ELSEVIER

Journal of Organometallic Chemistry 493 (1995) 77–82

Journal of Organometallic Chemistry

Pentahalophenyl palladium and platinum trinuclear complexes with tetrathiomolybdate and tetrathiotungstate

José Ruiz [a], Venancio Rodríguez [a], Gregorio López [a,*], Penny A. Chaloner [b], Peter B. Hitchcock [b]

[a] *Departamento de Química Inorgânica, Universidad de Murcia, 30071-Murcia, Spain*
[b] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK*

Received 14 September 1994

Abstract

The di-μ-hydroxo complexes $[NBu_4]_2[\{MR_2(\mu\text{-OH})\}_2]$ (M = Pd or Pt; R = C_6F_5 or C_6Cl_5) and $[\{(C_6F_5)(PPh_3)Pd(\mu\text{-OH})\}_2]$ react with $[NH_4]_2[M'S_4]$ (M′ = Mo or W) in 1:1 molar ratio to yield the trinuclear complexes $[NBu_4]_2[\{MR_2\}_2(\mu\text{-}M'S_4)]$ and $[\{(C_6F_5)(PPh_3)Pd\}_2(\mu\text{-}M'S_4)]$, respectively, with tetrathiomolybdate and tetrathiotungstate as bridging tetradentate ligands. Elemental analyses, conductance measurements and spectroscopic (IR, visible, ^{19}F, ^{31}P) methods have been used to characterize the new complexes. The X-ray crystal structure of $[Bu_4N]_2[\{Pd(C_6F_5)_2\}_2(\mu\text{-}WS_4)]$ has been established. Coordination at tungsten is tetrahedral and at palladium square, planar. The W–Pd distance indicates a metal–metal interaction.

Keywords: Palladium; Platinum; Trinuclear; Molybdenum; Tungsten; X-ray structures

1. Introduction

Tetrathiometallate compounds have been widely studied as ligands for many transition metals because of their possible relevance to biological electron transfer and nitrogen fixation. For example, they may be related to catalytic sites in nitrogen-fixing enzymes [1,2]. Binuclear and trinuclear complexes of the type $[L_2M'(MS_4)]$, $[M'(MS_4)_2]$ and $[(M'L_n)_2(\mu\text{-}MS_4)]$ (M = Mo or W; M′ = transition element) have been reported, in which the MS_4^{2-} ion coordinates either as bidentate terminal or as tetradentate bridging [3–9]. However, only a few compounds have been reported where $[MS_4]^{2-}$ is coordinated to organometallic compounds of groups [10–12]. The metathesis of halide by a thiometallate anion is a common method for the synthesis of organometallic derivatives of the thiometallates.

We have recently described the synthesis of the binuclear compounds $[\{MR_2(\mu\text{-OH})\}_2]^{2-}$ (M = Ni, Pd or Pt; R = C_6F_5 or C_6Cl_5) and $[\{(C_6F_5)(PPh_3)Pd(\mu\text{-OH})\}_2]$ which have proved to be excellent precursors for the synthesis of binuclear palladium or platinum complexes with double X bridges (X = azolate, amide, methoxide or dicyanomethanide) by reaction between the di-μ-hydroxo complexes and the corresponding protic acid HX [13–18]. The method should also be practicable for the preparation of MS_4^{2-}-bridged palladium and platinum complexes by the reaction of the di-μ-hydroxo complex with $[MS_4]^{2-}$ in the presence of acid.

The present work concerns the synthesis of organometallic anionic and neutral trinuclear complexes of palladium(II) and platinum(II) containing MS_4^{2-} (M = Mo or W) as a bridging tetradentate ligand. The results reported find precedent in the recent preparation of a number of nickel(II) tetrathiometallates by a route which is similar to that used in this work [19].

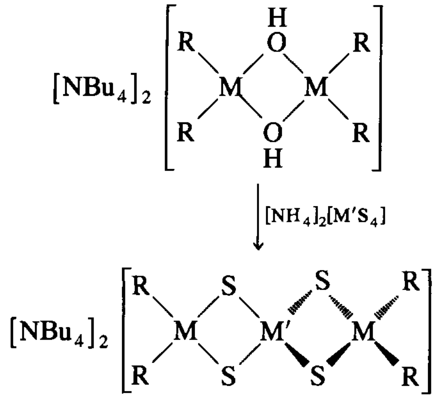
2. Results and discussion

The di-μ-hydroxo complexes $[NBu_4]_2[\{MR_2(\mu\text{-OH})\}_2]$ (M = Pd or Pt; R = C_6F_5 or C_6Cl_5) and $[\{(C_6F_5)(PPh_3)Pd(\mu\text{-OH})\}_2]$ react with $[NH_4]_2[M'S_4]$ (M′ = Mo or W) in 1:1 molar ratio to yield the trinuclear complexes with bridging tetrathiomolybdate and tetrathiotungstate $[NBu_4]_2[\{MR_2\}_2(\mu\text{-}M'S_4)]$ (com-

---

[*] Corresponding author.

SSDI 0022-328X(94)05338-3



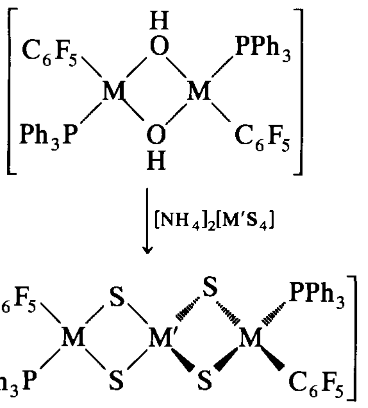
$M = Pd$, $M' = Mo$, $R = C_6F_5$ **1**
C_5Cl_5 **2**
$M' = W$, $R = C_5F_5$ **3**
C_6Cl_5 **4**
$M = Pt$, $M' = Mo$, $R = C_6F_5$ **5**
$M' = W$, $R = C_6F_5$ **6**

Scheme 1.

plexes **1–6**, Scheme 1) or $[\{(C_6F_5)(PPh_3)Pd\}_2(\mu\text{-}M'S_4)]$ (complexes **7** and **8**, Scheme 2. In both cases, the formation of the trinuclear compounds involves a two-stage process in which the hydroxo complex reacts with the acidic NH_4^+ ion to give $2H_2O + 2NH_3$ and the two MR_2 fragments are subsequently trapped by the tetrathiometallate ion, with formation of compounds **1–8**. When the reaction was carried out with a M : M' molar ratio of 1 : 2 the same products were obtained, and no binuclear complex of the type $[R_2MS_2M'S_2]^{2-}$ with terminal bidentate tetrathiometallate was formed. However, both types of complex were obtained for nickel [19].

The new complexes **1–8** have been characterized by partial elemental analysis (Table 1) and spectroscopic (IR, visible and ^{19}F) data (Table 2). In acetone solution complexes **1–6** behave as 2 : 1 electrolytes [20], which is consistent with the formulae shown in Scheme 1. Complexes **7** and **8** are non-conducting in the same solvent.

The IR spectra show bands attributed to the C_6F_5 (1630, 1490, 1460, 1050, and 950 cm^{-1}) [21] or the C_6Cl_5 (1315, 1285, 1220 and 670 cm^{-1}) [22] groups. Moreover, an absorption at ca. 800 cm^{-1} in the spectra of the bis(pentafluorophenyl) derivatives, or at ca. 830 cm^{-1} for the bis(pentachlorophenyl) derivatives, has been previously used for structural elucidation [23]. It is derived from the so-called halogen-sensitive mode in C_6F_5X and C_6Cl_5X (X = halogen) molecules, and in square-planar $[MR_2L_2]$ ($R = C_6F_5$ or C_6Cl_5) complexes it is related to the skeletal symmetry of the entire molecule [24], and behaves like a ν(M–C) vibration. A split band for this mode is characteristic of the *cis*-MR_2 fragment (complexes **1–6**). In the spectra of the bis(pentachlorophenyl) derivatives **2** and **4** a split band at *ca.* 610 cm^{-1}, assigned to ν(M–C) [22], also supports the *cis* geometry of the MR_2 moiety. The mono(pentafluorophenyl) complexes **7** and **8** give rise to a single band for the X-sensitive mode. The ν(M–S) bands of all trinuclear complexes are similar in energy to those of the uncoordinated mononuclear $[M'S_4]^{2-}$ (M' = Mo, W; 470 cm^{-1} and 458 cm^{-1}, respectively) [25].



$M = Pd$, $M' = Mo$ **7**
$M' = W$ **8**

Scheme 2.

Characteristic band shifts because of the complex formation are observed in the electronic spectra, which display strong absorptions [26] in the visible region, λ_{max} being in the range 400–570 nm (see Table 2 and Fig. 1 for complexes **1** and **5**). These absorptions may

Table 1
Analytical data, yields, and physical properties for the new complexes

Complex	Yield (%)	M.p. [b] (°C)	Analysis (%) [a] C	H	N	S	Λ_M [c]
1	80	146	42.1 (42.3)	4.8 (4.6)	1.7 (1.8)	8.3 (8.1)	211
2	61	223	35.1 (35.1)	3.8 (3.8)	1.4 (1.5)	6.9 (6.8)	197
3	80	161	40.2 (40.1)	4.4 (4.3)	1.9 (1.7)	7.4 (7.6)	207
4	60	213	33.8 (33.5)	3.6 (3.6)	1.4 (1.4)	6.7 (6.4)	220
5	89	291	38.2 (38.1)	4.1 (4.1)	1.7 (1.6)	7.0 (7.3)	213
6	82	311	36.6 (36.3)	4.0 (3.9)	1.7 (1.5)	6.7 (6.9)	215
7	77	203	44.7 (44.5)	2.5 (2.3)		9.4 (9.9)	
8	72	255	41.4 (41.7)	2.4 (2.2)		8.9 (9.3)	

[a] Calculated values in parentheses. [b] With decomposition. [c] S cm^2 mol^{-1} (in acetone).

Table 2
Spectroscopic data for the new complexes

Complex	Selected IR bands [a]		Visible		NMR data
	X-sensitive	$\nu(M'S)$	λ_{max} [b]	ϵ [c]	^{19}F $\delta(CFCl_3)$ [d]
1	780, 770	475	408.4	4580	-111.2 (d, 8 F_o, J_{om} 27.9)
			516.8	9190	-163.6 (t, 4 F_p, J_{mp} 19.7)
					-165.5 (m, 8 F_m)
2	830, 825	485	440.0	5690	
			519.2	5810	
3	780, 770	460	420.4	8040	-111.4 (d, 8 F_o, J_{om} 27.6)
			441.6	6540	-163.7 (t, 4 F_p, J_{mp} 19.7)
					-165.6 (m, 8 F_m)
4	830, 825	460	406.8	11500	
5	790, 780	470	570.8	9850	-113.8 (td, 8 F_o, J_{PtFo} 395, J_{om} 25.7)
			448.8	3390	-164.6 (t, 4 F_p, J_{mp} 19.8)
					-166.3 (m, 8 F_m)
6	790, 780	455	405.6	3910	-114.1 (td, 8 F_o, J_{PtFo} 407, J_{om} 27.6)
			442.4	5970	-164.8 (t, 4 F_p, J_{mp} 19.7)
			476.0	7680	-166.4 (m, 8 F_m)
7	780	480	505.2	10500	-114.5 (m, 2 F_o) [e]
					-114.9 (m, 2 F_o)
					-159.5 (t, 2 F_p, J_{mp} 19.5)
					-161.5 (m, 2 F_m)
					-162.2 (m, 2 F_m)
8	780	465	410.0	10800	-114.9 (m, 2 F_o) [f]
					-115.3 (m, 2 F_o)
					-159.6 (t, 2 F_p, J_{mp} 19.7)
					-161.6 (m, 2 F_m)
					-162.3 (m, 2 F_m)

[a] In Nujol mulls (cm^{-1}). [b] In nm (solvent acetone). [c] In mol^{-1} l cm^{-1}. [d] In $CDCl_3$ (J in Hz). [e] ^{31}P $\delta(H_3PO_4)$ 31.3 (t, J_{PFo} 6.1). [f] ^{31}P $\delta(H_3PO_4)$ 29.9 (t, J_{PFo} 7.5).

be attributed to charge-transfer transitions from a nonbonding molecular orbital with predominantly 3p (S) character to a 4d (Pd) or 5d (Pt) energy level [27,28].

The ^{19}F NMR spectra of complexes **1**–**6** show the expected set of three resonances with relative intensities of 2 : 1 : 2 because of the *ortho*-, *para*- and *meta*-F atoms of four equivalent C_6F_5 rings rotating freely about the metal–C_6F_5 bond. In complexes **5** and **6** the *ortho*-F central signal is flanked by the two satellites caused by coupling to ^{195}Pt. However, the spectra of **7** and **8** display two 1 : 1 resonance signals for the *ortho*-F atoms, and the same result is also observed in the *meta*-F region, indicating that rotation of the C_6F_5 rings about the metal–C_6F_5 is restricted. Obviously this is because of the presence of the bulky PPh_3 at the *cis* position.

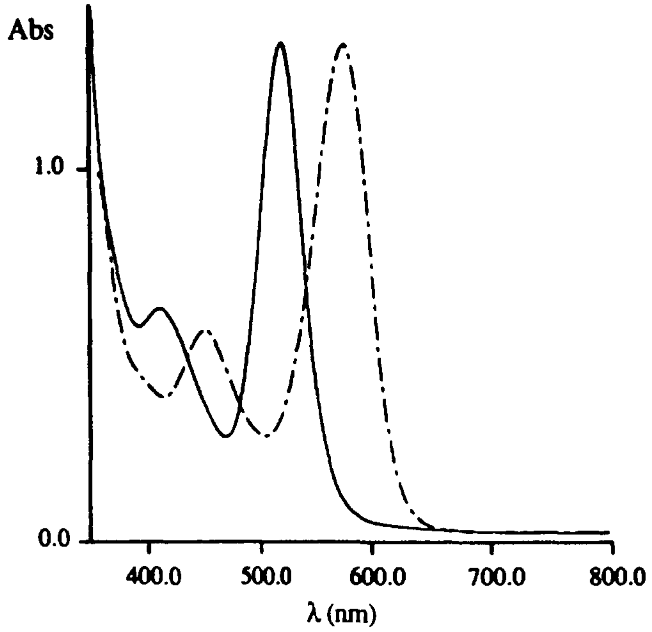


Fig. 1. Visible absorption spectra of complexes **1** (———) and **5** (-----) in acetone solution.

Fig. 2 shows a view of the anion of complex **3**, determined by X-ray analysis, together with the atom

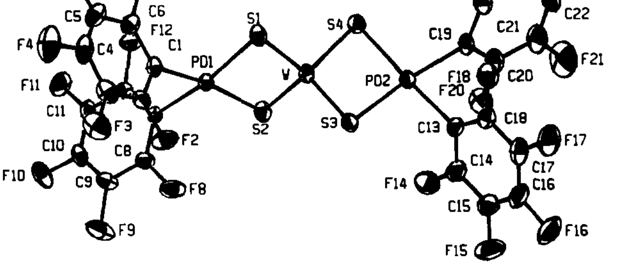


Fig. 2. Molecular structure of the anion of complex 3.

Table 3
Fractional atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	U_{eq} [a]
W	0.34387(3)	0.43396(3)	0.25909(1)	0.052(1)
Pd1	0.34829(6)	0.56125(5)	0.16734(2)	0.051(1)
Pd2	0.34627(6)	0.27727(5)	0.34438(2)	0.057(1)
S1	0.16977(22)	0.57912(20)	0.22782(8)	0.068(2)
S2	0.53017(22)	0.42107(20)	0.20960(8)	0.069(2)
S3	0.29218(24)	0.27197(18)	0.27024(8)	0.070(2)
S4	0.37833(23)	0.46145(18)	0.32783(8)	0.066(2)
F2	0.1995(6)	0.5013(4)	0.0961(2)	0.101(5)
F3	0.0101(6)	0.6266(6)	0.0359(2)	0.139(7)
F4	−0.0935(6)	0.8626(7)	0.0296(2)	0.152(8)
F5	−0.0076(7)	0.9677(5)	0.0573(3)	0.143(8)
F6	0.1818(6)	0.8421(4)	0.1477(2)	0.112(6)
F8	0.5022(6)	0.3904(4)	0.0913(2)	0.102(5)
F9	0.6728(6)	0.4155(5)	0.0153(2)	0.122(6)
F10	0.2417(6)	0.3926(5)	0.0058(2)	0.113(6)
F11	0.6710(5)	0.7693(4)	0.0517(2)	0.102(5)
F12	0.4933(5)	0.7499(4)	0.1258(2)	0.081(4)
F14	0.5540(6)	0.0391(5)	0.3184(2)	0.115(6)
F15	0.5472(8)	−0.1800(5)	0.3403(3)	0.149(8)
F16	0.3329(8)	−0.2270(5)	0.3924(3)	0.156(8)
F17	0.1181(7)	−0.0486(5)	0.4275(3)	0.141(7)
F18	0.1206(5)	0.1693(5)	0.4069(2)	0.098(5)
F20	0.6004(6)	0.1294(6)	0.4075(2)	0.118(7)
F21	0.6184(8)	0.0969(8)	0.4997(3)	0.185(10)
F22	0.4019(9)	0.2194(8)	0.5556(2)	0.178(10)
F23	0.1670(8)	0.3659(7)	0.5178(2)	0.152(8)
F24	0.1468(6)	0.3962(5)	0.4267(2)	0.112(6)
N1	0.1853(6)	0.5181(6)	0.6639(2)	0.063(6)
N2	0.4080(7)	0.0847(5)	0.1482(3)	0.072(6)
C1	0.2017(7)	0.6668(6)	0.1233(3)	0.055(6)
C2	0.1519(8)	0.6175(7)	0.0940(3)	0.067(7)
C3	0.0514(10)	0.6833(9)	0.0641(3)	0.092(9)
C4	0.0012(10)	0.8009(9)	0.0619(4)	0.097(10)
C5	0.0453(10)	0.8521(8)	0.0902(4)	0.090(10)
C6	0.1432(9)	0.7847(7)	0.1201(3)	0.071(8)
C7	0.4884(7)	0.5694(6)	0.1118(2)	0.048(6)
C8	0.5393(8)	0.4889(6)	0.0824(3)	0.064(7)
C9	0.6268(9)	0.5006(7)	0.0430(3)	0.074(7)
C10	0.6726(8)	0.5942(0)	0.0327(3)	0.069(8)
C11	0.6280(8)	0.6767(7)	0.0612(3)	0.063(7)
C12	0.5377(8)	0.6626(6)	0.0995(3)	0.056(6)
C13	0.3378(8)	0.1125(7)	0.3618(3)	0.064(7)
C14	0.4438(10)	0.0214(8)	0.3453(3)	0.086(9)
C15	0.4430(12)	−0.0918(9)	0.3564(4)	0.100(10)
C16	0.3371(11)	−0.1179(8)	0.3829(4)	0.100(10)
C17	0.2279(7)	−0.0288(6)	0.4002(3)	0.096(7)
C18	0.2317(6)	0.0847(5)	0.3890(2)	0.075(6)
C19	0.3738(6)	0.2633(5)	0.4130(2)	0.067(5)
C20	0.4901(7)	0.1901(6)	0.4339(2)	0.089(7)
C21	0.5005(8)	0.1736(7)	0.4819(3)	0.114(8)
C22	0.3900(9)	0.2362(7)	0.5086(2)	0.116(9)
C23	0.2762(8)	0.3087(7)	0.4899(2)	0.102(8)
C24	0.2680(7)	0.3217(6)	0.4429(2)	0.085(6)
C25	0.2883(7)	0.5121(6)	0.6204(2)	0.080(6)
C26	0.2246(9)	0.5785(7)	0.5762(3)	0.111(9)
C27	0.3328(11)	0.5666(9)	0.5356(3)	0.154(11)
C28	0.2722(18)	0.6290(12)	0.4905(4)	0.243(19)
C29	0.1135(7)	0.6442(5)	0.6726(2)	0.082(6)
C30	0.2119(8)	0.7092(6)	0.6769(3)	0.109(8)
C31	0.1391(12)	0.8281(8)	0.6874(5)	0.211(14)
C32	0.0588(17)	0.8496(11)	0.7153(7)	0.402(22)
C33	0.0727(6)	0.4723(5)	0.6576(2)	0.075(6)
C34	0.1205(7)	0.3480(6)	0.6481(3)	0.089(6)
C35	0.0001(8)	0.3106(7)	0.6432(3)	0.125(8)
C36	0.0420(10)	0.1929(8)	0.6333(4)	0.178(11)
C37	0.2710(6)	0.4465(5)	0.7040(2)	0.065(5)
C38	0.1889(7)	0.4485(7)	0.7509(2)	0.094(7)
C39	0.2658(7)	0.3563(7)	0.7875(3)	0.106(8)
C40	0.1862(9)	0.3487(9)	0.8337(3)	0.146(10)
C41	0.4704(7)	0.0485(5)	0.1016(2)	0.085(6)
C42	0.5387(9)	0.1271(6)	0.0688(3)	0.103(8)
C43	0.5980(9)	0.0812(7)	0.0253(3)	0.120(9)
C44	0.6861(9)	0.1414(7)	−0.0040(3)	0.124(9)
C45	0.5124(7)	0.1102(5)	0.1724(2)	0.081(5)
C46	0.6440(8)	0.0072(7)	0.1830(3)	0.111(8)
C47	0.7386(9)	0.0392(8)	0.2068(3)	0.136(10)
C48	0.8626(10)	−0.0580(12)	0.2202(4)	0.219(15)
C49	0.2822(7)	0.1980(5)	0.1423(3)	0.092(7)
C50	0.1623(9)	0.1934(8)	0.1193(4)	0.136(11)
C51	0.0400(11)	0.2965(10)	0.1233(5)	0.209(16)
C52	−0.0805(14)	0.3032(14)	0.1089(7)	0.283(23)
C53	0.3637(7)	−0.0156(5)	0.1770(3)	0.081(6)
C54	0.3021(8)	0.0000(6)	0.2260(3)	0.105(8)
C55	0.2510(9)	−0.0979(7)	0.2535(3)	0.128(10)
C56	0.3472(10)	−0.2058(8)	0.2575(4)	0.147(11)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

labelling used. Fractional atomic coordinates, and selected bond lengths and angles are presented in Tables 3 and 4, respectively. The coordination at tungsten is approximately tetrahedral, as expected, with S–W–S angles ranging from 106.96(8)° to 111.6(1)°. The coordination about each palladium is approximately square planar, but there is substantial distortion, with angles about Pd1 ranging from 85.4(3)° for C1–Pd–C7 to 97.56(8)° for S1–Pd1–S2. The related angles at Pd2 were 85.2(3)° and 97.67(8)°. As expected, the palladium coordination planes are approximately perpendicular to each other. The structures of the $[Bu_4N]$ cations are unremarkable, and there are no short anion–cation contacts.

The W–S distances average 2.199(4) Å. This is at the low end of the previously observed range [4,8,10b,11,28–31] for related complexes. It is, however, quite similar to the W–S distances (2.198(1) Å and 2.203(1) Å) observed in $[Rh_2(cod)_2(\mu\text{-}WS_4)]$, which is the only other structurally characterised example of a $[WS_4]^{2-}$ group bridging two square-planar metal centres bearing all-carbon ligands. The Pd–S distances average 2.349(12) Å. The Pd–W distances are 2.844(1) Å and 2.848(1) Å. This suggests strongly a metal–metal interaction. Such an interaction could be responsible for the distortion of the coordination planes of the palladium. Metal–metal interactions in bridged tetrathiometallate derivatives have long been proposed, and inter-metallic distances in, for example, $[Rh_2(cod)_2(\mu\text{-}WS_4)]$ (2.854(1) Å) [29], $[(Ph_3P)_2Ag(\mu\text{-}$

Table 4
Selected intramolecular distances (Å) and angles (°) with their e.s.d.'s

Bonds			
W–Pd1	2.844(1)	W–Pd2	2.848(1)
W–S1	2.195(2)	W–S2	2.203(2)
W–S3	2.196(3)	W–S4	2.203(3)
Pd1–S1	2.340(2)	Pd1–S2	2.359(2)
Pd1–C1	2.036(7)	Pd1–C7	2.021(7)
Pd2–S3	2.336(3)	Pd2–S4	2.359(3)
Pd2–C13	2.029(9)	Pd2–C19	2.038(6)
Angles			
Pd1–W–Pd2	171.51(2)	Pd1–W–S1	53.48(6)
Pd1–W–S2	53.94(6)	Pd1–W–S3	118.96(6)
Pd1–W–S4	134.09(6)	Pd2–W–S1	129.89(6)
Pd2–W–S2	123.10(6)	Pd2–W–S3	53.30(6)
Pd2–W–S4	53.87(6)	S1–W–S2	106.96(8)
S1–W–S3	109.05(9)	S1–W–S4	111.54(8)
S2–W–S3	110.81(9)	S2–W–S4	111.6(1)
S3–W–S4	106.94(9)	W–Pd1–S1	48.93(5)
W–Pd1–S2	49.02(6)	W–Pd1–C1	135.7(2)
W–Pd1–C7	138.2(2)	S1–Pd1–S2	97.56(8)
S1–Pd1–C1	88.4(2)	S1–Pd1–C7	172.1(2)
S2–Pd1–C1	171.4(2)	S2–Pd1–C7	89.2(2)
C1–Pd1–C7	85.4(3)	W–Pd2–S3	48.92(6)
W–Pd2–S4	48.96(6)	W–Pd2–C13	134.5(3)
W–Pd2–C19	140.1(2)	S3–Pd2–S4	97.67(8)
S3–Pd2–C13	86.3(3)	S4–Pd2–C19	170.2(2)
S4–Pd2–C13	174.0(3)	S4–Pd2–C19	91.1(2)
C13–Pd2–C19	85.2(3)	W–S1–Pd1	77.59(6)
W–S2–Pd1	77.04(6)	W–S3–Pd2	77.78(9)
W–S4–Pd2	77.18(9)		

$WS_4)Ag(PPh_3)]$ (3.056(2) Å and 2.886(2) Å) [30], $[\{Ru\{P(OMe)_3\}_4\}_2(\mu\text{-}WS_4)]^{2+}$ (2.988(2) Å and 3.002(2) Å) [8], $[\{Ru(PhNCS)(CO)(PPh_3)\}_2(\mu\text{-}WS_4)]$ (2.886(2) Å) [11], $[\{Ru(bipy)_2\}_2(\mu\text{-}WS_4)]^{2+}$ (2.838(1) Å) [4], $[\{Ru(Cp)(CNMe)\}_2(\mu\text{-}WS_4)]$ (2.870(2) Å) [10b], $[\{Au(PPh_2Me)\}_2(\mu\text{-}WS_4)]$ (2.836(1) Å, 2.843(1) Å) [31] and $[(FeCl_2)_2(\mu\text{-}WS_4)]$ (2.795(1) Å and 2.808(1) Å) [28] are consistent with this interpretation.

3. Experimental details

C, H, N and S analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance. Molar conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol dm^{-3}) with a Crison 525 conductimeter. The NMR spectra were recorded on a Bruker AC 200E (^1H) or a Varian Unity 300 (^{19}F, ^{31}P) spectrometer, using $SiMe_4$, $CFCl_3$ and H_3PO_4 as standards respectively. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. The precursors $[NBu_4]_2[\{M(R)_2(\mu\text{-}OH)\}_2]$ (M = Pd, R = C_6F_5 or C_6Cl_5; M = Pt, R = C_6F_5) [13,16,17] $[\{(C_6F_5)(PPh_3)Pd(\mu\text{-}OH)\}_2]$ [18] and $[NH_4]_2[M'S_4]$ (M' = Mo or W) [26] were prepared as described elsewhere.

3.1. Synthesis of the complexes

3.1.1. Complexes 1–4

To a solution of $[NBu_4]_2[\{PdR_2(\mu\text{-}OH)\}_2]$ (R = C_6F_5 or C_6Cl_5) (0.06 mmol) in methanol (6 cm^3) was added the corresponding tetrathiomethallate $[NH_4]_2[M'S_4]$ (M' = Mo or W) (0.06 mmol) with constant stirring at room temperature for 2 h to afford a suspension from which solvent was partially evaporated under reduced pressure. The precipitate was filtered off, washed with water and air-dried.

3.1.2. Complexes 5 and 6

To a solution of $[NBu_4]_2[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.1 g, 0.063 mmol) in methanol (8 cm^3) was added the corresponding tetrathiomethallate $[NH_4]_2[M'S_4]$ (M' = Mo or W; 0.063 mmol). The solution was heated under reflux for 7 h. The solvent was partially evaporated off under reduced pressure to afford a suspension which, after addition of water, was filtered off. The solid was washed with water and air-dried.

3.1.3. Complexes 7 and 8

To a solution of $[\{(C_6F_5)(PPh_3)Pd(\mu\text{-}OH)\}_2]$ (0.1 g, 0.09 mmol) in acetone (4 cm^3) was added a solution of the corresponding tetrathiomethallate $[NH_4]_2[M'S_4]$ (M' = Mo or W; 0.09 mmol) in methanol (4 cm^3) with constant stirring at room temperature for 2 h to afford a suspension from which solvent was partially evaporated off under reduced pressure. The precipitate was filtered off, washed with water, and air-dried.

3.2. Crystal structure determination of complex 3

Suitable crystals were grown from dichloromethane-diethyl ether. Data were collected using a crystal cut to 0.2 × 0.2 × 0.2 mm on an Enraf Nonius CAD-4 diffractometer in the θ–2θ mode. A total of 11928 unique reflections were measured in the range $2 < \theta < 25°$, h $0 \to 12$, k $-14 \to 14$, l $-34 \to 34$, and 8734 reflections with $F^2 > 2\ \sigma(F^2)$ where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/L_p$ were used in the refinement. The maximum change in two standard reflections measured every hour was −3.1%, and a decay correction was applied. An absorption correction (max, min 0.999, 0.894 from ψ scans) was applied. The structure was solved with routine heavy atom methods using SHELXS-86 [32] with refinement by full-matrix least-squares using the Enraf-Nonius MOLEN programs with non-hydrogen atoms anisotropic. Hydrogen atoms were fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom. The weighting scheme was $\omega = 1/\sigma^2(F)$ with $\Sigma\omega(F_o - F_c)^2$ minimised. The final residuals were $R = 0.041$, $R' = 0.044$, $s = 1.2$, $(\Delta/\sigma)_{max} = 0.2$, $\Delta\rho_{max,min} = +0.85, -0.29$. The crystal was triclinic, space group $P\bar{1}$(No. 2), $a = 10.230(1)$ Å, $b = 12.346(1)$ Å, $c =$

29.318(14) Å, $\alpha = 78.85(2)°$, $\beta = 81.83(3)°$, $\gamma = 69.53(1)°$, $U = 3391.9$ Å^3, $Z = 2$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1664$. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 24.5$ cm^{-1}, $T = 293$ K.

Additional material available from the authors or the Cambridge Crystallographic Data Centre comprises tables of anisotropic thermal parameters, bond distances and bond angles. Structure factor tables are available from the authors.

Acknowledgements

Financial support from the Spanish DGICYT (project PB91-0574) and the Dirección Regional de Educación y Universidad (Murcia) (project PSH94-19) is grateful acknowledged.

References

[1] R.H. Holm, *Chem. Soc. Rev.*, *10* (1981) 455.

[2] D. Coucouvanis, *Acc. Chem. Rev.*, *14* (1981) 201.

[3] A. Müller and E. Dieman, in *Comprehensive Coordination Chemistry*, Vol. 2, 1987 p. 559, and references therein.

[4] M.A. Greaney, C.L. Coyle, M.A. Harmer, A. Jordan and E.I. Stiefel, *Inorg. Chem.*, *28* (1989) 912.

[5] F. Bonomi, S. Iametti and D.M. Kurtz, jr., *Inorg. Chim. Acta*, *193* (1992) L125.

[6] S. Bernes, F. Sécheresse and Y. Jeannin, *Inorg. Chim. Acta*, *191* (1992) 11.

[7] D. Shaowun, Z. Nyanyong, C. Pengcheng, W. Xintao and L. Jiaxi, *J. Chem. Soc., Dalton Trans.*, (1992) 339; *Polyhedron*, *11* (1992) 109.

[8] T. Matsumoto, K. Matsumoto and T. Sato, *Inorg. Chim. Acta*, *202* (1992) 31.

[9] E. Bencini, F. Cecconi, C.A. Ghilardi, S. Midollini, F. Nuzzi and A. Orlandini, *Inorg. Chem.*, *31* (1992) 5339.

[10] (a) K.E. Howard, J.R. Lockemeyer, M.A. Massa, T.B. Rauchfuss, S.R. Wilson and X. Yang, *Inorg. Chem.*, *29* (1990) 4385; (b) K.E. Howard, T.B. Rauchfuss and S.R. Wilson, *Inorg. Chem.*, *27* (1988) 1710; (c) K.E. Howard, T.B. Rauchfuss and S.R. Wilson, *Inorg. Chem.*, *27* (1988) 3561; (d) K.E. Howard, T.B. Rauchfuss and A.L. Rheingold, *J. Am. Chem. Soc.*, *108* (1986) 297.

[11] M. Kato, M. Kawano, H. Taniguchi, M. Funaki, H. Moriyama, T. Sato and K. Matsumoto, *Inorg. Chem.*, *31* (1992) 26.

[12] A.R. Siedle, C.R. Hubbard, A.D. Mighell, R.M. Doherty and J.M. Stewart, *Inorg. Chim. Acta*, *38* (1980) 197.

[13] G. López, J. Ruiz, G. García, C. Vicente, J. Casabó, E. Molins and C. Miravit'les, *Inorg. Chem.*, *30* (1991) 2605.

[14] G. López, G. Sánchez, G. García, J. Ruiz, J. García, M. Martínez-Ripoll, A. Vegas and J.A. Hermoso, *Angew. Chem., Int. Edn. Engl.*, *30* (1991) 716.

[15] J. Ruiz, M.T. Martínez, C. Vicente, G. García, G. López, P.A. Chaloner and P.B. Hitchcock, *Organometallics*, *12* (1993) 4321.

[16] G. López, J. Ruiz, G. García, C. Vicente, J.M. Martí, J.A. Hermoso, A. Vegas and M. Martínez-Ripoll, *J. Chem. Soc., Dalton Trans.*, (1992) 53.

[17] G. López, J. Ruiz, G. García, J.M. Martí, G. Sánchez and J. García, *J. Organomet. Chem.*, *412* (1991) 435.

[18] G. López, J. Ruiz, G. García, C. Vicente, J.M. Martí and M.D. Santana, *J. Organomet. Chem.*, *393* (1990) C53.

[19] G. Sánchez, F. Momblona, G. García, G. López, E. Pinilla and A. Monge, *J. Chem. Soc., Dalton Trans.*, (1994) 2271.

[20] W.J. Geary, *Coord. Chem. Rev.*, *7* (1971) 81.

[21] D.A. Long and D. Steel, *Spectrochim. Acta*, *19* (1963) 1955.

[22] J. Casabó, J.M. Coronas and J. Sales, *Inorg. Chim. Acta*, *11* (1974) 5.

[23] G. López, J. Ruiz, C. Vicente, J.M. Martí, G. García, P.A. Chaloner, P.B. Hitchcock and R.M. Harrison, *Organometallics*, *11* (1992) 4091.

[24] E. Maslowski, *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, p. 437.

[25] R.P. Callahan and P.A. Piliero, *Inorg. Chem.*, *19* (1980) 2619.

[26] J.W. McDonald, G.D. Friesen, L.D. Rosenhein and W.E. Newton, *Inorg. Chim. Acta*, *72* (1983) 205.

[27] A. Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem., Int. Edn. Eng.*, *20* (1981) 934.

[28] D. Coucouvanis, E.D. Simhon, P. Stremple, M. Ryan, D. Swenson, N.C. Baenziger, A. Simopoulos, V. Papaefthymiou, A. Kostikas and V. Petrouleas, *Inorg. Chem.*, *23* (1984) 741.

[29] A.R. Siedle and W.B. Gleason, *Inorg. Chem.*, *25* (1986) 4054.

[30] A. Müller, H. Bögge and E. Königer-Albom, *Z. Naturforsch., Teil B*, *34* (1979) 1968.

[31] J.C. Huffman, R.S. Roth and A.R. Siedle, *J. Am. Chem. Soc.*, *98* (1976) 4340.

[32] G.M. Sheldrick in G.M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3*, Oxford University Press, Oxford, 1985, p. 175.