

### Cationic Rhodium(I) and Iridium(I) Complexes with Phosphorus–Sulfur Bidentate Ligands. Formation of Dioxygen Adducts

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There have been a number of studies on Rhodium(I) and Iridium(I) complexes containing chelating diphosphine ligands, particularly with respect to their use in the activation of small molecules and as homogeneous catalysts in hydrogenation and decarbonylation reactions [1]. By contrast, relatively few complexes of the above metal ions have been reported with hybrid bidentate ligands, in which one of the two phosphorus atoms has been replaced by a different donor atom, namely sulfur. Owing to the different binding properties of the two donor groups, complexes with hybrid ligands are expected to behave differently from the corresponding diphosphino-derivatives. In particular, a general feature of these compounds is their ability to undergo dissociation of the sulfur end of the chelate to generate coordinatively unsaturated species in solution, which could be active in homogeneous catalysis [2, 3].

We report here the synthesis of some cationic Rhodium(I) and Iridium(I) derivatives with the ligands  $(C_6H_5)_2P(CH_2)_2SR$  (PSR), where R is  $CH_3$  (PSMe),  $C_2H_5$  (PSEt) or  $C_6H_5$  (PSPh), of the type  $[M(PSR)_2]Y$ . Because we are currently interested in the activation of oxygen by transition metal complexes, we have also investigated the reactions of  $[M(PSR)_2]Y$  with  $O_2$ . It should be noted that some of the above complexes have been found to be able to promote catalytic oxidation of terminal olefins to methylketones [4].

#### Experimental

The PSR ligands were prepared by reacting the appropriate chloro-derivative  $Cl(CH_2)_2SR$  (R = Me, Et, Ph) with sodium diphenylphosphide in liquid ammonia [2].  $[Rh(COD)(acad)]$  [5],  $[Rh(COD)Cl]_2$  [6] and  $[Ir(cot)_2Cl]_2$  [7] were prepared by

published procedures. Microanalyses were performed by Mr L. Turiaco, Istituto di Chimica Analitica, University of Padova.  $^{31}P\{^1H\}$  NMR spectra were recorded on a Bruker WP-60 FT spectrometer in  $CH_2Cl_2$  solution by using an acetone- $d_6$  lock capillary and were referenced to external 85%  $H_3PO_4$ . Positive chemical shifts are downfields from  $H_3PO_4$ . Computer simulation of experimental spectra was performed with the ITRCAL programme provided by the Nicolet Instrument Co.

#### Preparation of the Complexes

All preparations were carried out under an inert atmosphere (nitrogen) and the solid products were stored under nitrogen at  $-20^\circ C$ . The complexes were prepared by a modification of the procedure of Lewis [8].

##### $[Rh(PSR)_2]BF_4$ (R = Me, Et, Ph)

A solution of  $[Rh(COD)(acad)]$  (0.3 g, 1 mmol) in dichloromethane (5 ml) was treated with a solution of trityltetrafluoroborate (0.32 g, 1 mmol) in 5 ml of the same solvent. The ligand (2 mmol) in dichloromethane (5 ml) was then added to the brown solution and after 30 min stirring the mixture was reduced in volume and finally treated dropwise with diethyl ether. The yellow solids were recrystallized from dichloromethane ether (yields 70–85%).

##### $[Rh(PSR)_2]B(C_6H_5)_4$ (R = Et, Ph)

A mixture of  $[Rh(COD)Cl]_2$  (0.66 g, 1.35 mmol) in methanol containing the ligands (5.4 mmol in 20 ml) was refluxed until a clear yellow solution was obtained. Sodium tetraphenylboron (0.92 g, 2.7 mmol) in methanol (5 ml) was added to the cooled filtered solution and yellow solids separated, which were recrystallized from dichloromethane methanol (yields 80–90%).

##### $[RhO_2(PSR)_2]B(C_6H_5)_4$ (R = Et, Ph)

A solution of  $[Rh(PSR)_2]B(C_6H_5)_4$  in dichloromethane was stirred under oxygen until the color changed to brown-orange. Methanol was added dropwise and the solvent allowed to slowly evaporate (yields 50–70%).

##### $[Ir(PSR)_2]B(C_6H_5)_4$ (R = Me, Et, Ph)

A mixture of  $[Ir(cot)_2Cl]_2$  (0.67 g, 1 mmol) and the ligand (4 mmol) in methanol (20 ml) was stirred until a clear solution was obtained. Sodium tetraphenylboron (0.68 g, 2 mmol) in methanol (5 ml) was added to the filtered solution and pale yellow solids separated, which were recrystallized from dichloromethane/methanol (yields 80–90%). The corresponding white dioxygen adducts  $[IrO_2(PSR)_2]B(C_6H_5)_4$  were obtained by simple expo-

TABLE I. Analytical Data of the Complexes.

Compound	Color	Anal. %					
		C		H		S	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
[Rh(P-SMe) <sub>2</sub> ]BF <sub>4</sub>	yellow	50.72	51.01	4.82	4.90	9.03	8.97
[Rh(P-SEt) <sub>2</sub> ]BF <sub>4</sub>	yellow	52.05	51.63	5.19	5.25	9.75	9.01
[Rh(P-SEt) <sub>2</sub> ]BPh <sub>4</sub>	yellow	69.32	69.49	6.02	6.06	6.61	6.36
[RhO <sub>2</sub> (P-SEt) <sub>2</sub> ]BPh <sub>4</sub>	brown	67.11	66.93	5.83	5.89	6.40	6.36
[Rh(P-SPh) <sub>2</sub> ]BF <sub>4</sub>	yellow	57.62	57.45	4.59	4.63	7.69	7.98
[Rh(P-SPh) <sub>2</sub> ]BPh <sub>4</sub>	yellow	72.09	71.79	5.48	5.37	6.01	5.78
[RhO <sub>2</sub> (P-SPh) <sub>2</sub> ]BPh <sub>4</sub>	brown	70.00	69.95	5.32	5.34	5.84	5.61
[IrO <sub>2</sub> (P-SMe) <sub>2</sub> ]BPh <sub>4</sub>	white	60.96	61.06	5.11	5.20	6.00	5.92
[IrO <sub>2</sub> (P-SEt) <sub>2</sub> ]BPh <sub>4</sub>	white	61.58	61.61	5.35	5.38	5.87	5.70
[IrO <sub>2</sub> (P-SPh) <sub>2</sub> ]BPh <sub>4</sub>	white	64.68	64.61	4.92	5.01	5.40	5.34

TABLE II. <sup>31</sup>P NMR Data<sup>a</sup> for the P-SR Ligands and their Complexes with Rh(I) and Ir(I).

Compound	Chem. shift, ppm <sup>b</sup> δ	Coordination chem. shift Δ <sup>c</sup>	Coupling const., Hz	
			J <sub>Rh-P</sub>	J <sub>P-P</sub>
P-SPh	-17.0			
P-SEt	-16.8			
P-SMe	-17.8			
[Rh(P-SPh) <sub>2</sub> ]BF <sub>4</sub>	63.7	80.7	163	
[Rh(P-SEt) <sub>2</sub> ]BF <sub>4</sub>	63.7	80.5	161	
[Rh(P-SMe) <sub>2</sub> ]BF <sub>4</sub>	63.8	81.6	159	
[Ir(P-SPh) <sub>2</sub> ]BPh <sub>4</sub>	46.5	63.5		
[Ir(P-SEt) <sub>2</sub> ]BPh <sub>4</sub>	47.3	64.1		
[Ir(P-SMe) <sub>2</sub> ]BPh <sub>4</sub>	47.4	65.2		
[RhO <sub>2</sub> (P-SPh) <sub>2</sub> ]BPh <sub>4</sub> <sup>d</sup>	50.9; 53.5	67.9; 70.5	132; 119	22.7
[RhO <sub>2</sub> (P-SEt) <sub>2</sub> ]BPh <sub>4</sub> <sup>d</sup>	51.8; 52.7	68.6; 69.5	135; 115	22.7
[RhO <sub>2</sub> (P-SMe) <sub>2</sub> ]BPh <sub>4</sub> <sup>e, f</sup>	53.5	71.3	121	
[IrO <sub>2</sub> (P-SPh) <sub>2</sub> ]BPh <sub>4</sub> <sup>g</sup>	16.2; 16.8	33.2; 33.8		10.5
[IrO <sub>2</sub> (P-SEt) <sub>2</sub> ]BPh <sub>4</sub> <sup>g</sup>	16.7; 17.6	33.5; 34.4		10.9
[IrO <sub>2</sub> (P-SMe) <sub>2</sub> ]BPh <sub>4</sub> <sup>g</sup>	17.2; 18.9	35.0; 36.7		9.2

<sup>a</sup>Run in CH<sub>2</sub>Cl<sub>2</sub> at 27 °C, unless otherwise noted. <sup>b</sup>With respect to external H<sub>3</sub>PO<sub>4</sub>; downfield shifts positive. <sup>c</sup>Δ = δ<sub>P coord</sub> - δ<sub>P free ligand</sub>. <sup>d</sup>ABX system. <sup>e</sup>In CH<sub>3</sub>OH. <sup>f</sup>Average value; no J<sub>P-P</sub>. <sup>g</sup>AB system.

sure to air of the solid [Ir(PSR)<sub>2</sub>]B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> compounds.

## Results and Discussion

Treatment of a suspension of [Rh(COD)Cl]<sub>2</sub> or of [Ir(cot)<sub>2</sub>Cl]<sub>2</sub> with two equivalents of the appropriate PSR ligand gave yellow-orange solutions, from which the yellow products [M(PSR)<sub>2</sub>]BPh<sub>4</sub>

(M = Rh, Ir) were isolated on addition of sodium tetraphenylboron. The more soluble [Rh(PSR)<sub>2</sub>]-BF<sub>4</sub> derivatives were prepared by reaction of two equivalents of PSR with [Rh(COD)(acac)] in dichloromethane in the presence of equivalent amounts of trityltetrafluoroborate. All the above complexes were characterized by elemental analysis (Table I) and were found to be 1:1 electrolytes in nitromethane.

The  $^{31}\text{P}$  NMR spectra of the  $[\text{Rh}(\text{PSR})_2]^+$  derivatives show doublet patterns (Table II) which are consistent with the expected planar structure. The large  $^{31}\text{P}$  coordination chemical shifts ( $\Delta \sim 60\text{--}80$  ppm) are in agreement with the observation that phosphorus containing five-membered ring systems show an analogous large downfield chemical shifts [9]. The rhodium–phosphorus coupling constants ( $J \sim 160$  Hz) are 20% higher than those of the  $[\text{Rh}(\text{diphosphine})_2]^+$  analogous [10], thus suggesting the structure



in which atoms with low *trans* influence (namely sulfur) are located *trans* to phosphorus. A survey of the data reported in the literature indicates that  $J(\text{Rh}\text{--}\text{P})$  increases as the *trans* influence of the ligand *trans* to phosphino groups decreases (in similar complexes a 30–40% decreasing is observed on going from *trans* P to *trans* Cl) [11].

Probably the  $[\text{Ir}(\text{PSR})_2]^+$  cations, whose  $^{31}\text{P}$  NMR spectra show only sharp singlets, have a similar configuration but additional evidence is needed in order to establish the structure. It is noteworthy that the square-planar complexes  $[\text{Pt}(\text{PSR})_2]^{2+}$  possess a similar *cis*-arrangement of the PSR ligands [12].

In the solid state the  $[\text{Rh}(\text{PSR})_2]\text{Y}$  complexes are moderately air-stable, while the corresponding iridium-derivatives readily react with atmospheric oxygen to yield well-defined dioxygen adducts of the type  $[\text{IrO}_2(\text{PSR})_2]\text{Y}$ . Manometric measurements show that in solution all the rhodium-complexes slowly add oxygen at ambient conditions. The  $\text{O}_2$ :Rh(I) ratio was measured for  $[\text{Rh}(\text{PSR})_2]\text{BF}_4$  in methanol (0.01 M) at 25 °C and was found to be dependent on the nature of the substituent at sulfur:  $\text{PPh} (\sim 0.6) < \text{PSet} (\sim 0.9) < \text{PSMe} (\sim 1)$ .

Dioxygen adducts  $[\text{RhO}_2(\text{PSR})_2]\text{BPh}_4$  have been isolated in the solid state by reacting an ethanol suspension of four-coordinate rhodium(I) cations in form of tetraphenylborate salts; in the same conditions the iridium(I) derivatives are converted into the colorless dioxygen-adducts in few minutes. Dioxygen complexes of Rhodium(I) and Iridium(I) usually exhibit an IR band between 800 and 900  $\text{cm}^{-1}$  [13]. However, in the case of  $[\text{MO}_2(\text{PSR})_2]\text{BPh}_4$  the  $\text{MO}_2$  bands could not be detected owing the strong absorptions of the ligands and the anion.

The geometry of the  $[\text{MO}_2(\text{PSR})_2]^+$  cations can be inferred from  $^{31}\text{P}$  NMR data. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{RhO}_2(\text{PSet})_2]\text{BPh}_4$  in dichloromethane solution saturated with oxygen consisted of an eight-line multiplet, which could be simulated by using an ABX (namely  $\text{P}_\text{A}\text{P}_\text{B}\text{Rh}$ ) model (Fig. 1). The ABX pattern is expected for a trigonal bipyramidal struc-

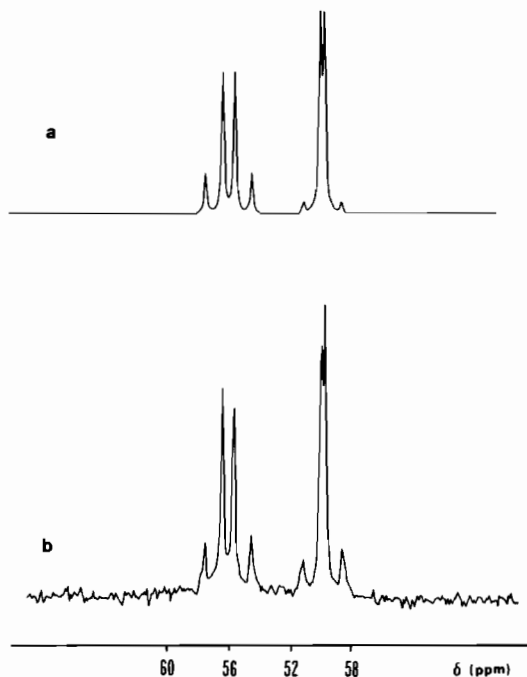


Fig. 1. Comparison of the simulated (a) and observed (b)  $^{31}\text{P}\{^1\text{H}\}$  FT NMR spectra of a solution of  $[\text{Rh}(\text{PSet})_2\text{O}_2]\text{BF}_4$  in  $\text{CH}_2\text{Cl}_2$  at 25 °C.

ture with an equatorial  $\text{O}_2$  and the PSet ligands spanning axial and equatorial positions (structure II).



The same geometry has been reported for the diphosphine analogues [1, 14, 15]. Dichloromethane solutions of  $[\text{RhO}_2(\text{PPh})_2]\text{BPh}_4$  show a similar eight-line spectrum, accompanied by a doublet at 63.7 ppm due to the presence of some amounts of uncomplexed  $[\text{Rh}(\text{PSR})_2]^+$  cation.

By contrast, the  $^{31}\text{P}$  NMR spectrum of  $[\text{RhO}_2(\text{PSMe})_2]^+$ , always in dichloromethane, displays only a sharp doublet, both at +35 °C and at –80 °C, thus suggesting either rapid intramolecular rearrangement of the above trigonal bipyramidal structure or possibly a square-pyramidal structure with axial  $\text{O}_2$ .

Assuming that all the  $[\text{RhO}_2(\text{PSR})_2]^+$  adducts have the same structure, it appears that steric factors are important in determining the dynamic of the rearrangement.

The  $^{31}\text{P}$  NMR spectra of the  $[\text{IrO}_2(\text{PSR})_2]^+$  cations show four-line multiplets, which were ana-

lyzed as AB systems. The data are again consistent with a geometry of the type II, with axial and equatorial phosphorus atoms.

Finally, from Table II it could be seen that the addition of dioxygen to the square-planar species moves  $^{31}\text{P}$  NMR resonances upfield, the difference being substantially larger for iridium-derivatives. Smaller Rh-P coupling constants in the five-coordinate adducts are in agreement with an increase in the formal oxidation state of Rhodium in the dioxygen derivatives [13].

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