Inorganica Chimica Acta, 154 (1988) 41–43

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 [Rh(diene)(acac)] (diene = cyclooctadiene or norbornadiene; acac = acetylacetonate) with bidentate ligands of the type $Ph_2P(CH_2)_nSR$ (n = 1, 2 or 3; R = Me, Et, Ph, not all combinations) or *cis*-$Ph_2PCH{=}CHPPh_2$ leads to $[Rh(diene)(LL)]^+$ or $[Rh(LL)_2]^+$, 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 $[M(PSR\text{-}C_2)_2]X$ (X = BPh_4, BF_4), where PSR-C_2 are the hybrid ligands $Ph_2P(CH_2)_2SR$ (R = Me, Et, 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 $^{31}P\{^1H\}$ NMR characterization of cationic rhodium(I) complexes $[Rh(diene)(LL)]^+$ and $[Rh(LL)_2]^+$ 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*-$Ph_2PCH{=}CHPPh_2$ are also reported.

Results and Discussion

The $[Rh(diene)(LL)]^+$ complexes, where diene is cycloocta-1,5-diene (COD) or bicyclo-hept-1,5-diene (NBD) and LL is $Ph_2P(CH_2)_nSR$ (n = 1, R = Ph, PSPh-C_1; n = 2, R = Ph, PSPh-C_2; n = 2, R = Me, PSMe-C_2; n = 2, R = Et, PSEt-C_2; n = 3; R = Ph, PSPh-C_3) or *cis*-1,2-bis(diphenylphosphino)ethylene (*cis*-VDP), were obtained by reacting [Rh(diene)(acac)] (acac = acetylacetonate) [4] with an equivalent of the appropriate ligand in the presence of stoichiometric amounts of trityltetrafluoborate in dichloromethane solution, following the procedure previously described in the literature [5]. The bis-chelate $[Rh(LL)_2]BF_4$ derivatives were prepared analogously, by reacting two equivalents of the ligands.

All the complexes behave as 1:1 electrolytes in nitromethane solution. The $^{31}P\{^1H\}$ NMR spectra of the $[Rh(diene)(LL)]BF_4$ 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 (R = Me, Et, 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(Rh–P) values for all the reported complexes (*ca.* 160 Hz, Table I) are similar to those observed for $[Rh(PSR\text{-}C_2)_2]BF_4$ [1], but are definitely larger than those exhibited by the $[Rh(diphosphine)_2]^+$ derivatives (*ca.* 110–140 Hz) [7]. It is concluded that a square planar structure **1** can be proposed for all the $[Rh(PSR)_2]^+$ cations, in which the two phosphorus atoms occupy a mutually *cis*-position.

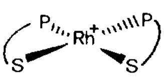
As previously reported [1], the cationic rhodium(I) complexes containing two chelate PSR-C_2 ligands, react with molecular oxygen leading to stable dioxygen 1:1 adducts, whose ^{31}P NMR spectra exhibit diagnostic ABX patterns indicative of a trigonal bipyramidal structure **2** with equatorial O_2 and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

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

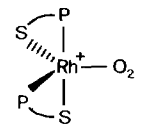
Compound	δ (ppm)	Δ (ppm)	J(Rh–P) (Hz)
PSPh-C_2	−17.00		
PSMe-C_2	−17.80		
PSEt-C_2	−16.80		
PSPh-C_1	−18.50		
PSPh-C_3	−17.20		
[Rh(NBD)(PSPh-C_2)]BF_4	55.90	72.90	161
[Rh(NBD)(PSMe-C_2)]BF_4	55.20	73.00	161
[Rh(NBD)(PSEt-C_2)]BF_4	55.80	72.60	163
[Rh(NBD)(PSPh-C_1)]BF_4	25.10	43.60	163
[Rh(NBD)(PSPh-C_3)]BF_4	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)(*cis*-VDP)]BF_4	66.30	94.50	152
[Rh(*cis*-VDP$)_2$]BF_4	70.10	98.30	134

[a] In CD_2Cl_2 at 27 °C.

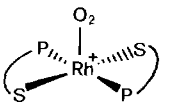
[Rh(PSMe-C_2)O_2]$^+$, we observed a clean doublet, attributable either to a rapid rearrangement of the proposed trigonal bipyramidal structure or to a square pyramidal arrangement with axial O_2. Now we have carefully monitored from time to time the $^{31}P\{^1H\}$ NMR spectrum of [Rh(PSEt-$C_2)_2$]BF_4 in CD_2Cl_2 under an O_2 atmosphere. At the beginning, only an eight line ABX multiplet is observed (δ = 51.8, 52.7; J(Rh–P) = 135 and 115 Hz; J(P–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(Rh–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 O_2 and the two phosphorus atoms in a mutually *trans*-position.



1



2



3

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, $^{31}P\{^1H\}$ relative to external 85% H_3PO_4; positive chemical shifts are downfield from the reference.

The PSR ligands were prepared by literature methods [8, 9]. [Rh(LL$)_2$]BF_4 and [Rh(LL)(diene)]BF_4 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 trityltetrafluoborate 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 $CDCl_3$) (t = triplet, b.s. = broad singlet, c.m. = complex multiplet) [Rh(NBD)(PSPh-C_2)]BF_4; 1.65 (c.m. NBD); 2.55–2.78 (c.m. 4H CH_2–CH_2); 4.14 (c.m. NBD); 4.90 (c.m. NBD); 7.30–7.53 (c.m. 15H C_6H_5); [Rh(NBD)(PSMe-C_2)]BF_4; 1.70 (c.m. NBD); 2.54 (b.s. 7H CH_3 and CH_2–CH_2); 4.14 (c.m. NBD); 4.42–5.61 (c.m. NBD); 7.48–7.57 (c.m. 10H C_6H_5); [Rh(NBD)(PSEt-C_2)]BF_4: 1.37 (t 3H CH_3, J(H–H) 7.3 Hz) 1.70 (c.m. NBD); 2.55–2.90 (c.m. 6H CH_2–CH_2–S–CH_2); 4.15 (c.m. NBD); 5.02 (c.m. NBD); 7.48–7.57 (c.m. 10H C_6H_5); [Rh(NBD)(PSPh-C_1)]BF_4: 1.30 (c.m. NBD); 3.40 (b.s. 2H CH_2); 3.84, 4.23, 4.80 (c.m. NBD); 7.48–7.57 (c.m. 15H C_6H_5); [Rh(NBD)(PSPh-C_3)]BF_4: 1.37 (c.m. NBD); 1.86–2.75 (c.m. 6H CH_2–CH_2–CH_2); 3.53–3.87 (c.m. NBD); 7.51 (c.m. 15H C_6H_5); [Rh(PSPh-$C_1)_2$]BF_4: 3.38 (c.m. 2H CH_2) 7.21–7.43 (c.m. 30H C_6H_5); [Rh(PSPh-$C_3)_2$]BF_4: 1.97, 2.46, 3.02 (c.m.

TABLE II. Analytical Data for Ligands and Complexes

Compound	Analysis: found (calc.) (%)		
	C	H	S
PSPh-C_1	74.08(74.00)	5.61(5.55)	10.47(10.39)
PSPh-C_3	74.92(74.98)	6.35(6.29)	9.61(9.53)
[Rh(NBD)(PSPh-C_1)]BF_4	53.10(52.91)	4.21(4.27)	5.52(5.42)
[Rh(NBD)(PSPh-C_2)]BF_4	53.70(53.67)	4.36(4.50)	5.65(5.29)
[Rh(NBD)(PSPh-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(PSPh-C_1)$_2$]BF_4	56.34(56.59)	4.62(4.25)	7.88(7.93)
[Rh(PSPh-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 CH_2–CH_2–CH_2); 7.23 (c.m. 30H C_6H_5); [Rh(COD)(*cis*-VDP)]BF_4: 2.38–5.17 (c.m. NBD); 7.16–7.55 (c.m. C_6H_5 and CH=CH); [Rh(*cis*-VDP)$_2$]BF_4: 7.15–7.20 (c.m. C_6H_5 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).