Reactions of the cationic bis(chelate) rhodium complex [Rh(P⌢O)₂]⁺ with SO₂, CS₂ and O₂/SO₂

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Abstract

The cationic bis(chelate) complex [Rh(P⌢O)₂][BPh₄] (1) (P⌢O: $\eta^2(O, P)$-chelated $(C_6H_{11})_2PCH_2CH_2OCH_3$ ligand) reacts with CS₂ and SO₂ to form the $\eta^2(C, S)$-coordinated carbon disulfide complex [RhCS₂(P⌢O)₂][BPh₄] (2) and the square-pyramidal η^1-SO₂ complex [Rh(η^1-SO₂)(P⌢O)₂][BPh₄] (4) respectively. According to the IR spectra, in complex 4 the RhSO₂ fragment adopts a pyramidal geometry. Upon treatment of the η^2-oxygen rhodium complex [RhO₂(P⌢O)₂][BPh₄] (3) with SO₂, the sulfato-O,O'-rhodium complex [RhSO₄(P⌢O)₂][BPh₄] (5) is accessible. The same compound is also available if complex 4 is reacted with oxygen. ¹⁰³Rh NMR investigations afford additional evidence for the coordination geometry in the complexes 1, 3, 4 and 5.

Keywords: Rhodium; Ether-phosphines; Sulfur dioxide; Carbon disulfide; ¹⁰³Rh NMR; Oxidation

1. Introduction

The activation of small molecules is still an important topic in transition metal catalyzed organic reactions. In particular, rhodium(I) and iridium(I) complexes are suitable catalysts for such reactions, and their mode of operation has already been reported [1]. In several cases [2] substantial improvement of these catalysts has been achieved by replacing classical tertiary phosphines by hemilabile ether-phosphine ligands. An example for this is the cobalt-catalyzed hydrocarbonylation of methanol to acetaldehyde [3]. Ether-phosphines are provided with a strong phosphorus donor and with an oxygen function incorporated in an open chain or cyclic ether moiety, which is able to stabilize coordinatively unsaturated metal complexes by formation of weak metal oxygen bonds [2]. Thus, the ether function may be regarded as an intramolecular solvent. A valuable starting compound for the activation of hydrogen, oxygen and methyl iodide proved to be the cationic bis(chelated) rhodium complex $[Rh(P⌢O)_2]^+$ (1) with $Cy_2PCH_2CH_2OCH_3$ as the O,P ligand [4,5]. In this investigation we want to report on the activation of CS₂, SO₂ and

SO₂/O₂ respectively. ¹⁰³Rh NMR measurements enable discrimination between the different geometries of the rhodium complexes obtained.

2. Results and discussion

To obtain additional information about the reactivity and stability of the bis(chelated) rhodium complex 1, it was allowed to react with CS₂ and SO₂. The octahedrally coordinated $\eta^2(C, S)$ carbon disulfide complex 2 is accessible by treatment of the starting compound 1 with an excess of CS₂ in dichloromethane at −40°C (Scheme 1). The reaction is accompanied by a spontaneous color change from orange to deep red and is quantitative within a few seconds. Complex 2 was obtained as a yellow powder which resists persistent efforts to crystallize. While 2 is rather stable in the solid state, in solution a gradual decomposition takes place even at −40°C. Probably the noncoordinated sulfur atom is cleaved from the carbon atom.

The composition of complex 2 was confirmed by an FD mass spectrum showing the M⁺ peak for the cation. In the ³¹P{¹H} NMR spectrum (Table 1) of 2 (−30°C) one observes an ABX pattern indicating two different phosphorus nuclei. The different ¹J(RhP) coupling con-

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stants are caused by inequivalent *trans* substituents, whereby the higher value is attributed to the phosphorus atom which is *trans* positioned to an ether oxygen donor. The oxygen function exerts a smaller *trans* effect than the sulfur atom, both are *trans* coordinated to the P ligands [6]. The ^2J(PP) coupling constant is in agreement with two phosphorus atoms in *cis* position. The ^{31}P chemical shift is characteristic of a five-membered chelate ring in which an ether-phosphine is involved. Recently we reported on the relationship between the ^{31}P chemical shift and the ring size [7]. Further support for the $\eta^2(O, P)$-coordination mode is furnished by the ^{13}C{^{1}H} NMR spectrum of 2 (Table 1); it reveals characteristic resonances for the carbon atoms in α-position to the ether oxygen atom [8]. The IR spectrum of 2 (Table 1) corroborates these NMR findings. Compared with the noncoordinated $Cy_2PCH_2CH_2OCH_3$ ligand, the antisymmetric C_2O vibration is shifted to lower wavelengths, which is diagnostic of rhodium–oxygen contact [9]. Additionally, an absorption at 1165 cm^{-1} is typical for an $\eta^2(C, S)$-coordination of the carbon disulfide [10].

If sulfur dioxide is bubbled into a dichloromethane solution of 1 at −40°C, the color changes immediately from orange to deep brown and formation of the complex [Rh(η^1-SO$_2$)(P⌒O)$_2$][BPh$_4$] (4) is accomplished within a few seconds. No reverse reaction with liberation of SO$_2$ is observed. Complex 4 precipitates from a dichloromethane/n-hexane solution as a pale yellow compound. At −30°C the ^{31}P{^{1}H} NMR spectrum of 4

Table 1
^{31}P{^{1}H} and selected ^{13}C{^{1}H} NMR (chemical shifts δ (ppm), coupling constants J (Hz)) and IR data (cm^{-1}) of complexes 2, 4 and 5

Complex	^{31}P NMR [a]			^{13}C NMR [b]		IR [c]
	δ	^1J(RhP)	^2J(PP)	CH$_2$O	OCH$_3$	ν_{as}(C$_2$O)
2	56.4 (dd)	153.7	17.8	72.33	61.72	1061 (m)
	43.4 (dd)	161.4	17.8	69.89	60.09	
4	60.9 (d)	174.2		72.90	64.04	1061 (m)
5	63.4 (dd)	140.2	24.4	79.43 [d]	67.31 [d]	1063 (m)
	40.7 (dd)	146.3	24.4	71.72 [d]	62.63 [d]	

[a] ^{31}P{^{1}H} NMR spectra obtained in CH$_2$Cl$_2$ at −30°C. [b] ^{13}C{^{1}H} NMR spectra obtained in CD$_2$Cl$_2$. [c] KBr. [d] ^{13}C{^{1}H} NMR spectrum obtained in acetone-d_6.

(Table 1) consists of an A_2X spin system which is explained by two equivalent phosphorus atoms in a square-pyramidal coordination sphere. The relatively large ^1J(RhP) coupling constant is in accordance with the lower *trans* influence of the ether oxygen atoms being *trans* positioned [11]. The ^{31}P chemical shift is in favor of a five-membered chelate ring, in which an ether-phosphine is involved. Moreover, the ^{13}C{^{1}H} chemical shifts (Table 1) of the carbon atoms in α-position to the ether oxygen function and the absorption of the antisymmetric C_2O stretching vibration in the IR spectrum of 4 are sufficient evidence for an $\eta^2(O, P)$-coordination of the ether-phophines.

According to Kubas [12] it is possible to determine the SO$_2$ geometry by means of the SO$_2$ stretching modes and the reactivity towards oxygen. The positions of both SO$_2$ bands, at 1033 and 1164 cm^{-1}, are in the expected range reported for an η^1-pyramidal RhSO$_2$ moiety. In particular, the fact that complex 4 is able to undergo sulfate formation within some minutes to give compound 5 (Scheme 1) with dioxygen provides further evidence for the presence of such a geometry [12]. Indeed, a solution of the dioxygen complex 3 in dichloromethane readily takes up sulfur dioxide at −40°C, whereupon the thermally stable sulfato complex 5 is isolated as a yellowish powder. It is soluble in polar organic solvents and its molecular composition is confirmed by a FAB mass spectrum. The ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra (Table 1) are similar to those of the precursor complex 3, hence the two ether-phosphines are chelated. A set of IR absorptions at 1265, 1228, 926, and 622 cm^{-1} is consistent with the presence of a bidentate $\eta^2(O, O')$ sulfate ligand [13].

The ability of dioxorhodium adducts to transfer oxygen atoms to inorganic and organic substrates has been well investigated [14], and reported in recent years for diphos [15], triphos [16] and $\eta^2(N, P)$-ligand [17] stabilized dioxorhodium complexes.

In recent years there has been an increased interest in NMR data of transition metals. ^{103}Rh NMR shifts have been correlated with stability constants, UV data, ki-

Anion : BPh$_4^-$
O,P = Cy$_2$PCH$_2$CH$_2$OCH$_3$
P⌒O = η^2(O,P)—coordinated ligand
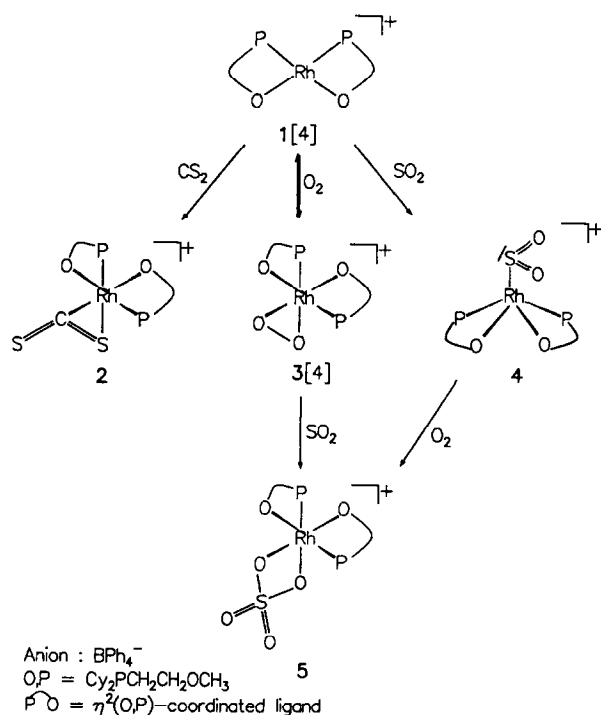
Scheme 1.

netic parameters, basicity of ligands, structural parameters, catalytic activity and other NMR parameters [18–21]. Because our investigations showed that compound 1 is catalytically active in CO_2 reduction [22], ^{103}Rh NMR shifts for complexes 1, 3, 4 and 5 have been determined in order to provide data in this context. The square-planar compound 1 ($\delta(^{103}$Rh$) = 65$ ppm) is strongly shielded compared with the octahedral complex 3 ($\delta(^{103}$Rh$) = 3770$ ppm) and 5 ($\delta(^{103}$Rh$) = 4063$ ppm). The shielding of the square-pyramidal complex 4 ($\delta(^{103}$Rh$) = 1950$ ppm) is between these extreme values. It is known that the oxidation state of the rhodium atom does not have much influence on the ^{103}Rh chemical shifts. The shielding is much more dependent on the coordination geometry, which has influence on the ΔE term of the paramagnetic contribution for the nuclear magnetic shielding. The shielding decreases from square-planar to octahedral symmetry due to the decrease in ligand field splitting [23]. This trend is confirmed by the chemical shift values of compound 1 versus compounds 3 and 5 and by other ^{103}Rh NMR measurements of neutral rhodium complexes [22]. The value for complex 4 indicates a different structure from square-planar or octahedral, thus suggesting the proposed square-pyramidal coordination.

3. Conclusion

In contrast to the behavior of the neutral mono(chelated) complex Rh(P⌢O)(P ~ O)Cl towards the above-mentioned small molecules, in all reported reactions the $\eta^2(O, P)$-coordination mode is preserved [22,24] because of the highly oxophilic property of the cationic rhodium system. Compared with the addition of hydrogen and oxygen [4], carbon disulfide and sulfur dioxide react with [Rh(P⌢O)$_2$][BPh$_4$] (1) in an irreversible way.

There is considerable interest in the activation of carbon dioxide by metal complexes [25]. Examples for the complexation of this unreactive molecule to transition metal complexes are rare [26]. Much use has been made, however, of the heterocumulenes OCS and CS$_2$ as more reactive models for carbon dioxide activation [10]. In the context of our efforts to hydrogenate carbon dioxide with [Rh(P⌢O)$_2$][BPh$_4$] (1) [22], compound 2 was synthesized as a model for the CO$_2$-fixation in a catalytic cycle.

The formation of an $\eta^2(O, O')$ sulfato rhodium complex is diagnostic of a pyramidal RhSO$_2$ fragment and a common reaction for low valent dioxygen complexes, indicating the peroxidic nature of the coordinated dioxygen.

4. Experimental section

All manipulations were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried over appropriate reagents and stored under argon. IR spectra were recorded on a Bruker IFS 48 FT-IR spectrometer. FD mass spectra were recorded on a Finnigan MAT 711 A instrument (8 kV, 60°C), modified by AMD; FAB mass spectra were obtained on a Finnigan TSQ 70 (10 kV, 50°C). Elemental analyses were performed with a Carlo Erba 1106 analyzer and a Perkin-Elmer Model 4000 atomic absorption spectrometer. Sulfur analyses were carried out according to Schöniger [27] and analyzed as described by Dirschel and Erne [28] and Wagner [29]. ^{1}H, ^{31}P{^{1}H}, ^{31}C{^{1}H} and ^{103}Rh{^{1}H} NMR spectra were measured with a Bruker DRX 250 spectrometer at 250.13, 101.25, 62.90 and 7.9 MHz. Chemical shifts were measured relative to partially deuterated solvent peaks which are reported relative to TMS. The ^{103}Rh-NMR resonances were measured using a 2D (^{31}P, ^{103}Rh){^{1}H} experiment [30] for compounds 1 and 5. Resonances for compounds 3 and 4 could only be determined by a ^{31}P{^{103}Rh, ^{1}H} DECP90 experiment owing to their fast decomposition. Chemical shift values are referred to Ξ(Rh) = 3.16 MHz [31]. (C$_6$H$_{11}$)$_2$PCH$_2$CH$_2$OCH$_3$ [32] and the complexes 1, 3 [4] were prepared as previously described.

4.1. Cis-bis[dicyclohexyl(2-methoxyethyl)phosphine-O,P](η²-C,S-carbon disulfide)rhodium(I) tetraphenylborate (2)

A solution of 1 (62 mg, 0.1 mmol) in 5 ml of dichloromethane was treated with CS$_2$ at − 40°C. Instantaneously the reaction mixture turned to deep red. 10 ml of *n*-hexane were added to the solution. The precipitate was collected, washed three times with 2 ml of *n*-hexane and dried in vacuo to yield 93 mg (92%) of complex 2; m.p. 93°C (dec); MS (FD, 8 kV, 35°C) *m/e* 693 [M$^+$–BPh$_4$]. Anal. Found: C, 63.68 [33]; H, 8.33; Rh, 9.73. C$_{55}$H$_{78}$BO$_2$P$_2$RhS Calc.: C, 65.21; H, 7.96; Rh, 10.16%. ^{113}C{^{1}H} NMR (62.90 MHz, CD$_2$Cl$_2$, − 30°C) 164.3 (q, ^1J(CB) 48.4 Hz, *ipso*-C of BPh$_4$), 136.2–122.6 (m, C–Ph), 37.26–35.54 (m, PCH).

4.2. Cis-bis[dicyclohexyl(2-methoxyethyl)phosphine-O,P](η¹-S-sulfur dioxide) rhodium(I) tetraphenylborate (4)

Sulfur dioxide was bubbled into a solution of 1 in 5 ml of dichloromethane at − 40 °C. A spontaneous color change from orange to dark brown occured. After 5 min of stirring an orange–yellow solid was precipitated with *n*-hexane (15 ml), which was dried in vacuo to yield 88 mg (89%) of 4; m.p. 94°C (dec); MS (FAB, 50°C) *m/e*

679 [M^+–BPh$_4$]. Anal. Found: C, 63.73 [33]; H, 7.66; Rh, 10.42. $C_{54}H_{78}BO_4P_2RhS$ Calc.: C, 64.93; H, 7.87; S, 3.21; Rh, 10.30%. $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_2Cl_2) 164.45 (q, $^1J(CB)$ 47.2 Hz, *ipso*-C of BPh$_4$), 136.4–122.3 (m, C–Ph), 39.21–35.15 (m, PCH).

4.3. Cis-bis[dicyclohexyl(2-methoxyethyl)phosphine-O,P](η^2-O,O'-sulfate)rhodium(III) tetraphenylborate (5) (prepared from 3)

Sulfur dioxide was passed through a solution of 3 (94 mg, 0.1 mmol) at $-40°C$. After 5 min of stirring the pale yellow compound was precipitated with *n*-hexane (15 ml) and dried in vacuo to yield 97 mg (94%); m.p. 107°C (dec); MS (FAB) m/e 711 [M^+–BPh$_4$]. Anal. Found: C, 60.49 [33]; H, 7.69; S, 3.13; Rh, 9.61. $C_{54}H_{78}BO_6P_2RhS$ Calc.: C, 62.91; H, 7.63; S, 3.11; Rh, 9.98%. $^{13}C\{^1H\}$ NMR (62.90 MHz, acetone-d_6) 164.9 (q, $^1J(CB)$ 47.9 Hz, *ipso*-C of BPh$_4$), 137.0–122.4 (m, C–Ph), 38.0–36.6 (m, PCH).

4.4. Cis-bis[dicyclohexyl(2-methoxyethyl)phosphine-O,P](η^2-O,O'-sulfate)rhodium(III) tetraphenylborate (5) (prepared from 4)

Dioxygen was bubbled into a solution of 4 in 5 ml of dichloromethane at $-40°C$. After 10 min of stirring a pale yellow solid was precipitated with *n*-hexane (15 ml) and dried in vacuo to yield 89 mg (86%). The compound was characterized by its $^{31}P\{^1H\}$ NMR spectrum (101.25 MHz, CD_2Cl_2) 63.4 (dd, $^1J(RhP)$ 140.2, $^2J(PP)$ 24.4 Hz), 40.7 (dd, $^1J(RhP)$ 146.3, $^2J(PP)$ 24.4 Hz).

Acknowledgements

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