Heterobimetallic Group 6-rhodium complexes III [*]. [M(CO)₃(NN)(dppm-P)] (M = Mo, W; NN = phen or bpy) as P-donor in M–Rh complexes

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Abstract

A new synthetic route to heterobimetallic M–Rh (M = Mo or W) complexes has been explored. The procedure is the reaction of Rh^I complexes of the type [{RhCl(diolefin)}₂] (diolefin = NBD or COD) with the complexes of monodentate dppm [M(CO)₃(NN)(dppm-P)] (NN = phen or bpy), which are potential phosphine ligands.

The products obtained were studied by IR, ^{31}P-NMR and ^{1}H-NMR spectroscopies and formulated as [(CO)₂(NN)M(μ-CO)-(μ-dppm)RhCl(diolefin)] (M = Mo or W; diolefin = NBD or COD; NN = phen or bpy) containing a M–Rh bond bridged by dppm and semibridged by CO.

Keywords: Molybdenum; Tungsten; Dinuclear diphosphine complexes; Heterobimetallic complexes; Rhodium–Group 6 complexes; Diphenylphosphinemethane

1. Introduction

It is well known that [{RhCl(CO)₂}₂] reacts readily with phosphines [1]. This reaction has been used to synthesize heterobinuclear complexes with bridging diphosphine dppm (Ph₂PCH₂PPh₂) or dppe (Ph₂-PCH₂CH₂PPh₂) [2–5]. Most of these compounds have two bridging dppm, but a few examples with only one bridging dppm have been described [6,7].

For several years we have been interested in producing bimetallic M–Rh (M = Mo or W) systems bridged by one dppm and some other ligands [8,9]. In these complexes the proximity of the bridged metal centres involved should favour cooperative effects which might be used in catalytic processes [10]. In a previous paper we reported the compounds [(CO)₃M(μ-Cl)(μ-CO)(μ-dppm)Rh(NBD)] (M = Mo or W) obtained by reaction of [RhCl(NBD)]₂ with [M(CO)₄(dppm-PP')], which were characterized as bimetallic systems containing only one bridging dppm. X-ray analysis of the molybde-num derivative confirmed the presence of a Rh–Mo bond bridged by dppm, carbonyl and chloride [8].

Following the above, in this work we describe a synthetic route using [M(CO)₃(NN)(dppm-P)] (NN = phen or bpy) [11] as a phosphine ligand in their reactions with [{RhCl(diolefin)}₂] (diolefin = NBD or COD).

2. Results and discussion

The reactions between [{RhCl(NBD)}₂] and [M-(CO)₃(NN)(dppm-P)] (M = Mo or W; NN = phen or bpy) in a 1:2 molar ratio in CH₂Cl₂ solution at −20°C yield the binuclear heterobimetallic complexes [(CO)₂-(NN)M(μ-CO)(μ-dppm)RhCl(NBD)] [M = Mo, NN = phen (1a); M = Mo, NN = bpy (1b), M = W, NN = phen (1c); M = W, NN = bpy (1d)]. The compounds were isolated as dark blue solids, slightly soluble in all common solvents but only stable at −20°C. A quantitative analysis by X-ray fluorescence showed a 1:1 Mo/Rh ratio. A tungsten anticathode and an analyser crystal of LiF(200) 2D = 4.0267 Å were used in the X-ray tube; Rh Kα = 0.6147 Å, Mo Kα = 0.7107 Å.

When the reactions were carried out at room temperature, a mixture of the above dinuclear compounds with others is formed, from which we were unable to separate the desired complexes despite repeated attempts. By column chromatography in silica gel using CH_2Cl_2 as eluent, [{RhCl(CO)(dppm)}$_2$] [12] and decomposition products were obtained from orange and subsequent bands, respectively.

The low-temperature requirement for the isolation and stabilization of the new dinuclear compounds was deduced by an IR study of the solution reaction. The $\nu(CO)$ absorption region (2200–1600 cm^{-1}) was monitored for each compound at ten minute intervals during 2 h. As an example, we describe the reaction of [W(CO)$_3$(bpy)(dppm-P)] with [{RhCl(NBD)}$_2$] (Fig. 1). In the first scan, in addition to the three bands at 1905, 1810 and 1785 cm^{-1} attributed to $\nu(CO)$ of the starting carbonyl tungsten compound, two new bands at 1780 and 1750 cm^{-1} were also observed.
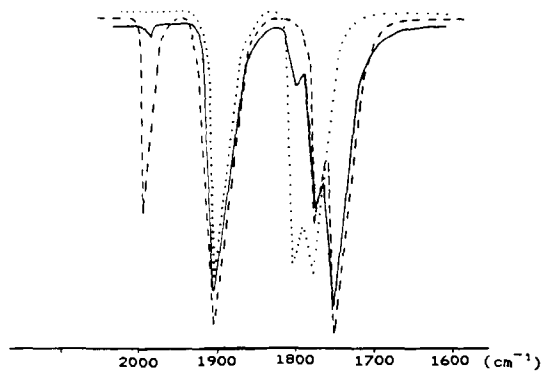

Fig. 1. IR spectra in the carbonyl region of reaction solutions in CH_2Cl_2 of [W(CO)$_3$(bpy)(dppm-P)] with [{RhCl(NBD)}$_2$]. · · · · · [W(CO)$_3$(bpy)(dppm-P)]. ——— [W(CO)$_3$(bpy)(dppm-P)]+[RhCl(NBD)]$_2$ (after 10 min). - - - - - [W(CO)$_3$(bpy)(dppm-P)]+[RhCl(NBD)]$_2$ (after 2 h).

Table 1
IR (cm^{-1}) and ^{1}H-NMR (δ (ppm), J (Hz)) spectroscopic data of new complexes [(CO)$_2$(NN)M(μ-CO)(μ-dppm)RhCl(NBD)] (**1a–d**) and [(CO)$_2$(phen)W(μ-CO)(μ-dppm)RhCl(COD)] (**2**)

IR [a]					^{1}H-NMR [b]		
Complex	CO ν(CO) KBr	CH_2Cl_2	NBD β(CH)	COD β(CH)	NBD	COD	CH$_2$ in dppm
1a	1890vs	1905vs	1310m		5.76 (s, C–H)		2.87 (t)
	1785sh	1790s			4.19 (s, C–H)		^2J(H–P) = 10.6
	1760vs	1765s			3.99 (s, –C–H)		
					1.18 (s, CH$_2$)		
1b	1890vs	1905vs	1310m		5.70 (s, C–H)		2.89 (t)
	1785sh	1790s			4.20 (s, C–H)		^2J(H–P) = 10.1
	1755vs	1760vs			3.97 (s, –C–H)		
					1.19 (s, CH$_2$)		
1c	1880vs	1895vs	1310m		5.82 (s, C–H)		3.09 (t)
	1775sh	1780s			4.19 (s, C–H)		^2J(H–P) = 10.7
	1750vs	1755vs			3.99 (s, –C–H)		
					1.18 (s, CH$_2$)		
1d	1880vs	1905vs	1310m		5.79 (s, C–H)		3.16 (t)
	1775sh	1780sh			4.21 (s, C–H)		^2J(H–P) = 10.8
	1745vs	1750vs			3.96 (s, –C–H)		
					1.26 (s, CH$_2$)		
2	1895vs			1505w		5.60 (s, C–H)	3.40 (t)
	1775sh			1300w		3.52 (s, C–H)	^2J(H–P) = 10.6
	1745vs					2.37 (s, CH$_2$)	
						1.90 (s, CH$_2$)	

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [b] In CD$_2$Cl$_2$ at −20°C. s, singlet; t, triplet

Table 2
^{31}P-NMR (δ (ppm), J (Hz)) spectroscopic data of new complexes [(CO)$_2$(NN)M(μ-CO)(μ-dppm)RhCl(NBD)] (1a–d) and [(CO)$_2$(phen)W(μ-CO)(μ-dppm)RhCl(COD)] (2)

Complex	δ (P$_A$)	δ (P$_B$)	$^d \Delta\delta$(P$_A$)	$^c \Delta\delta$(P$_B$)	^2J(P$_A$–P$_B$)	^1J(P$_A$–Rh)	^1J(P$_A$–W)
[a] 1a	22.76 (d)	33.00 (dd)	44.46	60.50	83.3	164.9	–
[a] 1b	22.25 (d)	33.50 (dd)	43.95	61.00	81.5	166.0	–
[b] 1c	11.96 (d)	34.43 (dd)	33.66	62.23	76.6	165.6	227.8
[b] 1d	12.11 (d)	35.07 (dd)	33.81	62.77	75.3	166.7	233.5
[c] 2	13.00 (d)	37.60 (dd)			74.5	159.0	

[a] In CD$_2$Cl$_2$/C$_6$D$_6$ solution at -50°C. [b] In CD$_2$Cl$_2$/C$_6$D$_6$ solution at -20°C. [c] In CDCl$_3$ solution at -20°C. [d] See text [e] See text
d = doublet, dd = doublet of doublets.

The intensity of the bands at 1810 and 1785 cm^{-1} decreased with time and after 2 h both disappeared. Simultaneously, an increase in the intensity of the other three bands, at 1905, 1780 and 1750 cm^{-1}, was observed (Fig. 1) and therefore these are assigned to ν(CO) of the new bimetallic compound. The absorption at 1750 cm^{-1} was attributed to ν(CO) of a semibridging carbonyl group, consistent with the values found for the stretching band of this group in related compounds [13,14]. The band at ca. 2000 cm^{-1}, attributed to ν(CO) of [{RhCl(CO)(dppm)}$_2$] [12] was present from the first scan and increased in intensity with time. However, at lower temperature the intensity of this band decreases, and at about -20°C it disappears altogether. We deduce that the temperature required to prevent the formation of this unwanted compound is -20°C, allowing the isolation of the pure bimetallic compounds [1a–d].

The IR spectra of the new compounds (Table 1) were also recorded in KBr pellets and show ν(CO) in the same range, 1890–1755 cm^{-1} (1a, b) and 1880–1745 cm^{-1} (1c, d). The pattern of bands suggests a *fac* carbonyl environment, similar to the parent compound, but with a semibridging carbonyl group. In the lower frequency region there is no evidence of an absorption band due to ν(RhCl). However, this has already been observed in chloroRh[III] heterobimetallic complexes containing dppm [15].

The ^{31}P-NMR spectra were obtained in CD$_2$Cl$_2$/C$_6$D$_6$ (Table 2) under N$_2$ at -50°C (1a, b) and -20°C (1c, d). These temperatures were required to allow adequate resolution without decomposition. The spectra consist of two resonances at δ(35.5–33.0) ppm and δ(22.8–11.5) ppm (Fig. 2). The former, which is a doublet of doublets, was assigned to the phosphorus atom bonded to rhodium (P$_B$) (^1J(P$_B$–Rh) = 164.9–166.7 Hz) and the other signal (a doublet) to the phosphorus atom bonded to Mo(W)(P$_A$). Satellites due to the P$_A$–W coupling (^1J(P$_A$–W) = 233.5 Hz, NN = bpy, 227.8 Hz, NN = phen) were observed in the tung-

sten derivatives. The coordination shifts $\Delta\delta$(P$_A$)($\Delta\delta$-(P$_A$) = δP$_{bimetallic\ complex}$ − δP$_{free\ phosphine}$) (Table 2) follow the expected order W < Mo, depending on the metal. In contrast, longer donation from P$_B$ to the rhodium
is deduced from the $\Delta\delta$(P$_B$) values ($\Delta\delta$(P$_B$) = δP$_{bimetallic\ complex}$ − δP$_{initial\ tricarbonylic\ complex}$)[1] in the tungsten complexes compared to the molybdenum. In these complexes it appears that, for the same μ-P$_A$–P$_B$, P$_A$-metal donation to the Group 6 metals falls, giving rise to an increase in P$_B$–Rh donation.

The ^{1}H-NMR spectra, in CD$_2$Cl$_2$ at -20°C (Table 1) show NBD signals at H$_1$$\delta$(5.70–5.82), and H$_2$-$\delta$(4.19–4.21), H$_3$ δ(3.96–3.99) and H$_4$ δ(1.18–1.26) ppm (Fig. 3) as well as a single resonance in the range δ (2.87–3.16) ppm (^2J(H–P) 10.1–10.8 Hz), which suggests the equivalence of the methylene protons of the dppm.

We have two suggestions to explain the non-equivalence of the NBD olefinic protons. The first assumes that the diolefin is fluxional, showing non-equivalent olefinic bonds at -20°C, probably due to two different orientations of the NBD.

A fair number of dienes in four- and five-coordinate rhodium complexes have been found to reorient [16], but this behaviour has not always been observed for NBD derivatives; so it is remarkable that [{Rh(NBD)-(OAc)}$_2$] showed restricted rotation of NBD groups [17].

In addition, five-coordinate complexes of the type [B(pz)$_4$Rh(diene)] (diene = NBD or COD) showed very rapid exchange between the axial and equatorial sites

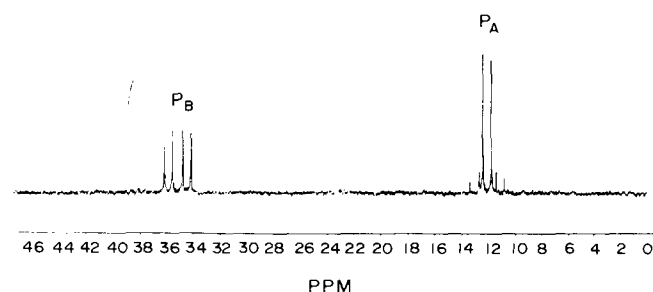46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0

PPM

Fig. 2. ^{31}P-NMR spectrum of [(CO)$_2$(bpy)W(μ-CO)(μ-dppm)RhCl-(NBD)].

[1] The initial complex [M(CO)$_3$(NN)(dppm-*P*)] with an uncoordinated phosphorus atom (P$_B$) was used as reference.
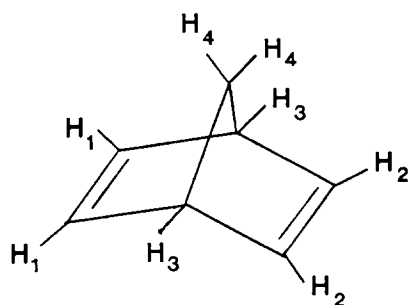
Fig. 3. Position of H_1, H_2, H_3 and H_4.

Fig. 5. Two different resonances for the olefinic protons, H_1 and H_2.

on the NMR time scale even at $-89.6°C$ [18]. The complexes (1a–d) may be stereochemically non-rigid, but our NMR data are not adequate to prove this.

One alternative explanation emerges from considering the static structures proposed for (1a–d) (Fig. 4), in which the asymmetric environment at rhodium could be distorted by interaction at molybdenum through a semibridging CO group, giving rise to the non-equivalence of olefinic protons H_1 and H_2. However, in the absence of a variable-temperature NMR study, which is not possible due to the instability of compounds, we were unable to decide between these rationalizations.

On the basis of the above results we conclude that the reactions of [{RhCl(NBD)}$_2$] and [M(CO)$_3$(NN)-(dppm-P)] give rise to new MoRh and WRh bimetallic compounds, bridged by a dppm and a CO as depicted in Fig. 4.

The coordination polyhedron around Mo(W) atom is constituted of the same ligands as in the starting compounds, and the rhodium atom is almost five coordinated via the bidentate diolefin and a chloride ligand as well as a bridging dppm and a semibridging CO. An additional bond between the two metals M–Rh (M = Mo or W) would satisfy a 36e$^-$ configuration and is
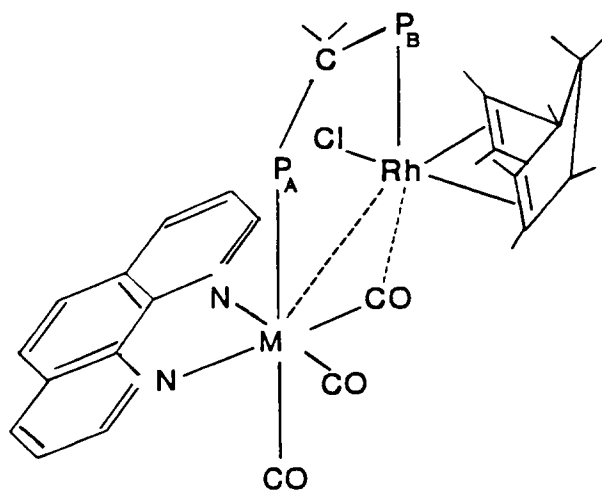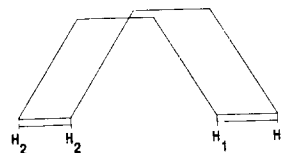
consistent with the metal proximity produced by the two bridges.

In order to obtain additional support for the above structural proposal, and due to the failure of attempts to grow suitable crystals for structural X-ray determination even at low temperature, we have studied the behaviour of a related reaction using [{RhCl(COD)}$_2$] as starting compound.

Treatment of a dichloromethane solution of [{RhCl-(COD)}$_2$] with [W(CO)$_3$(phen)(dppm-P)] in 1:2 molar ratio at $-20°C$ gave the heterobimetallic complex [(CO)$_2$(phen)W(μ-CO)(μ-dppm)RhCl(COD)]. The compound is a dark blue solid, stable for several weeks at $-20°C$ and slightly soluble in common organic solvents.

A spectroscopic study (IR, ^{31}P and ^{1}H-NMR) was carried out under the conditions used for the other compounds. Tables 1 and 2 summarize the main results.

The ^{1}H-NMR spectrum shows two different resonances for the olefinic protons H_1 and H_2 of the COD (Fig. 5).

This has already been observed in a RhMo compound, for which a square-plane coordination at the rhodium atom was suggested [19]. However, this structure does not appear adequate to describe the rhodium coordination environment in [(CO)$_2$(phen)W(μ-CO)-(μ-dppm)RhCl(COD)] because its IR spectrum indicates the presence of a semibridging CO group, similar to those shown in the related NBD derivatives.

The rest of the spectroscopic data show that the structure established for the NBD compounds is also possible for the COD complex, suggesting the same coordination behaviour in both derivatives.

3. Experimental section

3.1. General

All reactions were performed under dioxygen-free dry dinitrogen, using freshly distilled, dried and degassed solvents.

NMR spectra were recorded on Varian XL-300 and Bruker 300 spectrometers with (CH$_3$)$_4$Si as internal standard for ^{1}H and 85% phosphoric acid as external standard for ^{31}P. IR spectra were recorded on a Perkin-Elmer 1300 spectrophotometer. Analyses (C, H,

Fig. 4. Proposed molecular rearrangement for the complexes (1a, 1b, 1c, 1d).

N) were performed by Elemental Micro-Analysis Ltd Laboratories, Devon, UK.

The complexes [M(CO)$_3$(NN)(dppm-P)] (M = Mo or W) and [{RhCl(NBD)}$_2$], were prepared by previously described methods [11,20].

3.2. Reactions

3.2.1. Preparation of [(CO)$_2$(phen)Mo(μ-CO)(μ-dppm)-RhCl(NBD)]

A solution of [{RhCl(NBD)}$_2$](0.130 mmol) in CH$_2$Cl$_2$ (30 ml) was added to a solution of [Mo(CO)$_3$-(phen)(dppm-P)] (0.260 mmol) in CH$_2$Cl$_2$ (15 ml). The mixture was stirred for 2 h at −20°C and petroleum ether was added to precipitate a dark blue solid, which was filtered off and dried in vacuo. The solid was recrystallized from CH$_2$Cl$_2$/petroleum ether and dried in vacuo. Anal. Found: C, 57.95; H, 3.94; N, 2.85. Calc. for C$_{47}$H$_{38}$ClMoN$_2$O$_3$P$_2$Rh: C, 57.86; H, 3.89; N, 2.87%.

3.2.2. Preparation of [(CO)$_2$(bpy)Mo(μ-CO)(μ-dppm)-RhCl(NBD)]

The synthesis of this complex is analogous to that described above. Anal. Found: C, 56.90; H, 3.98; N, 2.92. Calc. for C$_{45}$H$_{38}$ClMoN$_2$O$_3$P$_2$Rh: C, 56.80; H, 3.99; N, 2.94%.

3.2.3. Preparation of [(CO)$_2$(phen)W(μ-CO)(μ-dppm)-RhCl(NBD)]

This compound is obtained by a similar procedure to the above. Anal. Found: C, 53.10; H, 3.60; N, 2.63. Calc. for C$_{47}$H$_{38}$ClN$_2$O$_3$P$_2$RhW: C, 53.07; H, 3.57; N, 2.63%.

3.2.4. Preparation of [(CO)$_2$(bpy)W(μ-CO)(μ-dppm)Rh-Cl(NBD)]

The procedure was similar to that for the other derivatives. Anal. Found: C, 51.90; H, 3.65; N, 2.68. Calc. for C$_{45}$H$_{38}$ClN$_2$O$_3$P$_2$RhW: C, 51.99; H, 3.65; N, 2.69%.

3.2.5. Preparation of [(CO)$_2$(phen)W(μ-CO)(μ-dppm)-RhCl(COD)]

This complex was prepared by a similar procedure. Anal. Found: C, 53.42; H, 3.90; N, 2.60. Calc. for C$_{48}$H$_{42}$ClN$_2$O$_3$P$_2$RhW: C, 53.40; H, 3.89; N, 2.59%.

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