

Synthesis and NMR Characterization of Cationic Rhodium(I) Complexes Containing Phosphorus–Sulfur Bidentate Ligands

CARLO BONUZZI, MARIO BRESSAN, FRANCO MORANDINI and ANTONINO MORVILLO

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Centro C.N.R., University of Padua, via Marzolo 1, 35131 Padua, Italy

(Received April 8, 1988)

Abstract

The reaction of $[\text{Rh}(\text{diene})(\text{acac})]$ (diene = cyclooctadiene or norbornadiene; acac = acetylacetonate) with bidentate ligands of the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{SR}$ ($n = 1, 2$ or 3 ; $\text{R} = \text{Me}, \text{Et}, \text{Ph}$, not all combinations) or *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ leads to $[\text{Rh}(\text{diene})(\text{LL})]^+$ or $[\text{Rh}(\text{LL})_2]^+$, depending on the stoichiometry of the reaction. The complexes were fully characterized by ^1H and ^{31}P NMR spectroscopy.

Introduction

In a previous paper [1] we reported the synthesis and multinuclear NMR characterization of new rhodium(I) and iridium(I) complexes of general formula $[\text{M}(\text{PSR-C}_2)_2]\text{X}$ ($\text{X} = \text{BPh}_4, \text{BF}_4$), where PSR-C_2 are the hybrid ligands $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{SR}$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$). On the basis of NMR arguments, the complexes are assigned a square-planar geometry, with the two phosphorus in the *cis* position [1]. Here we report the synthesis and $^{31}\text{P}\{^1\text{H}\}$ NMR characterization of cationic rhodium(I) complexes $[\text{Rh}(\text{diene})(\text{LL})]^+$ and $[\text{Rh}(\text{LL})_2]^+$ with a series of phosphorus–sulfur ligands spanning different carbon chain lengths between the two donor atoms. The complexes have been found to be effective catalysts in the O_2 -oxidation of terminal olefins to methylketones [2] and also in the hydrogenation of olefins and ketones [3]. The preparation and characterization of new complexes containing the ligand *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ are also reported.

Results and Discussion

The $[\text{Rh}(\text{diene})(\text{LL})]^+$ complexes, where diene is cycloocta-1,5-diene (COD) or bicyclo-hept-1,5-diene (NBD) and LL is $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{SR}$ ($n = 1$, $\text{R} = \text{Ph}$, PSPH-C_1 ; $n = 2$, $\text{R} = \text{Ph}$, PSPH-C_2 ; $n = 2$, $\text{R} = \text{Me}$, PSMe-C_2 ; $n = 2$, $\text{R} = \text{Et}$, PSEt-C_2 ; $n = 3$; $\text{R} = \text{Ph}$, PSPH-C_3) or *cis*-1,2-bis(diphenylphosphino)ethylene (*cis*-VDP), were obtained by reacting $[\text{Rh}(\text{diene})$

(acac)] (acac = acetylacetonate) [4] with an equivalent of the appropriate ligand in the presence of stoichiometric amounts of trityltetrafluoroborate in dichloromethane solution, following the procedure previously described in the literature [5]. The bis-chelate $[\text{Rh}(\text{LL})_2]\text{BF}_4$ derivatives were prepared analogously, by reacting two equivalents of the ligands.

All the complexes behave as 1:1 electrolytes in nitromethane solution. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the $[\text{Rh}(\text{diene})(\text{LL})]\text{BF}_4$ complexes, as well as those of the bis-chelate ones (Table I), show doublets due to the coupling of the phosphorus with the rhodium atom. The high deshielding of the ^{31}P NMR chemical shift upon coordination, found for the complexes containing the PSR-C_2 ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) ligands, is a well documented fact for five-membered chelate rings containing phosphorus atoms [6]. It is to be noted that the coordination chemical shifts (Δ in Table I) are larger for the bis-chelate adducts than for the mono-chelate ones (80 [1] *versus* 73 ppm), the former values being closer to that observed for the corresponding complexes containing the diphosphines DPPE [6]. On the contrary, the Δ values for the mono- and bis-chelate complexes containing PSPH-C_1 or PSPH-C_3 , agree with those reported for the analogous complexes containing related diphosphines, *i.e.* giving rise to four- or six-membered chelate rings [6]. $J(\text{Rh-P})$ values for all the reported complexes (*ca.* 160 Hz, Table I) are similar to those observed for $[\text{Rh}(\text{PSR-C}_2)_2]\text{BF}_4$ [1], but are definitely larger than those exhibited by the $[\text{Rh}(\text{diphosphine})_2]^+$ derivatives (*ca.* 110–140 Hz) [7]. It is concluded that a square planar structure 1 can be proposed for all the $[\text{Rh}(\text{PSR})_2]^+$ cations, in which the two phosphorus atoms occupy a mutually *cis*-position.

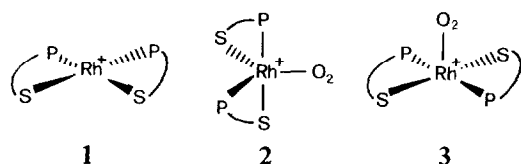
As previously reported [1], the cationic rhodium(I) complexes containing two chelate PSR-C_2 ligands, react with molecular oxygen leading to stable dioxygen 1:1 adducts, whose ^{31}P NMR spectra exhibit diagnostic ABX patterns indicative of a trigonal bipyramidal structure 2 with equatorial O_2 and two non-equivalent phosphorus atoms. Only in the case of

TABLE I. $^{31}\text{P}\{^1\text{H}\}$ NMR Data of Ligands and Rhodium(I) Complexes^a

Compound	δ (ppm)	Δ (ppm)	$J(\text{Rh}-\text{P})$ (Hz)
PSPh-C ₂	-17.00		
PSMe-C ₂	-17.80		
PSEt-C ₂	-16.80		
PSPh-C ₁	-18.50		
PSPh-C ₃	-17.20		
[Rh(NBD)(PSPh-C ₂)]BF ₄	55.90	72.90	161
[Rh(NBD)(PSMe-C ₂)]BF ₄	55.20	73.00	161
[Rh(NBD)(PSEt-C ₂)]BF ₄	55.80	72.60	163
[Rh(NBD)(PSPh-C ₁)]BF ₄	25.10	43.60	163
[Rh(NBD)(PSPh-C ₃)]BF ₄	15.90	33.10	154
[Rh(PSPh-C ₁) ₂]]BF ₄	20.10	38.60	155
[Rh(PSPh-C ₃) ₂]]BF ₄	23.40	40.60	167
[Rh(COD)(<i>cis</i> -VDP)]BF ₄	66.30	94.50	152
[Rh(<i>cis</i> -VDP) ₂]]BF ₄	70.10	98.30	134

^a In CD₂Cl₂ at 27 °C.

[Rh(PSMe-C₂)O₂]⁺, we observed a clean doublet, attributable either to a rapid rearrangement of the proposed trigonal bipyramidal structure or to a square pyramidal arrangement with axial O₂. Now we have carefully monitored from time to time the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of [Rh(PSEt-C₂)₂]]BF₄ in CD₂Cl₂ under an O₂ atmosphere. At the beginning, only an eight line ABX multiplet is observed (δ = 51.8, 52.7; $J(\text{Rh}-\text{P})$ = 135 and 115 Hz; $J(\text{P}-\text{P})$ = 22.7 Hz). However, after 15 h standing at room temperature, this pattern has completely disappeared, being replaced by a doublet centered at 52.4 ppm ($J(\text{Rh}-\text{P})$ = 127 Hz). Therefore, a slow isomerization of the trigonal bipyramidal structure takes place in solution, thus demonstrating that the observed doublet arises from a new rearrangement of the ligands, likely a square pyramidal structure **3** in solution with axial O₂ and the two phosphorus atoms in a mutually *trans*-position.



Experimental

All experiments were carried out under nitrogen and the solid products were stored at -20 °C. All solvents and reagents were reagent grade and were dried and purified before use.

The NMR spectra were obtained with a Jeol FX90Q (90 MHz) instrument operating in FT mode.

¹H chemical shifts are reported relative to internal tetramethylsilane, $^{31}\text{P}\{^1\text{H}\}$ relative to external 85% H₃PO₄; positive chemical shifts are downfield from the reference.

The PSR ligands were prepared by literature methods [8, 9]. [Rh(LL)₂]]BF₄ and [Rh(LL)(diene)]-BF₄ complexes were prepared as reported elsewhere [1, 2, 9]. In a typical procedure, a solution of [Rh-(diene)(acac)] (1 mmol) in 5 ml of dichloromethane was treated with a solution of 1 mmol of trityltetrafluoroborate in 5 ml of the same solvent. The ligand (1 or 2 mmol) was then added to the brown solution and after 30 min the stirring mixture was concentrated in vacuum and treated dropwise with diethylether. The crude products were recrystallized from dichloromethane-diethylether. Yields were in the range 70–90% and satisfactory elemental analyses were obtained (Table II).

¹H NMR (in CDCl₃) (t = triplet, b.s. = broad singlet, c.m. = complex multiplet) [Rh(NBD)(PSPh-C₂)]BF₄: 1.65 (c.m. NBD); 2.55–2.78 (c.m. 4H CH₂-CH₂); 4.14 (c.m. NBD); 4.90 (c.m. NBD); 7.30–7.53 (c.m. 15H C₆H₅); [Rh(NBD)(PSMe-C₂)]BF₄: 1.70 (c.m. NBD); 2.54 (b.s. 7H CH₃ and CH₂-CH₂); 4.14 (c.m. NBD); 4.42–5.61 (c.m. NBD); 7.48–7.57 (c.m. 10H C₆H₅); [Rh(NBD)(PSEt-C₂)]BF₄: 1.37 (t 3H CH₃, $J(\text{H}-\text{H})$ 7.3 Hz) 1.70 (c.m. NBD); 2.55–2.90 (c.m. 6H CH₂-CH₂-S-CH₂); 4.15 (c.m. NBD); 5.02 (c.m. NBD); 7.48–7.57 (c.m. 10H C₆H₅); [Rh(NBD)-(PSPh-C₁)]BF₄: 1.30 (c.m. NBD); 3.40 (b.s. 2H CH₂); 3.84, 4.23, 4.80 (c.m. NBD); 7.48–7.57 (c.m. 15H C₆H₅); [Rh(NBD)(PSPh-C₃)]BF₄: 1.37 (c.m. NBD); 1.86–2.75 (c.m. 6H CH₂-CH₂-CH₂); 3.53–3.87 (c.m. NBD); 7.51 (c.m. 15H C₆H₅); [Rh(PSPh-C₁)₂]]BF₄: 3.38 (c.m. 2H CH₂) 7.21–7.43 (c.m. 30H C₆H₅); [Rh(PSPh-C₃)₂]]BF₄: 1.97, 2.46, 3.02 (c.m.

TABLE II. Analytical Data for Ligands and Complexes

Compound	Analysis: found (calc.) (%)		
	C	H	S
PSPPh-C ₁	74.08(74.00)	5.61(5.55)	10.47(10.39)
PSPPh-C ₃	74.92(74.98)	6.35(6.29)	9.61(9.53)
[Rh(NBD)(PSPPh-C ₁)]BF ₄	53.10(52.91)	4.21(4.27)	5.52(5.42)
[Rh(NBD)(PSPPh-C ₂)]BF ₄	53.70(53.67)	4.36(4.50)	5.65(5.29)
[Rh(NBD)(PSPPh-C ₃)]BF ₄	54.21(54.37)	4.80(4.53)	5.25(5.19)
[Rh(NBD)(PSEt-C ₂)]BF ₄	49.61(49.67)	4.74(4.89)	5.73(5.75)
[Rh(NBD)(PSMe-C ₂)]BF ₄	48.34(48.74)	4.54(4.65)	5.61(5.90)
[Rh(PSPPh-C ₁) ₂]BF ₄	56.34(56.59)	4.62(4.25)	7.88(7.93)
[Rh(PSPPh-C ₃) ₂]BF ₄	58.11(58.47)	5.05(4.87)	7.31(7.43)
[Rh(COD)(cis-VDP)]BF ₄	58.52(58.82)	5.01(4.93)	
[Rh(cis-VDP) ₂]BF ₄	63.97(64.27)	4.77(4.56)	

12H CH₂-CH₂-CH₂); 7.23 (c.m. 30H C₆H₅); [Rh-(COD)(cis-VDP)]BF₄: 2.38-5.17 (c.m. NBD); 7.16-7.55 (c.m. C₆H₅ and CH=CH); [Rh(cis-VDP)₂]BF₄: 7.15-7.20 (c.m. C₆H₅ and CH=CH).

Acknowledgements

The authors wish to thank Mr A. Ravazzolo, C.N.R., for the helpful assistance and Ministero della Pubblica Istruzione for financial support.

References

- 1 M. Bressan, F. Morandini and P. Rigo, *Inorg. Chim. Acta*, **77**, L139 (1983).
- 2 M. Bressan, F. Morandini, A. Morvillo and P. Rigo, *J. Organomet. Chem.*, **280**, 139 (1985).
- 3 C. Bonuzzi, M. Bressan, F. Morandini and A. Morvillo, to be published.
- 4 R. Cramer, *Inorg. Synth.*, **15**, 16 (1974).
- 5 B. F. G. Johnson, J. Lewis and D. A. White, *J. Chem. Soc. A*, 2699 (1971).
- 6 P. E. Garrou, *Chem. Rev.*, **81**, 229 (1981).
- 7 B. R. James and D. Mahajan, *Can. J. Chem.*, **57**, 180 (1979).
- 8 P. Rigo and M. Bressan, *Inorg. Chem.*, **14**, 149 (1975).
- 9 A. Morvillo and M. Bressan, *Inorg. Chim. Acta*, **121**, 219 (1986).