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Heterobimetallic Group 6-rhodium complexes

II *. Reactions of $[Rh(S_2CNEt_2)(CO)_2]$ with the complexes $[M(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})]$ (M = Mo or W) and $[Mo(CO)_4(\eta^2\text{-dppm})]$ as P-donor systems

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Abstract

Reactions of $[Rh(S_2CNEt_2)(CO)_2]$ with the complexes $[M(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})]$ (M = Mo or W) and $[Mo(CO)_4(\eta^2\text{-dppm})]$ led to new heterobimetallic compounds $[(CO)(\eta^2\text{-phen})M(\mu\text{-CO})_2(\mu\text{-dppm})Rh(S_2CNEt_2)]$ (M = Mo, **1a**; M = W, **1b**) and $[(CO)_4Mo(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]$ (**2**). The first two involve bonding of the uncoordinated P atom of the transition metal Mo(W) starting complex to the rhodium. In addition a dative bond Rh → Mo(W) assisted by two carbonyl groups is proposed. A similar Rh → Mo bonding bridged by dppm was deduced for complex **2**. However, in this case, it is produced by opening of the MoPP ring in the parent complex.

Introduction

Heterobimetallic complexes with metal–metal bonds have been the subject of much current research, in view of the catalytic potential and the possibility that cooperative effects between different metal centres may influence reactivity.

Recently many bimetallic complexes containing bridging diphosphine ligands such as $Ph_2PCH_2PPh_2$ have been described [1]. By far the most common type of such complexes has two dppm ligands, but in contrast, there are very few examples with a single, bridging dppm. In a previous paper we described the formation of the heterobimetallic complexes $[(CO)_3M(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})Rh(NBD)]$ by reaction of the Rh^I derivative $[\{RhCl(NBD)\}_2]$ with $[M(CO)_4(\eta^2\text{-dppm})]$ (M = Mo or W) [2]. The crystal structure of the molybdenum derivative revealed the presence of a Rh–Mo bond bridged by dppm, carbonyl and chloride ligands [2].

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We have also recently described the chemistry of $[Rh(S_2CNEt_2)(CO)_2]$ which showed facile and fast substitution reactions with triarylphosphine ligands to produce $[Rh(S_2CNEt_2)(CO)(P(4\text{-}XC_6H_4)_3)]$ and $[Rh(S_2CNEt_2)(P(4\text{-}XC_6H_4)_3)_2]$ (X = F, Cl, CH_3, or CH_3O) [3].

In order to produce bimetallic Rh–Mo(W) systems bridged by dppm, we then studied the reactions of $[Rh(S_2CNEt_2)(CO)_2]$ with $[M(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})]$ (M = Mo or W) (a) and $[Mo(CO)_4(\eta^2\text{-dppm})]$ (b) as potential P-donors systems. We reasoned that complexes (a) should coordinate to a second metal (Rh) via the free phosphorus atom. However, in (b), opening of the 4-membered chelate ring might occur, producing bimetallic systems containing the $M(\mu\text{-dppm})M'$ moiety. A metal–metal bond assisted by dppm and possibly with some other bridging ligands could be formed.

In the present paper, we report the study of new binuclear complexes containing rhodium bonded to molybdenum or tungsten, formed by treating the complexes $[M(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})]$ and $[Mo(CO)_4(\eta^2\text{-dppm})]$ with $[Rh(S_2CNEt_2)(CO)_2]$.

Results and discussion

The compound $[Rh(S_2CNEt_2)(CO)_2]$ reacts with the complexes $[M(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})]$ (M = Mo or W) in a 1:1 molar ratio and CH_2Cl_2 as solvent. After 2 h at room temperature, the reaction was completed and new heterobimetallic species $[(CO)(\eta^2\text{-phen})M(\mu\text{-CO})_2(\mu\text{-dppm})Rh(S_2CNEt_2)]$ (M = Mo, **1a**; M = W, **1b**) were produced in 80% yield. In all cases, evolution of carbon monoxide was observed (0.50 equiv.). The compounds are green-blue stable solids, insoluble in most common solvents, but adjudged pure from thin layer chromatography.

On the other hand, the treatment of an equimolar mixture of $[Rh(S_2CNEt_2)(CO)_2]$ and $[Mo(CO)_4(\eta^2\text{-dppm})]$ in acetone for 3 h at room temperature gave the heterobimetallic complex $[(CO)_4Mo(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]$ (**2**) in 60% yield. The product was a red-orange solid, slightly stable in air in the solid state for several days, but sensitive to sunlight in solution. It is slightly soluble in common solvents. When the tungsten derivative $[W(CO)_4(\eta^2\text{-dppm})]$ was used in the above reaction, a mixture of products which could not be separated was produced.

Analytical and IR, ^1H and ^{31}P-NMR spectroscopy data (Tables 1 and 2) were consistent with the formulations proposed. Qualitative analysis by X-ray fluorescence indicated a 1:1 metal/metal ratio. A tungsten anticathode and an analyst crystal of LiF (200) $2D = 4.0267$ Å were used in the X-ray tube; Rh-$K_\alpha = 0.6147$ Å, Mo-$K_\alpha = 0.7107$ Å.

The IR spectra in the carbonyl region of **1a** and **1b** exhibited $\nu(CO)$ bands typical of both terminal and bridging carbonyls (Table 1) [4–10]. However, compound **2** shows five strong bands. The absorption at 1980 cm^{-1} is attributed to CO bonded to rhodium [3] and the other four bands show the characteristic pattern of tetracarbonyl complexes, but the values of these absorptions are very different to those of the starting compounds [11]. There was no evidence of bridging carbonyls.

The diethyldithiocarbamate ligands are probably bidentate [12–14]. The ^1H NMR assignments are also shown in the tables. The triplet at 3.46 ppm assigned to the equivalent methylene protons of the dppm ligand in the tungsten derivative was obscured by the $Et_2NCS_2^-$ resonances in the molybdenum analogue. The 3.81

Table 1

IR (cm^{-1}) and ^1H-NMR (δ (ppm), J (Hz)) spectroscopic data for the complexes $[(CO)(\eta^2\text{-phen})M(\mu\text{-}CO)_2(\mu\text{-dppm})Rh(S_2CNEt_2)]$ (M = Mo **1a**; M = W **1b**)

	IR [a]		^1H NMR [b]	
	CO	$Et_2NCS_2^-$	$Et_2NCS_2^-$	CH_2 in dppm
	$\nu(CO)$	$\nu(CN)$	δ	δ
1a	1860vs	1490s	1.22 (m, CH_3)	(*)
	1710sh		3.68 (m, CH_2)	
	1690vs			
1b	1855vs	1485s	1.10 (m, CH_3)	3.46 t
	1705sh		3.60 (m, CH_2)	
	1685vs			

[a] In KBr pellets. [b] In $CDCl_3$ solution. vs, very strong; s, strong; sh, shoulder; m, multiplet; t, triplet; (*), the signal is occluded by the quadruplet of CH_2 group of diethyldithiocarbamate ligand.

ppm (q) resonance of **2** includes an additional signal arising from the dithiocarbamate, consistent with the unequivalence of its ethyl groups. The low solubilities of **1a** and **1b** prevented us from obtaining satisfactory ^{31}P and ^{13}C spectra.

The ^{31}P NMR spectrum of **2** shows a doublet at 26.5 ppm, assigned to the phosphorus atom bonded to molybdenum and a double doublet at 32.6 ppm assigned to the phosphorus atom bonded to rhodium.

On the basis of the above data for **1a** and **1b**, we propose a structure in which one dppm ligand and two carbonyl groups are bridging, while the $Et_2NCS_2^-$ is bidentate on the Rh and the two other ligands are terminal. In addition, in order to satisfy an 18-electron configuration at the $Mo(W)^0$, a Rh → Mo(W) metal–metal bond is formulated. The rhodium atom can be viewed as occupying the seventh coordination site of Mo(W).

This is not exceptional and the ability of Rh^I complexes to act as Lewis bases is well documented [15], and single dative interactions between metals have already been proposed for a number of bimetallic complexes [16–18].

In the absence of ^{31}P NMR data, it was not possible to infer the positions of nitrogen atoms with respect to the phosphorus atom of the dppm. However, the

Table 2

IR (cm^{-1}), ^1H, ^{31}P NMR (δ (ppm), J (Hz)) spectroscopic data for the complex $[(CO)_4Mo(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]$

IR [a]			NMR [b]		
$\nu(CO)$		$\nu(CN)$	$\delta(^1H)$		$\delta(^{31}P)$
KBr	CH_2Cl_2	$Et_2NCS_2^-$	$Et_2NCS_2^-$	dppm	dppm
2020vs	2020vs	1510m	1.27 (t, CH_3)	3.10 (t, CH_2)	26.5 (d, P_A)
1980vs	1975vs		1.35 (t, CH_3)	^2J(H–P) = 10.4	32.6 (dd, P_B)
1900vs	1905vs		3.81 (q, CH_2)	7.15–7.80 (m, C_6H_5)	^1J (P_B–Rh) = 155.1
1890vs	1880vs		^3J(H–H) = 7.0		^2J(P_A–P_B) = 68.6
1840vs	1850vs				

[a] vs, very strong; m, medium. [b] t, triplet; q, quadruplet; m, multiplet; d, doublet; dd, doublet of doublets.

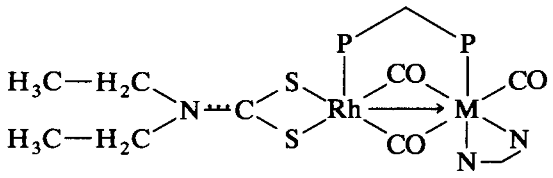


Fig. 1.

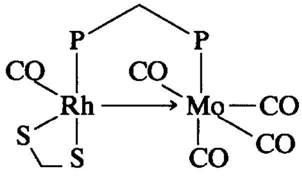


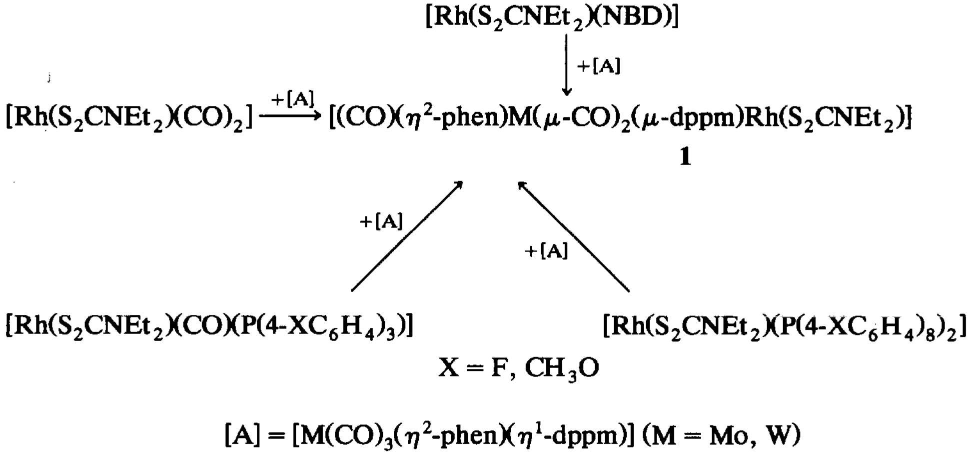
Fig. 2.

related compound [H(η^2-dppm)Ru(μ-H)(μ-Cl)(μ-dppm)Rh(COD)] contains two dppm ligands, chelating and bridging, with a cis and trans disposition of the phosphorus atoms of the chelating dppm ligand with respect to the phosphorus atom of the bridging dppm ligand [19,20]. We propose a similar arrangement (Fig. 1).

For compound **2**, we suggest a structure (Fig. 2) in which only one dppm ligand is bridging between the two metals, the other ligands occupying terminal positions. An additional Rh → Mo dative interaction provides 16-electron and 18-electron environments for either metal.

The differences between the proposed structures for **1a**, **1b** and **2** suggested the study of related reactions using rhodium compounds with fewer carbonyl ligands, such as [Rh(S_2CNEt_2)(NBD)], [Rh(S_2CNEt_2)(CO)(P(4-XC_6H_4)$_3$)], and [Rh (S_2CNEt_2)(P(4-XC_6H_4)$_3$)$_2$] (X = F or CH_3O).

The treatment of the above rhodium compounds with an equimolar amount of [M(CO)$_3$(η^2-phen)(η^1-dppm)] again gave **1a** and **1b** (Scheme 1). However, with



Scheme 1.

$$\begin{tikzcd}
 & {[Rh(S_2CNEt_2)(NBD)]} \arrow[d, "+{[B]}"] \\
{[Rh(S_2CNEt_2)(CO)_2]} \arrow[r, "+{[B]}"] & {[(CO)_4Mo(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]} \quad \mathbf{2} \\
 & {[Rh(S_2CNEt_2)(CO)(P(4\text{-}XC_6H_4)_3)]} \arrow[u, "+{[B]}"']
\end{tikzcd}$$

$X = F, CH_3O$

$[B] = [Mo(CO)_4(\eta^2\text{-dppm})]$

Scheme 2.

$[Mo(CO)_4(\eta^2\text{-dppm})]$, we were only able to obtain positive results with $[Rh(S_2CNEt_2)(NBD)]$ and $[Rh(S_2CNEt_2)(CO)(P(4\text{-}XC_6H_4)_3)]$. In both cases, **2** was the final product.

No reaction occurs under any of the conditions investigated when $[Rh(S_2CNEt_2)(P(4\text{-}XC_6H_4)_3)_2]$ was used. This is consistent with the difficult displacement of the phosphine from complexes $[Rh(S_2CNEt_2)(P(4\text{-}XC_6H_4)_3)_2]$.

We were very surprised that $[Mo(CO)_4(\eta^2\text{-dppm})]$ and the monocarbonyl or $[Rh(S_2CNEt_2)(NBD)]$ all gave the Rh–Mo complex **2**. The yield was much lower than when the dicarbonyl rhodium complex was used. We consider that $[Rh(S_2CNEt_2)(NBD)]$ can undergo carbonylation reactions under very mild conditions. Possibly $[Mo(CO)_4(\eta^2\text{-dppm})]$ carbonylates it, yielding $[Rh(S_2CNEt_2)(CO)_2]$, which then produces complex **2**. If the $Rh(S_2CNEt_2)(CO)$ moiety is necessary (Fig. 2), it is not surprising that reaction does not occur if $[Rh(S_2CNEt_2)(P(4\text{-}XC_6H_4)_3)_2)]$ is used. The formation of the heterobimetallic complexes **1** from $[M(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})]$ requires only the $Rh(S_2CNEt_2)$ group (Fig. 1).

Electrochemistry

Figure 3 shows a typical cyclic voltammetric curve recorded with a solution of $[(CO)_4Mo(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]$ (approx. 1 m*M*) and 0.2 *M* tetrabutylammonium hexafluorophosphate in CH_2Cl_2.

An anodic–cathodic peak system A'_1/A_1, typical of a quasi-reversible ($\Delta E_{p,a}$ = 120 mV, $E_{1/2} = 0.435$ V) redox process is observed. A further oxidation at A_2 ($E_{p,a} = 0.95$ V) can also be detected. No cathodic process takes place in the potential range available in our solvent medium. The results suggest the formation at peak A'_1 of a $[Rh^{II}Mo^0]^{1+}$ complex. An $E_{1/2}$ value of 0.435 V *versus* SCE, computed as the half-sum of anodic and cathodic peak potentials of the A'_1/A_1 system, was estimated for the $[Rh^IMo^0]/[Rh^{II}Mo^0]^{1+}$ couple.

The second anodic peak A_2, can be assigned to a new oxidation process, Rh^{2+}/Rh^{3+}. The two single-electron transfer might be expected by loss of two electrons from a Rh–Mo orbital, with unequal contributions from the two metals.

Experimental

General

All reactions were performed under oxygen-free dry dinitrogen. Solvents used in the preparation of the complexes were of commercial grade and were thoroughly

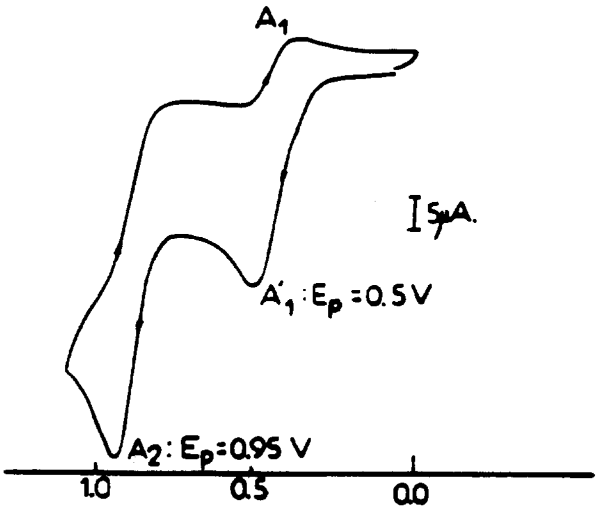


Fig. 3. Cyclic voltammogram of [(CO)$_4$Mo(μ-dppm)Rh(S$_2$CNEt$_2$)(CO)] (1 mM in CH$_2$Cl$_2$ with 0.2 M ^{n}Bu$_4$NPF$_6$, Pt working electrode and SCE as reference electrode).

deoxygenated prior to use. NMR spectra were recorded on Varian XL-300 and Bruker 300 spectrometers with $(CH_3)_4Si$ as internal standard for ^1H and 85% phosphoric acid as external standard for ^{31}P; the solvent was $CDCl_3$. IR spectra were recorded on a Perkin–Elmer 1300 spectrophotometer. X-Ray fluorescence measurements were realized with a Philips PW 1.540 spectrometer. Analyses (C,H,N) were performed by Elemental Micro-Analysis Ltd. Laboratories, Devon, UK. Cyclic voltammetry was performed with an A 305 HQ function generator and an AMEL 552 potentiostat. Cyclic voltammograms were recorded with a RIKEN-DENSHI F-35,X-Y. All experiments were carried out in an argon atmosphere.

The complex [Mo(CO)$_4$(η^2-dppm)] was prepared by published methods [11]. The complexes [Rh(S$_2$CNEt$_2$)(CO)$_2$], Rh(S$_2$CNEt$_2$)(NBD)], [Rh(S$_2$CNEt$_2$)(CO)-(P(4-XC$_6$H$_4$)$_3$)], [Rh(S$_2$CNEt$_2$)(P(4-XC$_6$H$_4$)$_3$)$_2$)] and [M(CO)$_3$(η^2-phen)(η^1-dppm)] were described in recent papers from this laboratory [3,21].

Reactions

Preparation of [(CO)(η^2-phen)Mo(μ-CO)$_2$(μ-dppm)Rh(S$_2$CNEt$_2$)]. A solution of [Rh(S$_2$CNEt$_2$)(CO)$_2$] (0.260 mmol) in CH$_2$Cl$_2$ (20 ml) was added to a solution of [Mo(CO)$_3$(η^2-phen)(η^1-dppm)] in CH$_2$Cl$_2$ (15 ml). The colour of the solution slowly turned from blue to green. The mixture was stirred for 3 h and the precipitate formed was filtered off, washed with dichloromethane and dried *in vacuo*. Anal. Found: C, 54.02; H, 4.16; N, 4.10. Calc: C, 54.26; H, 4.01; N, 4.22%.

Preparation of [(CO)(η^2-phen)W(μ-CO)$_2$(μ-dppm)Rh(S$_2$CNEt$_2$)]. The synthesis of this complex is analogous to that described above. Anal. Found: C, 49.50; H, 3.72; N, 3.83. Calc: C, 49.85; H, 3.69; N. 3.87%.

Preparation of [(CO)$_4$Mo(μ-dppm)Rh(S$_2$CNEt$_2$)(CO)]. A solution of [Mo (CO)$_4$(η^2-dppm)] (0.168 mmol) in acetone (15 ml) was treated with a solution of [Rh(S$_2$CNEt$_2$)(CO)$_2$] (0.168 mmol) in acetone (20 ml). The resultant mixture was stirred for 3 h and then concentrated to 10 ml; n-hexane was added to precipitate a red-orange solid, which was filtered off and washed with diethyl ether and dried *in vacuo*. The solid was recrystallized from acetone/*n*-hexane as red-orange needles. Anal. Found: C, 48.25; H, 3.60; N, 1.68. Calc: C, 48.21; H, 3.67; N, 1.60%.

Acknowledgments

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