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PREPARATION AND PROPERTIES OF NEW TRIPLY-BRIDGED DI-μ-PYRAZOLATE (μ-CARBONYL)DIRHODIUM COMPLEXES WITH PENTAMETHYLCYCLOPENTADIENYL AND DIPHOSPHINE LIGANDS

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Summary

Cationic complexes of formula $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(L{-}L)]BPh_4$ were prepared by treating a methanolic suspension of $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2]$ with $NaBPh_4$ in the presence of the bidentate ligands L–L (L–L = bis(diphenylphosphino)methane(dppm), 1,4-bis(diphenylphosphino)butane (dppb), *cis*-1,2-bis(diphenylphosphino)ethylene (dppen), 1,2-bis(diphenylarsino)ethane (dpae)). The intermediate complex $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)(dppen)]BPh_4$ was isolated. The formation of the related compounds $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)L]BPh_4$ (L = PPh_3, PCy_3) is also reported.

Introduction

Very recently we reported the synthesis of the heterovalent Rh^{III}–Rh^{I} complex $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2]$ (I) [1]. This complex reacts with 1,3-bis(diphenylphosphino)propane (dppp) in methanol to yield an unusual triply-heterobridged complex of formulae $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppp)]^+$ (II), which was characterized by X-ray diffraction [2]. It seemed of interest to prepare some related derivatives in order to explore the effect of the nature of the diphosphine ligand on the reactivity. It was already known that in some CO substitution reactions of rhodium complexes the nature of the products depends on the chain length of the chelate diphosphine present [3,4].

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TABLE 1

ANALYSES, MOLAR CONDUCTIVITIES, IR DATA AND YIELDS FOR THE COMPLEXES III–X

Complex	Analyses (Found (calcd.)(%))			Λ_M (Ω^{-1} cm^2 mol^{-1})	ν(CO) [a] (cm^{-1})	Yield (%)
	C	H	N			
$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)(dppen)]BPh_4$ (III)	65.5 (65.5)	4.9 (5.1)	4.0 (4.5)	71	2080, 1725	66
$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppen)]BPh_4$ (IV)	64.4 (66.0)	5.6 (5.2)	4.1 (4.6)	72	1785	98
$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)(PPh_3)]BPh_4$ (V)	–	–	–	–	2060, 1830	–
$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)(PCy_3)]BPh_4$ (VI)	63.4 (63.8)	6.9 (6.6)	4.9 (4.95)	78	2035, 1830	30
$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppm)]BPh_4$ (VII)	66.3 (65.7)	5.2 (5.3)	4.45 (4.6)	75	1767	63
$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppb)]BPh_4$ (VIII)	64.7 (66.4)	5.6 (5.6)	4.2 (4.5)	71	1765	63
$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dpae)]BPh_4$ (IX)	62.4 (63.3)	4.9 (5.0)	4.3 (4.3)	75	1750	28
$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppb)]BF_4$ (X)	52.8 (53.2)	4.9 (4.9)	5.1 (5.5)	122	1770	45

[a] Nujol mulls.

TABLE 2

SELECTED ^1H AND ^{31}P NMR DATA[a] FOR THE PREPARED COMPLEXES

Complex	^1H NMR			$^{31}P\{^1H\}$NMR	
	C_5Me_5	H(4)[b]	$(CH_2)_n$	δ(P)	^1J(Rh–P)
II	1.45 s	5.92 bs	2.49 m	22.4 d	137.6
III[c]	1.79 s	5.69 t[d]	6.42[e] m	–	–
IV[c]	1.47 s	6.15 bs	6.30[e] m	72.0	147.8
VI	1.53 s	6.20 bs	–	46.3	124.6
VII	1.42 s	6.23 bs	4.20 m	–21.3 d	124.6
VIII	–	–	–	22.4 d	136.8
IX	1.32 s	6.16 t[f]	2.42 m	–	–
X	1.30 s	5.92 bs	–[g]	–	–

[a] Spectra were measured in $CDCl_3$ solution at 200 and 32.43 MHz for ^1H and ^{31}P respectively. Chemical shifts are given in δ(ppm) relative to TMS (^1H) or H_3PO_4 (^{31}P) and coupling constants in Hz. A negative sign indicates a resonance to higher field of the reference. s singlet, d doublet, t triplet, m multiplet, b broad. [b] H(4) represents the proton on the C(4) of the pyrazolate ring. [c] ^1H NMR spectrum measured in acetone-d_6 solution. [d] Pseudotriplet with ^3J(HH) 2 Hz. [e] Chemical shift of the CH=CH of the diphosphine protons. [f] Pseudotriplet with ^3J(HH) 2.2 Hz. [g] Very broad multiplet.

Results and discussion

The addition of *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) to a methanolic suspension of the orange complex I, containing $NaBPh_4$ gives a dark red solid. The IR spectrum (in Nujol) of this material shows the presence of two ν(CO) absorptions, at 2080 and 1725 cm^{-1}, attributable to terminal and bridging carbonyl ligands, respectively. Its ^1H NMR spectrum, in acetone-d_6 solution, presents resonances at δ 1.79(s), 6.42(m) and 5.69(t) ppm in 15/2/2 ratio, assigned respectively to a C_5Me_5 ring, to the CH=CH vinyl group of one dppen ligand and to the H(4) protons of two equivalents pyrazolate groups, along with a complex multiplet in the 6.8–8 ppm region. On the basis of these data and of the analytical and conductivity measurements (Table 1) we conclude that the product should be formulated as $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)(dppen)]BPh_4$ (III).

When complex III is dissolved in acetone, chloroform or dichloromethane, the initial dark red colour of the solution slowly changes to orange, and the IR spectra show the disappearance of the ν(CO) bands of the starting material and the parallel appearance of a new ν(CO) band at 1790 cm^{-1} (CH_2Cl_2 solution). After 72 h reaction the complex $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppen)]BPh_4$ (IV) was isolated as an orange solid; its analytical and spectroscopic data (Tables 1 and 2) were consistent with this formulation for the cation in complex IV, involving two pyrazolate and one CO group acting as bridging ligands. Thus in solution complex III slowly loses the terminal CO group to give IV (eq. 1):

$$[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)(dppen)]^+ \xrightarrow{-CO} \underset{(IV)}{[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppen)]^+} \quad (1)$$

In this context it is noteworthy that reaction of complex I with monodentate tertiary phosphines, such as PPh_3 or PCy_3, under similar conditions (i.e. with methanol as solvent and in the presence of $NaBPh_4$) gives the new cationic species $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)L]BPh_4$ (L = PPh_3 (V), PCy_3 (VI)) (eq. 2),

$$[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2] \xrightarrow[NaBPh_4]{L} [(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)L] + [(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(CO)L]^+ \qquad (2)$$

(L = PPh_3, PCy_3)

related to complex III (for spectroscopic data see Tables 1 and 2), along with the recently reported neutral complexes $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)L]$ [1], formed by partial displacement of the coordinated carbonyl groups * (eq. 2). Complex VI was obtained analytically pure, but complex V was not.

The formation of the complexes II and IV by reaction of dppp or dppen with complex I seems to be a general reaction. Thus, other diphosphines such as bis(diphenylphosphino)methane (dppm) or 1,4-bis(diphenylphosphino)butane (dppb) or the diarsine 1,2-bis(diphenylarsino)ethane (dpae) react with complex I in methanol and in the presence of $NaBPh_4$ to give the complexes $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(L\text{–}L)]BPh_4$ (L–L = dppm (VII), dppb (VIII), dpae (IX)). That complexes IV and VII–IX must have similar structures to complex II is indicated by the virtually identical spectroscopic data (Tables 1 and 2) [2]. It is of interest that the dppm ligand acts as a chelate, in spite of its well known tendency to act as binucleating ligand [5]. In this connection it is relevant to note previously prepared and structurally characterized dinuclear rhodium complexes containing pyrazolate and dppm as bridging groups (e.g. $[Rh_2(\mu\text{-pz})(\mu\text{-dppm})_2(CO)_2]^+$, $[Rh_2I_2(\mu\text{-pz})(\mu\text{-dppm})_2(CO)_2]^+$ and $[Rh_2I_2(\mu\text{-pz})_2(\mu\text{-dppm})(CO)_2]$) [6].

The cationic complexes of formulae $[(C_5Me_5)Rh(\mu\text{-pz})(\mu\text{-pz})_2(\mu\text{-CO})Rh(L\text{–}L)]^+$ could also be prepared treating I with silver salts and the corresponding L–L ligand, as exemplified for dppb in eq. 3:

$$[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)_2] + AgBF_4 + dppb \xrightarrow{\text{acetone}} \underset{(X)}{[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(dppb)]BF_4} + AgCl + CO \qquad (3)$$

This complex has similar spectroscopic data to those for the related BPh_4 derivative (VIII), except for the expected differences due to the presence of a BF_4 anion.

It should be noted that attempts to prepare a complex analogous to complexes II, IV, and VII–IX but containing the bidentate ligand bis(diphenylarsino)methane (dpam) have been unsuccessful. This failure could be due to the rather low tendency of this ligand to act as chelate [7]. On the other hand, the good chelating ligands 2,2′-bipyridine and 1,10-phenanthroline do react with I in refluxing methanol, in the presence of $NaBPh_4$ but only unidentified, products not containing CO ligands, were detected.

In summary, the reaction of I with chelating diphosphines, in methanol and in the presence of Na^+, gives $[(C_5Me_5)Rh(\mu\text{-pz})_2(\mu\text{-CO})Rh(L\text{–}L)]^+$ complexes. The di-

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* In dichloromethane and in the absence of $NaBPh_4$ these neutral $[(C_5Me_5)ClRh(\mu\text{-pz})_2Rh(CO)L]$ complexes are the only products from the reaction of complex I with L [1].

phosphine ligands react with the Rh^I atom of the complex $[(C_5Me_5)ClRh(\mu\text{-}pz)_2Rh(CO)_2]$ (I), forcing one of the carbonyl ligands to move from the terminal position to the bridging site. This carbonyl group coordinates at the vacant position generated in the other rhodium centre by the abstraction of the chloride ligand by the sodium cation. The final products of the reaction are the markedly stable $[(C_5Me_5)Rh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh(L\text{-}L)]^+$ complexes (II, IV, VII–IX). The isolation of the intermediate complex III (L–L = dppen), the detection of V, and the characterization of VI support these suggestions.

The complexes reported in this paper and the homovalent dinuclear rhodium complex $[(PPh_3)IRh(\mu\text{-}dmp)_2(\mu\text{-}CO)RhI(PPh_3)]$ (dmp = 3,5-dimethylpyrazolate) reported by Powell et al. [8] are the only examples of complexes containing a "$Rh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh$" framework.

These results, along with those of previous work on rhodium chemistry in different formal oxidation states (I, II or III), confirm the remarkable ability of the pyrazolate ligands to stabilize a variety of triply-bridged situations of the type "$Rh(\mu\text{-}pz)_{3-x}(\mu\text{-}Y)_xRh$" ($x = 1$; Y = CO [2, 8, this work], dppm [6b], OH [9], HgCl [10]. $x = 2$; Y = OMe [9], dppm [6a]).

Experimental

Reactions were carried out in air. The solvents were dried by standard methods and distilled before use. C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. Conductivities were measured at 20°C in ca. 5×10^{-4} *M* acetone solutions using a Philips 9501/01 conductimeter. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets or in dichloromethane or chloroform solutions between NaCl plates. ^1H NMR spectra were recorded on a Varian XL 200 Spectrometer at room temperature and ^{31}P NMR spectra were recorded on a Bruker AM 80 instrument.

Complexes I and II were prepared by published procedures [1,2].

Preparation of the complex $[(C_5Me_5)Rh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh(CO)(dppen)]BPh_4$ *(III)*

To a suspension of complex I (117.4 mg, 0.21 mmol) in methanol (15 ml) were added successively $NaBPh_4$ (75.6 mg, 0.22 mmol) and dppen (88.3 mg, 0.21 mmol). The solids dissolved and a slow precipitation of a dark red solid began immediately. The mixture was stirred for 22 h then the solid was filtered off, washed with MeOH and Et_2O, and air-dried.

Preparation of the complex $[(C_5Me_5)Rh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh(dppen)]BPh_4$ *(IV)*

Complex III (60.9 mg, 0.05 mmol) was dissolved in $CHCl_3$ (10 ml). The initial dark red colour of the solution slowly changed to orange. After 72 h stirring the solution was concentrated under reduced pressure (ca. 2 ml) and complex IV was precipitated in almost quantitative yield by addition of n-hexane (20 ml). Similar results were obtained with acetone or dichloromethane as solvents.

Preparation of the complexes $[(C_5Me_5)Rh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh(CO)(L)]BPh_4$ *($L = PPh_3$ (V), PCy_3 (VI))*

To a suspension of complex I (0.30 mmol) in methanol (20 ml) were added successively $NaBPh_4$ (0.33 mmol) and a solution of the corresponding L ligand (0.30 mmol) in the same solvent (3 ml). The solids dissolved and a slow precipitation of an orange solid began immediately. The suspensions were stirred for 24 h and the mixture of solids was then filtered off. Extraction with acetone (3 × 10 ml, room temperature) gave an orange-red solution, which was concentrated under reduced pressure. Subsequent addition of n-hexane (20 ml) gave a precipitate of analytically pure complex VI.

Preparation of the complexes $[(C_5Me_5)Rh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh(L\text{-}L)]BPh_4$ *(L–L = dppm (VII), dppb (VIII), dpae (IX))*

To a suspension of complex I (0.20 mmol) in methanol (12 ml) were successively added $NaBPh_4$ (0.26 mmol) and a solution of the corresponding L–L ligand (0.20 mmol) in the same solvent (3 ml). The solids dissolved and a slow precipitation of dark red (dppm) or orange (dppb, dpae) solids began immediately. The mixtures were stirred for 20 h (dppm, dpae) or 87 h (dppb) and the solid formed was filtered off. The products were washed with MeOH and Et_2O then air dried.

Preparation of the complex $[(C_5Me_5)Rh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh(dppb)]BF_4$ *(X)*

To a suspension of complex I (108.7 mg, 0.20 mmol) in methanol (15 ml) was added a solution of $AgBF_4$ (37.8 mg, 0.20 mmol) in the same solvent (2 ml). The complex dissolved and AgCl was immediately precipitated. The mixture was stirred for 20 min and the AgCl was filtered off. To the resulting filtrate were added 81.5 mg (0.20 mmol) of dppb, and the orange solution was stirred for 1.5 h then concentrated under reduced pressure (ca. 2 ml). Addition of Et_2O (15 ml) gave an orange precipitate, which was filtered off, washed with Et_2O, air-dried, and recrystallized from CH_2Cl_2/Et_2O.

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