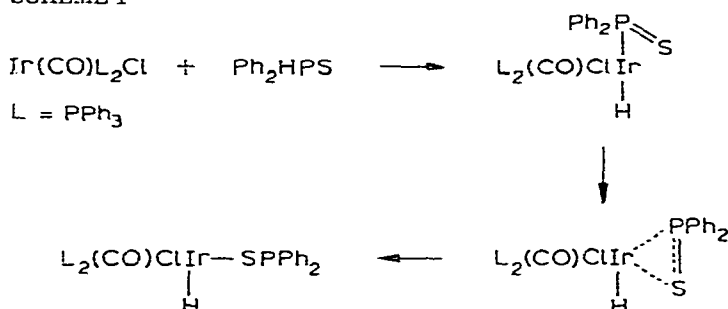
The high field 1H NMR spectrum of I exhibits the hydrido ligand resonance as a triplet at 26.1τ ($J(H-P) \cong 12$ Hz); the IR spectrum has $\nu(Ir-H)$ at 2215 cm^{-1} and the $\nu(CO)$ at 2032 cm^{-1} ; in the far-infrared spectrum characteristic bands at 315 cm^{-1} (medium-weak) and at 265 cm^{-1} (medium-strong) are observed. We assign the band at lower wavenumbers to $\nu(Ir-Cl)$ because it is absent in the iodo-derivative $Ir(CO)H(PPh_3)_2(SPPH_2)I$, obtained by treating I with LiI . The band at 315 cm^{-1} can be tentatively assigned to $\nu(Ir-S)$ [1]. If the complex had configuration Ib, the $\nu(Ir-H)$ absorption would be expected to be low, owing to the high *trans*-influence of the carbonyl group [10–12]; similarly a resonance at lower NMR fields would be observed [10–15]. Moreover, no significant interaction between the vibrational states of metal-hydrogen and carbonyl was observed, as shown by comparison of the spectra of the hydrido and deuterido-complex [16]; in the latter the $\nu(CO)$ remains unshifted and the $\nu(Ir-D)$ was observed at 1590 cm^{-1} . A choice between configurations Ia and Ic is possible

from the far-infrared spectrum. The $\nu(\text{Ir}-\text{Cl})$ absorption at 265 cm^{-1} is consistent with configuration Ic, in accordance with the high *trans*-influence of the hydrido ligand [10–15]; for configuration Ia, the $\nu(\text{Ir}-\text{Cl})$ would be expected to be in the $290\text{--}320\text{ cm}^{-1}$ region.

The $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ seems to react at room temperature in benzene with diphenylphosphine sulphide to give an equilibrium. Allowing the mixture to react for a long time and using an excess of ligand gives a product mixed with the starting compound, and all attempts to purify it failed. The product does not show a $\text{Rh}-\text{H}$ stretching frequency band, and the $\nu(\text{CO})$ band at 1975 cm^{-1} (CH_2Cl_2 solution) rules out the formation of a rhodium(III) compound; moreover the analytical data and the IR spectrum indicate that it does not contain chlorine. On this basis, the product can be formulated as $\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{SPPH}_2)$. It thus seems that, as for the iridium(I) substrate, a rhodium(III) hydrido-complex may be formed; by reductive elimination of HCl this could yield the product. Such a reaction is frequently observed in oxidative addition reactions on rhodium(I) substrates [17]. The complex $\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{SPPH}_2)$ is not sufficiently soluble to give a satisfactory ^{31}P NMR spectrum; the presence of a sulphur-rhodium bond is postulated by analogy with I.

Scheme 1 seems a reasonable scheme for the reaction of I with diphenylphos-

SCHEME 1



phine sulphide in the light of some aspects of the chemistry of the secondary phosphine sulphides [1–3,18]. The first step involves formation of a labile iridium(III) hydrido-complex which contains a phosphorus(V) bonded to the metal. We suggest that this intermediate isomerizes by an intramolecular mechanism, involving a three-centre transition state, to give the final product in which the Ph_2PS group is S-bonded. Compounds containing a phosphorus(V) atom bonded to a transition metal have been isolated [4,19–22], and, in some cases, they give the S-bonded isomer on UV irradiation in non polar solvents [21]. On the other hand, quantitative isomerization of the dimethylphosphine sulphide complex $\text{Mn}(\text{CO})_4(\text{SPHMe}_2)$ ($\text{X} = \text{Cl}, \text{Br}$) from S- to P-bonded has been observed on raising the temperature [3]. The alternative mechanism involving formation, under equilibrium condition, of a five-coordinated iridium(I) complex in which the diphenylphosphine sulphide is S-bonded to metal and further nucleophilic attack at the metal, with $\text{P}-\text{H}$ bond breaking, seems to be unlikely, because of the low ability of five-coordinated iridium(I) species to undergo oxidative additions [17].

MeI and EtI react with I to give the known $\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_2\text{ClI}$, characterized

by comparison with an authentic sample [23]. Thus, the reaction probably occurs initially by S-alkylation of the coordinated Ph_2PS group, and can be related to the S-alkylation reactions of coordinated thio-groups [24]. A mechanism involving an electrophilic attack of the alkyl group at sulphur with formation of a labile cationic complex, which in turn undergoes a fast rearrangement involving coordination of the halogen to the metal and release of the mercaptophosphine seems reasonable. Unfortunately, we were unable to isolate the formed mercaptophosphine. S-Alkylation of coordinated thio-group with subsequent displacement of the thioether sulphur donor by halide has been observed in some cases [24]. In the absence of kinetic data we cannot rule out initial attack of the alkyl group of MeI or EtI at the phosphorus atom of the coordinated SPPH_2 group, though this seems unlikely owing to the lower nucleophilicity of phosphorus than of sulphur.

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