New Approach to the Chemistry of Polysulfides Using Diphosphanylmethanide Complexes of Manganese(I)

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Abstract: The study of the nucleophilic degradation of S_8 by the methanide complex $[\mathrm{Mn(CO)_4\{(PPh_2)_2CH\}}]$ (**2**) has led to the preparation of a unique class of polysulfide derivatives of formula $[\mathrm{(CO)_4Mn\{(PPh_2)_2C{-}S_{\mathit{n}}{-}C(PPh_2)_2\}Mn(CO)_4}]$. The structures of **3** ($n = 6$), **4** ($n = 2$), and **7** ($n = 1$) have been determined by X-ray crystallography, whereas those polysulfides with the sulfur chains S_7, S_5, S_4, and S_3 have been detected by spectroscopic methods. The polysulfides with $n > 2$ lose sulfur spontaneously, a process that can be accelerated by treatment with PPh_3 or Na/Hg. Complexes **3**, **4**, and **7** were protonated at the two methanide carbon atoms to give the cationic dinuclear derivatives $[\mathrm{(CO)_4Mn\{(PPh_2)_2C(H){-}S_{\mathit{n}}{-}C(H)(PPh_2)_2\}Mn(CO)_4}]^{2+}$ (**8**, $n = 6$; **9**, $n = 2$; **10**, $n = 1$). The ^1H NMR spectrum of **9** suggests the existence of intramolecular $C{-}H \cdots S$ interactions, in agreement with the X-ray structural determination of this complex. By treatment of **4** and **7** with one equivalent of HBF_4 it is possible to selectively protonate just one methanide carbon atom, which allows the isolation of the mixed cationic derivatives $[\mathrm{(CO)_4Mn\{(PPh_2)_2C(H){-}S_{\mathit{n}}{-}C(PPh_2)_2\}Mn(CO)_4}]^+$ (**11**, $n = 2$; **6**, $n = 1$). Additionally, heterometallic complexes containing a bridging disulfide unit, of general formula $[\mathrm{(CO)_4Mn\{(PPh_2)_2C(AuPPh_3)S{-}SC(AuPPh_3)(PPh_2)_2\}Mn(CO)_4}]^{2+}$ (**12**) and $[\mathrm{(CO)_4Mn\{(PPh_2)_2C(H)S{-}SC(AuPPh_3)(PPh_2)_2\}Mn(CO)_4}]^+$ (**13**), were prepared by reaction of **4** and **11**, respectively, with $[\mathrm{AuCl(PPh_3)}]$ in the presence of $TlPF_6$.

Keywords: diphosphanylmethanides · manganese · polysulfides · sulfur

Introduction

Polysulfides of general formula $R{-}S_n{-}R$, also referred to as substituted polysulfanes, and their cyclic and polymeric congeners are important compounds that have found applications in many areas of chemistry. Thus, a plethora of organic polysulfides are used as coupling agents in rubber vulcanization,[1] and certain polysulfide polymers such as thiokol are extensively utilized for adhesives, sealants, and insulators, among other things.[2] Polysulfide-containing molecules are also of considerable biological importance, as the S–S bond is present in a variety of natural products and contributes significantly to the tertiary structures of many proteins;[3] polysulfides are also involved in DNA-cleaving processes.[4] Recently, a number of ferrocenyl polysulfide derivatives, including polymers, have been prepared and have displayed interesting electronic and structural features.[5] Some of these derivatives have been used as chiral ligands for rhodium- and iridium-catalyzed asymmetric reactions.[6] Metallic polysulfides are also of considerable importance, and a rich coordination chemistry of polysulfido chelate ligands has been developed.[7]

With all of these precedents the synthesis of new types of polysulfide-containing molecules, which could open routes to the study of unexplored chemical behavior and properties of these materials, appears to be an interesting goal. Herein we describe the preparation of the unique class of anionic polysulfides $[\mathrm{(PPh_2)_2C{-}S_{\mathit{n}}{-}C(PPh_2)_2}]^{2-}$ coordinated through the four phosphorus atoms to form dinuclear complexes of

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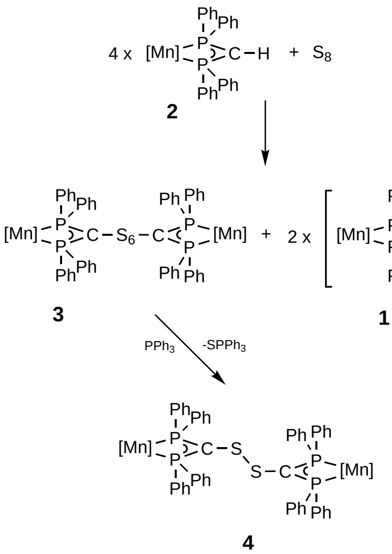
manganese(I). We have reported, in a preliminary form, that the diphosphanylmethanide complex $[Mn(CO)_4\{(PPh_2)_2CH\}]$ (**2**) readily reacts with cyclooctasulfur, affording the hexasulfur-linked tetraphosphanylbis(methanide) dinuclear derivative $[(CO)_4Mn\{(PPh_2)_2C{-}S_6{-}C(PPh_2)_2\}Mn(CO)_4]$(**3**).[8] We now give a detailed account of the nucleophilic degradation reactions of S_8 by **2** and of the further sulfur extrusion processes involved therein, which afford a number of polysulfur-bridged dimetallic complexes of general formula $[(CO)_4Mn\{(PPh_2)_2C{-}S_n{-}C(PPh_2)_2\}Mn(CO)_4]$ ($n = 1-7$). We also describe the controlled protonation reactions of these bimetallic species at the methanide carbon atoms to give several complexes containing the new tetraphosphanyl–polysulfide anionic and neutral ligands $[(PPh_2)_2C(H){-}S_n{-}C(PPh_2)_2]^-$ and $[(PPh_2)_2C(H){-}S_n{-}C(H)(PPh_2)_2]$, respectively.



Scheme 1. Formation of the dinuclear hexasulfide **3** by reaction of the methanide complex **2** with S_8 and shortening of the S_6 chain in **3** to give the disulfide **4**. $[Mn] = Mn(CO)_4$.

Results and Discussion

Bis(diphosphanylmethanide)polysulfide bridging ligands: The treatment of a solution of the diphosphanylmethanide complex **2** in dichloromethane with S_8 results in the formation of **3** and **1**, after a few minutes of stirring at room temperature (Scheme 1).[9] The ratio of the products **3** and **1** in the reaction mixture is approximately 1:2, regardless of whether a stoichiometric amount or an excess of S_8 is added. Both complexes were easily separated by column chromatography on alumina and **3** was finally crystallized from CH_2Cl_2/hexane, resulting in yellow crystals. The structure of **3** determined by X-ray diffraction is given in Figure 1. Selected bond lengths and angles are given in Table 1. The complex has approximate C_2 symmetry with the pseudo twofold axis passing through the

Abstract in Spanish: *El estudio de la degradación nucleofílica de* S_8 *por el complejo metanuro* $[Mn(CO)_4\{(PPh_2)_2CH\}]$ (**2**) *ha conducido a la preparación de una clase única de derivados polisulfuro de fórmula* $[(CO)_4Mn\{(PPh_2)_2C{-}S_n{-}C(PPh_2)_2\}{-}Mn(CO)_4]$. *Las estructuras de* **3** ($n = 6$), **4** ($n = 2$) *y* **7** ($n = 1$) *han sido determinadas mediante cristalografía de rayos-X, mientras que los polisulfuros con cadenas de azufre* S_7, S_5, S_4 *y* S_3 *han sido detectados mediante métodos espectroscópicos. Para* $n > 2$ *estos complejos son inestables y pierden azufre espontáneamente, un proceso que puede ser acelerado por tratamiento con* PPh_3 *ó Na/Hg. Estos polisulfuros fueron protonados sobre los dos átomos de carbono metanuro dando los complejos catiónicos dinucleares* $[(CO)_4Mn\{(PPh_2)_2C(H){-}S_n{-}C(H)(PPh_2)_2\}Mn(CO)_4]^{2+}$ (**8**: $n = 6$, **9**: $n = 2$, **10**: $n = 1$). *El espectro de* ^1H *RMN de* **9** *es llamativo sugiriendo la existencia de interacciones intramoleculares* $C{-}H\cdots S$, *en consonancia con la determinación estructural de rayos-X para este compuesto. Mediante tratamiento de* **4** *y* **7** *con un equivalente de* HBF_4 *es posible protonar selectivamente un único átomo de carbono metanuro lo que permite aislar los derivados catiónicos mixtos* $[(CO)_4Mn\{(PPh_2)_2C(H){-}S_n{-}C(PPh_2)_2\}Mn(CO)_4]^+$ (**11**, $n = 2$; **6**, $n = 1$). *Mediante reacción de* **4** *y* **11** *con* $[AuCl(PPh_3)]$ *en presencia de* $TlPF_6$ *se han obtenido además complejos heterometálicos que contienen una unidad disulfuro puente, de fórmula general* $[(CO)_4Mn\{(PPh_2)_2C(AuPPh_3)S{-}SC(AuPPh_3)(PPh_2)_2\}Mn(CO)_4]^{2+}$ (**12**) *y* $[(CO)_4Mn\{(PPh_2)_2C(H)S{-}SC(AuPPh_3)(PPh_2)_2\}Mn(CO)_4]^+$ (**13**).

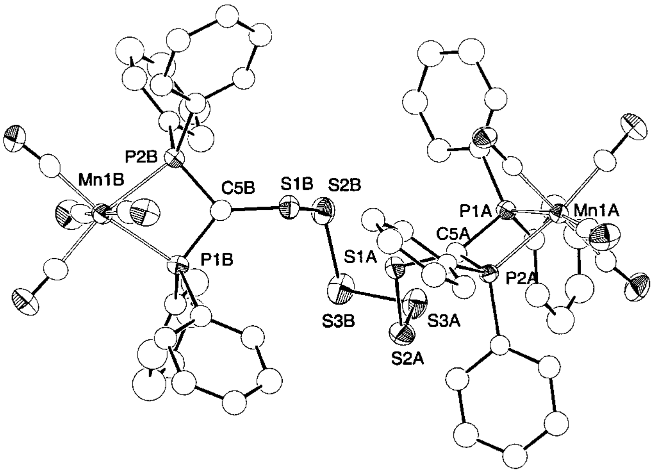


Figure 1. The molecular structure of **3** (ORTEP, 30% probability level).

Table 1. Selected bond lengths [Å] and angles [°] for **3**.

Mn1A–P1A	2.347(3)	Mn1B–P1B	2.339(3)
Mn1A–P2A	2.339(2)	Mn1B–P2B	2.355(3)
S1A–S2A	2.113(4)	S1B–S2B	2.113(4)
S1A–C5A	1.718(8)	S1B–C5B	1.717(7)
S2A–S3A	2.054(5)	S2B–S3B	2.053(4)
S3A–S3B	2.054(4)		
P1A–C5A	1.760(8)	P1B–C5B	1.758(8)
P2A–C5A	1.750(9)	P2B–C5B	1.761(8)
P1A–Mn1A–P2A	70.2(1)	P1B–Mn1B–P2B	70.5(1)
P1A-C5A-P2A	100.3(4)	P1B-C5B-P2B	100.7(4)
S2A-S1A-C5A	110.0(3)	S2B-S1B-C5B	112.8(3)
S1A-S2A-S3A	107.3(2)	S1B-S2B-S3B	107.2(2)
S2A-S3A-S3B	107.2(2)	S3A-S3B-S2B	106.7(2)

midpoints of the S1A⋯S1B and S3A–S3B segments. The atoms of the two related halves of the molecule are labeled as A and B, respectively. The S_6 unit bridges two complexes **2**, displacing two methanide hydrogen atoms. The structural features in the two halves are very similar. The octahedral coordination around the Mn atom involves four terminal carbonyl groups and two chelating P atoms from the tetraphosphanylbis(methanide) derivative. The two four-membered chelate rings are bent, with the two metal atoms 0.367(1) and 0.484(1) Å out of the planes formed by the P_2CS fragments, which are almost orthogonal to the C–S–S planes. The two P–Mn–P bite angles are very small, 70.2(1) and 70.5(1)°, respectively. In the S_6 chain the two terminal S–S bond lengths are significantly greater than the three internal ones. The short 3.506(3) Å separation between the two terminal S atoms of the chain is noteworthy. The S atoms form a six-membered ring with a chair conformation. The torsion angles starting from S1A–S2A are: 57.0(2), −87.1(2), 93.8(2), −84.8(2), 56.5(2), and −49.4(2)°. The two bulky substituents in the ring occupy equatorial positions.

Compound **3** spontaneously loses some sulfur when maintained in solution for several days, leading to a mixture of dinuclear complexes with shorter polysulfur chains. Furthermore, the hexasulfur chain in **3** can be quickly shortened by different desulfurization processes, such as treatment with PPh_3 or reduction with Na/Hg, which abstract sulfur as $SPPh_3$ and Na_2S, respectively (Scheme 1). In each case the final stage in the reduction of the chain length is the disulfide derivative **4**. Although efforts have been made to isolate the other polysulfide complexes, those corresponding to S_5, S_4, and S_3 chains, we have not been successful because they always appear as mixtures even if strict control over the reaction conditions for the chain reduction is maintained. It must be noted that it is difficult to distinguish between the different polysulfides by most spectroscopic methods. Thus, in the IR spectra in CH_2Cl_2 few changes were observed in the ν(CO) region on going from the hexasulfide **3** to the disulfide **4** (Table 2). In the ^{31}P NMR spectra a very broad signal appears centered at $\delta = 24.1$ for **3**, $\delta = 22.1$ for **4**, and in between for the mixtures of the other polysulfide derivatives. Spectroscopic detection of these polysulfides in the different reaction mixtures was therefore carried out by mass spectrometry or, indirectly, by ^1H NMR spectroscopy of their protonated derivatives by observing the signal of the $P_2C(H)–S_n–C(H)P_2$ protons, as we will see below (see Table 5).

Table 2. Selected spectroscopic data for the neutral polysulfides **3**, **4**, and **7**.

	IR[a] ν(CO) [cm^{-1}]	$^{31}P\{^1H\}$ NMR[b] δ
3	2074 (s), 1992 (vs), 1967 (s)	24.1 (br)
4	2070 (s), 1992 (vs), 1963 (s)	22.1 (br)
7	2068 (s), 1987 (vs), 1958 (s)	18.2 (br)

[a] In CH_2Cl_2. [b] In CD_2Cl_2.

The structure of **4** was also determined by X-ray methods (Figure 2), allowing a comparison of its structural parameters with those of the hexasulfide derivative **3**. Selected bond lengths and angles are given in Table 3. The complex has crystallographic C_i symmetry with the inversion center on the midpoint of the S–S bond. The S_2 unit in **4** essentially replaces the S_6 unit of **3**, and **4** can be seen as derived from **3** by cleavage of the two longest S–S bonds. The octahedral coordination around the Mn atoms is quite similar to that found in **3**. The two four-membered chelate rings are bent, with the metal atoms 0.250(4) Å out of the plane formed by the P_2CS fragment, which is, as in **3**, almost orthogonal to the C–S–S plane. The P–Mn–P bite angles are 69.8(3)°. The S–S bond length (2.177(13) Å) is much greater than the longest ones found in **3**. The C–S–S–C fragment is planar with the C atoms in *trans* positions. This conformation is rather uncommon, having been found, to our knowledge, in only three other structures.[10] The closely related diselenide cation $[(PPh_3)_2C–Se–Se–C(PPh_3)_2]^{2+}$ has been described and its structure determined by X-ray crystallography.[11]

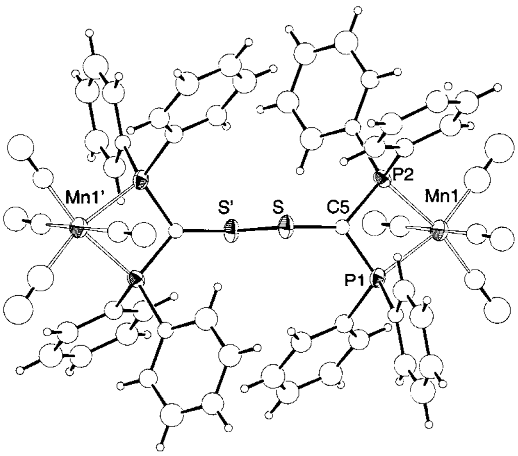


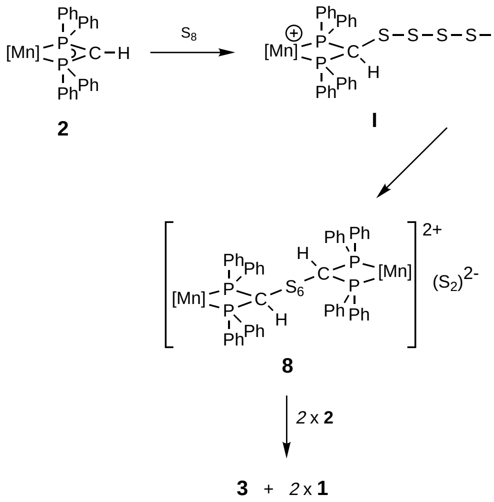
Figure 2. The molecular structure of **4** (ORTEP, 30 % probability level).

Table 3. Selected bond lengths [Å] and angles [°] for **4**.[a]

Mn1–P1	2.354(8)	Mn1–P2	2.361(8)
P1–C5	1.74(2)	P2–C5	1.74(2)
S–C5	1.71(2)	S–S′	2.177(13)
P1-Mn1-P2	69.8(3)	P1-C5-P2	101.3(11)
C5-S-S′	106.0(9)		

[a] Symmetry transformations used to generate equivalent atoms: ′: $-x+1/2, -y+1/2, -z+1$

Some mechanistic considerations: Taking into account the widely admitted mechanism for the nucleophilic degradation of cyclooctasulfur by bases,[12] it seems reasonable to assume that the reaction of the diphosphanylmethanide complex **2** with S_8 proceeds through the formation of the intermediate species **I** which contains an open octasulfur chain (Scheme 2). Then the attack of a new methanide molecule on **I** would not follow the usual behavior, which would lead to the formation of eight equivalents of the corresponding mercaptide species; instead the dinuclear hexasulfide derivative **8** should be formed after the elimination of the S_2^{2-} ion. Finally, the two $P_2C(H)–S_6–C(H)P_2$ protons in **8** should be transferred to two additional molecules of **2**, resulting in the experimentally observed 1:2 mixture of **3** and **1**. The formation of **I** must be the rate-determining step as the **3**:**1** ratio is approximately independent of the amount of S_8 added. Although **8** was not

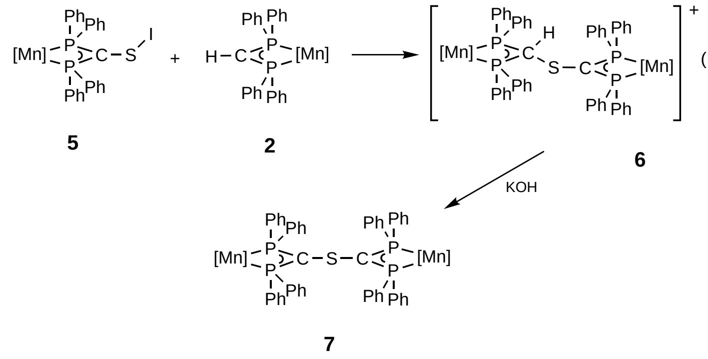


Scheme 2. Proposed mechanism for the nucleophilic degradation of S_8 by the methanide complex **2**. [Mn] = Mn(CO)$_4$.

detected in the course of this reaction, it could be prepared in an independent experiment by treatment of **3** with acids, as we will describe in detail below.

In principle, the attack of **2** on **I** could take place at different sulfur atoms in the octasulfur chain. However, attack on a sulfur atom placed in the vicinity of the diphosphane fragment is not very probable because of the steric hindrance imposed by the bulky diphenylphosphanyl groups. Nucleophilic attack on a sulfur atom near to the terminal sulfur, which supports the negative charge, is also unlikely, owing to electronic repulsions. The isolation of the hexasulfur species **3** in this reaction suggests that attack at the sixth sulfur atom in **I** is particularly favored as a compromise between the steric and electronic limitations. However, a careful analysis of the crude reaction mixture of **2** and S_8 by mass spectrometry and by ^{1}H NMR spectroscopy of the corresponding protonated species showed that, although the hexasulfide derivative **3** is the major product, some of the pentasulfide, the tetrasulfide and even, to a lesser extent, the heptasulfide derivatives were also formed (see Table 5). This means that the hexasulfide complex **3** is not the sole polysulfide species formed in this reaction, though the nucleophilic attack of the methanide **2** on the octasulfur chain seems to be very favored in the sixth position.

The monosulfide case: The dinuclear monosulfide derivative $[(CO)_4Mn\{(PPh_2)_2C{-}S{-}C(PPh_2)_2\}Mn(CO)_4]$ (**7**) could not be obtained from the disulfide complex **4**, with either PPh_3 or Na/Hg as sulfur the abstractor. Unlike the sulfur extrusion process from the hexasulfide **3** to form the disulfide **4**, in which two S–S bonds must be broken in each step, the formation of the monosulfide **7** would imply not only the scission of the S–S bond but also of one S–C bond, which is stronger than a single bond, as shown in the X-ray study of this molecule (S–C = 1.71(2) Å). Moreover, both reduction with Na and nucleophilic attack by the phosphane on the disulfide unit, with both sulfur atoms directly bonded to the methanide carbon atoms, appear to be very unlikely owing to electronic repulsions. However, although the disulfide complex **4** is resistant to sulfur extrusion, the S–S bond can easily be broken by oxidation reactions to give mononuclear species, as we have shown in a recent communication.[13] An example is the reaction of **4** with I_2 to give the sulfenyl iodide derivative **5**. We have now found that **5** is a suitable starting material for the synthesis of the monosulfane dinuclear complex **7** (Scheme 3). Treatment of **5** with one equivalent of **2** gives the intermediate **6** through a nucleophilic substitution of iodide by the methanide, which is then deprotonated with KOH to yield **7**. The stretching frequencies of the carbonyl groups of **7** are slightly lowert than those of the disulfide **4** (Table 2). This follows the general trend observed in this series of polysulfide derivatives, in which the carbonyl stretching frequencies are lowered as the sulfur chain length is reduced. The same trend is followed by the ^{31}P NMR signals of these complexes (Table 2).



Scheme 3. Formation of the monosulfide derivative **7** by reaction of **5** with **2**. [Mn] = Mn(CO)$_4$.

Yellow crystals of **7** were obtained from CH_2Cl_2/hexane and its structure was determined by X-ray crystallography (Figure 3). Two molecules of the complex, labeled A and B, respectively, were found in the asymmetric unit, and one of them is shown in Figure 3. A selection of bond lengths and angles is shown in Table 4. Each molecule has approximate C_2 symmetry with the pseudo twofold axis passing through the central sulfur atom and bisecting the C9–S1–C10 angle, which is 113(1)° and 115(1)° in the A- and B-labeled complexes, respectively. Both molecules have very similar structural features, as can be seen from the other data in Table 4. Moreover both parts of each molecule have virtually identical structural parameters too, with only small differences arising from the fairly disordered phenyl groups.

Proton transfer processes: The $[(CO)_4Mn\{(PPh_2)_2C{-}S_n{-}C(PPh_2)_2\}Mn(CO)_4]$ complexes can be protonated at the two methanide carbon atoms by treatment with an excess of HBF_4, yielding their cationic derivatives $[(CO)_4Mn\{(PPh_2)_2C(H){-}S_n{-}(H)C(PPh_2)_2\}Mn(CO)_4]^{2+}$ (**8**, $n = 6$; **9**, $n = 2$; **10**, $n = 1$) (Scheme 4). The reaction can easily be reversed by treatment with KOH.

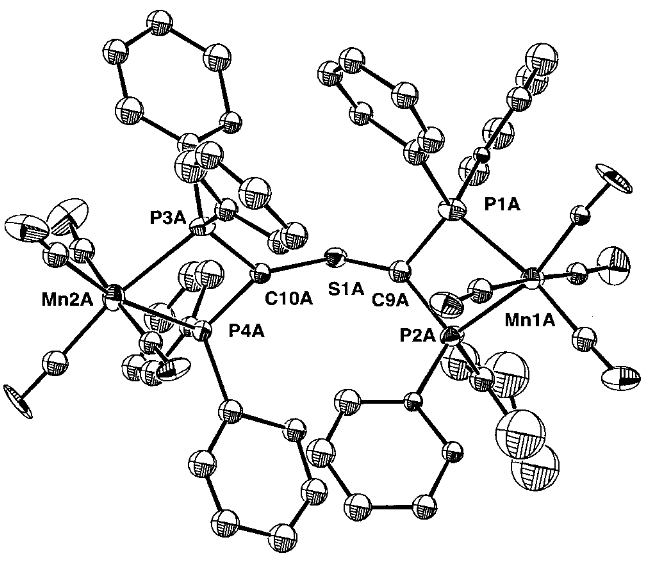
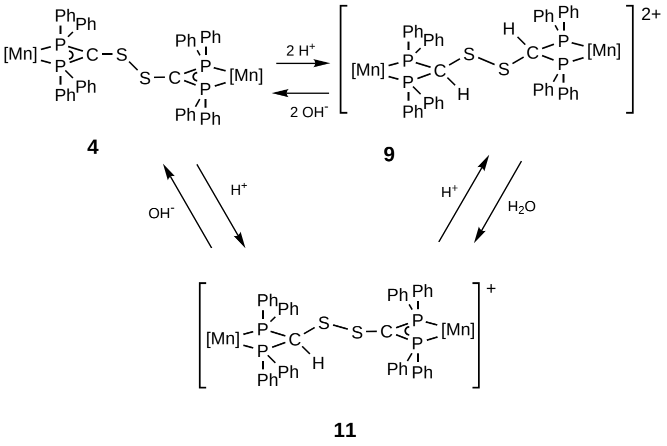


Figure 3. The molecular structure of **7** (ORTEP, 50% probability level).

Table 4. Selected bond lengths [Å] and angles [°] for **7**.

Mn1A–P1A	2.337(10)	Mn1B–P1B	2.358(9)
Mn1A–P2A	2.347(9)	Mn1B–P2B	2.343(9)
Mn2A–P3A	2.340(9)	Mn2B–P3B	2.344(10)
Mn2A–P4A	2.322(10)	Mn2B–P4B	2.336(8)
P1A–C9A	1.78(3)	P1B–C9B	1.78(2)
P2A–C9A	1.74(3)	P2B–C9B	1.76(2)
C9A–S1A	1.77(3)	C9B–S1B	1.77(2)
C10A–S1A	1.69(3)	C10B–S1B	1.78(3)
P1A-Mn1A-P2A	68.9(3)	P1B-Mn1B-P2B	69.9(3)
P3A-Mn1A-P4A	69.2(3)	P3B-Mn2B-P4B	69.3(3)
P1A-C9A-P2A	97.9(13)	P1B-C9B-P2B	99.0(10)
P3A-C10A-P4A	95.6(15)	P3B-C10B-P4B	99.4(14)
C9A-S1A-C10A	112.8(14)	C9B-S1B-C10B	115.3(12)



Scheme 4. Reversible proton transfer processes in **4**. [Mn] = Mn(CO)$_4$.

The spectroscopic data for these new complexes are presented in Table 5. Their IR spectra show a strong shift of the ν(CO) bands toward higher frequencies (40 cm^{-1} on average) with respect to their neutral precursors. In the ^{1}H NMR spectra the chemical shift of the P$_2$C(H)–S$_n$–C(H)P$_2$ protons proved to be very sensitive to the sulfur chain length, appearing as a triplet at $\delta = 6.09$, 6.99, and 5.70 for **8**, **9**, and **10**, respectively. This feature allowed us to spectroscopically characterize the other polysulfide derivatives, corresponding to the S$_7$, S$_5$, S$_4$, and S$_3$ sulfur chains, present in the different reaction mixtures (Table 5 and Figure 4). It is noteworthy that the signals of these protons appear in a narrow range of frequencies for $n = 7-3$ (from $\delta = 6.07$ to 6.26), whereas in the disulfide derivative **9** the signal appears at a very high chemical shift ($\delta = 6.99$) dropping sharply to $\delta = 5.70$ in the monosulfide species **10**. Also of note is the value of the $^2J_{\mathrm{P,H}}$ coupling constant in **9** (7 Hz), which is significantly smaller than that corresponding to the other of polysulfides (11 Hz). The chemical shifts in the ^{31}P NMR spectra of **9** ($\delta = 34.0$) and **10** ($\delta = 52.5$) are also peculiar and very different to those of the other polysulfide derivatives, which fall in the range of $\delta = 42-44$. To rationalize the above spectroscopic data we suggest that two weak C–H···S interactions may exist between the P$_2$C(H)–S$_n$–C(H)P$_2$ protons and the β-sulfur atoms of the sulfur chain (Scheme 5). In fact it has been reported that the ^{1}H NMR signals for protons involved in such hydrogen bonds usually shift to high frequencies.[14] This interaction is absent in the monosulfide **10** as it lacks the β-sulfur atoms, causing

Table 5. Selected spectroscopic data for the cationic polysulfides of formula [(CO)$_4$Mn{(PPh$_2$)$_2$C(H)–S$_n$–C(H)(PPh$_2$)$_2$}Mn(CO)$_4$]$^{2+}$ and for complexes **6**, **11**, **12**, and **13**.

n (complex)	IR[a] ν(CO) [cm^{-1}]	^{31}P{^{1}H} NMR[b] δ	^{1}H NMR[b] δ ($^2J_{\mathrm{P,H}}$)
7			6.07 (t, 11 Hz)
6 (**8**)	2096 (s), 2037 (m) 2014 (vs)	44.0 (br)	6.09 (t, 11 Hz)
5			6.16 (t, 11 Hz)
4			6.20 (t, 11 Hz)
3			6.26 (t, 11 Hz)
2 (**9**)	2094 (s), 2036 (m) 2011 (vs)	34.0 (br)	6.99 (t, 7 Hz)
1 (**10**)	2095 (s), 2035 (m) 2012 (vs)	52.5 (br)	5.70 (t, 11 Hz)
6	2091 (s), 2076 (s) 2031 (m), 2008 (vs) 1992 (s), 1975 (m)	46.0 (br), 27.0 (br)	5.93 (t, 12 Hz)
11	2093 (s), 2077 (s) 2033 (m), 2010 (vs) 1993 (s), 1974 (m)	41.0 (br), 26.4 (br)	5.77 (t, 11 Hz)
12	2090 (s), 2030 (m) 2007 (vs)	45.0, 44 (br)	
13	2093 (s), 2031 (m) 2008 (vs)	41.3 (br), 38.1	6.40 (t, 14 Hz)

[a] In CH$_2$Cl$_2$. [b] In CD$_2$Cl$_2$.

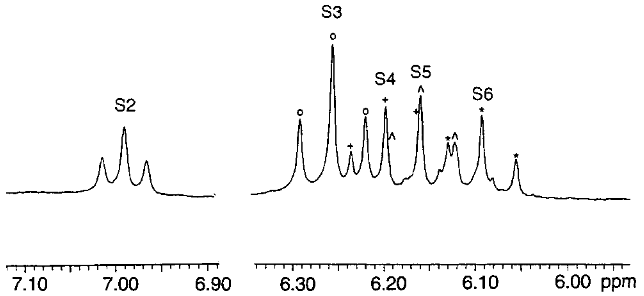
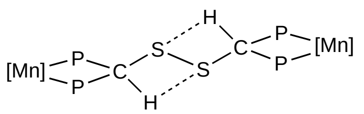


Figure 4. ^{1}H NMR of a mixture of cationic polysulfide complexes of formula [(CO)$_4$Mn{(PPh$_2$)$_2$C(H)–S$_n$–C(H)(PPh$_2$)$_2$}Mn(CO)$_4$]$^{2+}$ ($n = 2-6$).



Scheme 5. Schematic representation of the proposed C–H$\cdots$S interactions in **9**.

the chemical shift of the protons to lower. In the disulfide **9** the interaction should be stronger than in all other polysulfide derivatives (as is evidenced by the notably higher chemical shift of these protons in **9**), perhaps owing to a cooperative effect,[15] as the two proposed C–H$\cdots$S hydrogen bonds are interconnected (Scheme 5). In order to support this proposition we carried out an X-ray structural determination on **9**. The structure of the cation is shown in Figure 5 and a selection of bond lengths and angles is presented in Table 6. Unlike the neutral precursor **4**, complex **9** does not have C_i symmetry because the two tertiary hydrogen atoms break that symmetry by both pointing towards the same side of the molecule. The S1$\cdots$H10 (3.074(3) Å) and S2$\cdots$H9 (3.121(3) Å) distances are not very short but they are comparable to the van der Waals separation, allowing the existence of weak C–H$\cdots$S interactions in the solid state as well, in agreement with the spectroscopic data of this complex in solution. It is also worth remarking the S–S bond length of 2.056(4) Å, which is much shorter than the corresponding length in the neutral complex **4** (2.177(13) Å).

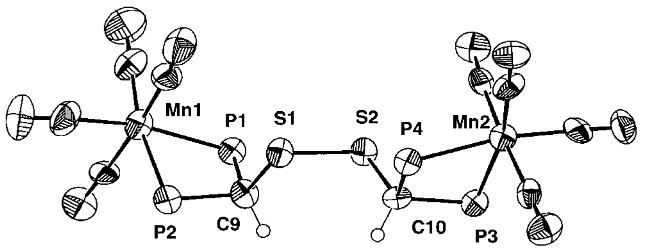


Figure 5. Structure of the cation **9** (ORTEP, 50% probability level). Phenyl groups have been omitted for clarity.

Table 6. Selected bond lengths [Å] and angles [°] for **9**.

Mn1–P1	2.355(3)	Mn2–P3	2.301(4)
Mn1–P2	2.295(4)	Mn2–P4	2.339(3)
P1–C9	1.880(11)	P3–C10	1.845(10)
P2–C9	1.841(11)	P4–C10	1.893(10)
C9–S1	1.824(10)	C10–S2	1.815(10)
S1–S2	2.056(4)		
P1-Mn1-P2	71.79(12)	P3-Mn2-P4	72.17(12)
P1-C9-P2	94.2(5)	P3-C10-P4	94.0(5)
C9-S1-S2	102.4(4)	C10-S2-S1	100.8(3)

Very interestingly, complex **9** can be selectively deprotonated by treatment with H_2O in CH_2Cl_2 to give the monocationic dinuclear complex **11**, in which the bridging ligand contains both a diphosphane and a diphosphanylmethanide fragment (Scheme 4). This complex was also formed by reaction of **4** with one equivalent of HBF_4. Compound **11** was obtained by both methods in quantitative yield as a pale yellow solid. The semiprotonated monosulfide derivative **6**, which was previously detected during the synthesis of **7** (Scheme 3), can also be prepared in the same manner as **11**. The formation of these semiprotonated polysulfide derivatives suggests the existence of an electronic connection between both metallic fragments through the sulfur chain, a feature which is also evidenced in the infrared spectra of these complexes (Table 5). Thus, the IR spectrum of **11** in the ν(CO) region consists of two groups of bands, the one at higher frequencies corresponding to the $Mn(CO)_4$ moiety bonded to the protonated $(PPh_2)_2C(H)S$– fragment of the bridging ligand (2093, 2033, and 2010 cm^{-1}), and the one at lower frequencies corresponding to the $Mn(CO)_4$ moiety bonded to the diphosphanylmethanide unit $(PPh_2)_2CS$– (2077, 1993, and 1974 cm^{-1})(Figure 6). Note that this last group of signals appears at higher frequencies (6 cm^{-1} on average) than those corresponding to the fully deprotonated complex **4** (2070, 1993, and 1963 cm^{-1}), indicating that the first protonation process on **4** to give **11** induces some electronic changes in the remaining deprotonated $Mn(CO)_4(PPh_2)_2CS$– fragment, rendering it more difficult to protonate and allowing the isolation of **11** in a pure form (instead of a statistical mixture of **4**, **9**, and **11**). Curiously, in the IR spectrum of **11** the ν(CO) absorptions corresponding to the protonated fragment appear almost at the same values than those of the fully protonated derivative **9** (at just 1.5 cm^{-1} lower frequencies on average, see Table 2 and Table 5), suggesting that the electronic connection through the diphoshanylmethanide unit is nearly disrupted on protonation.

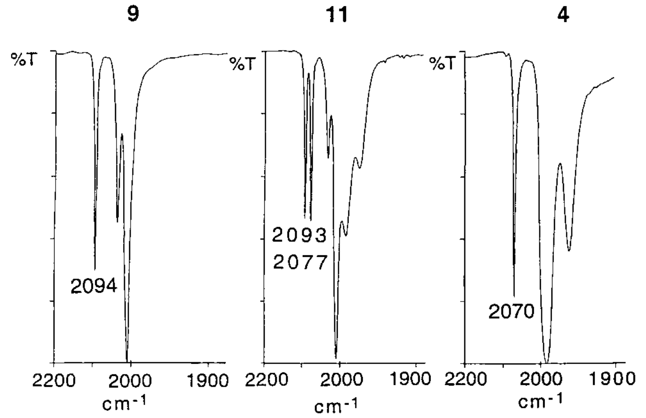
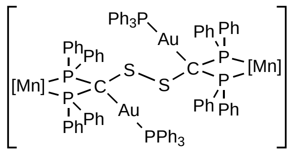
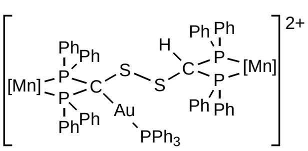


Figure 6. Monitoring by IR spectroscopy of the controlled protonation process on **4** to give **11** and **9**.

On the other hand, in parallel reactions to those described above, it is also possible to introduce a metallic fragment into the P_2C–S–S–CP_2 chain of **4**. Thus **4** readily reacts with two equivalents of $[AuCl(PPh_3)]$ in the presence of $TlPF_6$ as chloride abstractor, affording **12** . Similarly, **11** reacts with one equivalent of $[AuCl(PPh_3)]$ under the same conditions to give the mixed derivative **13**. Although we have been unable to prepare suitable crystals of **12** and **13** for X-ray analysis, their spectroscopic data (Table 5) are similar to those of the related complexes $[Mn(CO)_4\{(PPh_2)_2C(AuPPh_3)_2\}]^+$ and $[Mn(CO)_4\{(PPh_2)_2C(H)(AuPPh_3)\}]^+$,[16] suggesting that the gold atoms in **12** and **13** are directly bonded to the methanide carbon atoms, though some Au$\cdots$S contact can not be



12



13

excluded. In this regard it has been reported that bis(trithiaferrocenophane) derivatives can coordinate transition metal ions through the polysulfur chains, allowing the synthesis of remarkable heterometallic species.[17]

Interestingly, the signal of the P$_2$C(H)$-$S$_2$$-$C(AuPPh$_3$)P$_2$ proton in the ^{1}H NMR spectrum of **13** appears 0.60 ppm lower in frequency than that of the P2C(H)$-$S$_2$$-$C(H)P$_2$ protons in **9**, and is near to the range found for the other cationic polysulfide derivatives (Table 5). This lowering of frequency could be attributed to the disappearance of the above mentioned cooperativity in the interaction of those protons with the disulfide unit.

Conclusion

We have synthesized the unique polysulfide derivatives [(CO)$_4$Mn{(PPh$_2$)$_2$C$-$S$_n$$-$C(PPh$_2$)$_2$}Mn(CO)$_4$], in which the bridging polysulfur chain is linked to carbonyl complexes of Mn^I through diphosphanylmethanide units. Although the polysulfides with $n > 2$ are unstable toward sulfur extrusion, the sulfur chain length can be relatively controlled, allowing the X-ray structural characterization of **3** ($n = 6$), **4** ($n = 2$), and **7** ($n = 1$), whereas those polysulfides with the S$_7$, S$_5$, S$_4$, and S$_3$ sulfur chains were spectroscopically detected. The bridging polysulfidebis(diphosphanylmethanide) ligands contain both electrophilic and nucleophilic centers, a feature which determines their reactivity. Thus, the central sulfur atoms of the polysulfur chain behave as electrophiles when reacting with PPh$_3$ or Na/Hg, whereas the methanide carbon atoms are nucleophilic, as shown in their reactions with HBF$_4$ or [AuCl(PPh$_3$)].

These results can potentially be extended to the synthesis of metal-containing polysulfide polymers with interesting properties such as pH dependent electronic connectivity between the metal centers. These studies are currently under investigation.

Experimental Section

General: All reactions were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Solvents were dried and purified by standard techniques and distilled under nitrogen prior to use. All reactions were monitored by IR spectroscopy (Perkin–Elmer FT 1720-X and Paragon 1000 spectrophotometers). Elemental analyses were performed on a Perkin–Elmer 240B elemental analyzer. ^{1}H and ^{31}P NMR spectra were measured with Bruker AC-300 and AC-200 instruments. Chemical shifts are given in ppm relative to internal SiMe$_4$ (^{1}H) or external 85% H$_3$PO$_4$ (^{31}P). FAB-MS spectra were obtained from the University of Oviedo Mass Spectroscopic Service. The complexes [Mn(CO)$_4${(Ph$_2$P)$_2$CH}] (**2**),[16] [Mn(CO)$_4${(Ph$_2$P)$_2$C$-$S$-$I}] (**5**),[13] and [AuCl(PPh$_3$)][18] were prepared as described elsewhere. All other reagents were commercially obtained and used without further purification.

Reaction of 2 with S$_8$: A solution of [Mn(CO)$_4${(Ph$_2$P)$_2$CH}] (**2**) (200 mg, 0.36 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise to S$_8$ (29 mg, 0.11 mmol) over 15 min at room temperature with continuous stirring. The resultant yellow solution was filtered through an alumina column (activity III) to eliminate the cationic complex **1**. The solvent was evaporated to dryness, yielding a yellow solid consisting of a mixture of polysulfide complexes of general formula [(CO)$_4$Mn{(PPh$_2$)$_2$C$-$S$_n$$-$C(PPh$_2$)$_2$}Mn(CO)$_4$]. MS (FAB): *m/z* (%): 1324.0 (1) [$M^+ + 2$H]($n = 7$), 1292.0 (5) [$M^+ + 2$H]($n = 6$), 1259.9 (3) [$M^+ +$ 2H]($n = 5$), 1227.8 (2) [$M^+ + 2$H]($n = 4$), 1195.6 (2) [$M^+ + 2$H]($n = 3$), 1163.6 (2) [$M^+ + 2$H]($n = 2$). The ^{1}H NMR spectra of this mixture, after protonation with HBF$_4$, did not show signals corresponding to polysulfides with $n = 3$ and 2. The crude yellow solid was then chromatographed through an alumina column (activity III). Elution with CH$_2$Cl$_2$/hexane (1:2 v/v) gave a yellow solid, which was recrystallized by diffusion of hexane into a CH$_2$Cl$_2$ of the complex, affording yellow crystals of **3** suitable for X-ray diffraction studies (40% yield). Elemental analysis calcd (%) for C$_{58}$H$_{40}$Mn$_2$O$_8$P$_4$S$_6$ (1291.1): C 53.96, H 3.12; found: C 54.19, H 3.34.

Compound 4: A solution of **3** (40 mg, 0.30 mmol) in THF (30 mL) was added to an excess of sodium amalgam (15 g, 0.8%) at room temperature. After 30 min of stirring the solvent was removed in vacuo. The residue was extracted with CH$_2$Cl$_2$ (50 mL), filtered, and evaporated to dryness. The remaining yellow solid was chromatographed on alumina (activity III) using hexane, diethyl ether, and CH$_2$Cl$_2$ as eluants. Elution first with hexane and then with diethyl ether gave mixtures of different polysulfides. Finally, elution with CH$_2$Cl$_2$/hexane (4:1) afforded **4** as a yellow solid (33% yield). Crystals of **4** suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. MS (FAB): *m/z* (%): 1163.6 (25) [$M^+ + 2$H]; elemental analysis calcd (%) for C$_{58}$H$_{40}$Mn$_2$O$_8$P$_4$S$_2$ (1162.9): C 59.91, H 3.47; found: C 59.71, H 3.45.

Compound 7: A solution of **2** (50 mg, 0.09 mmol) in CH$_2$Cl$_2$ (5 mL) was added dropwise to a solution of **5** (64 mg, 0.09 mmol) in CH$_2$Cl$_2$ (9 mL) and stirred for 30 min. The color of the solution changed from red to yellow. An excess of KOH (0.40 g, 7.1 mmol) was added and the mixture stirred for 30 min. The solution was filtered through diatomaceous earth and the solvent evaporated to dryness under vacuum. The yellow residue was washed with hexane (4 × 15 mL). Yield 76%. Crystals of **7** suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. Elemental analysis calcd (%) for C$_{58}$H$_{40}$Mn$_2$O$_8$P$_4$S (1130.8): C 61.61, H 3.57; found: C 61.35, H 3.64.

Compound 8-(BF$_4$)$_2$: Tetrafluoroboric acid/diethyl ether complex (48 μL, 0.28 mmol, 85%) was added to a solution of **3** (150 mg, 0.116 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature with continuous stirring. The solution instantly changed from yellow to colorless. The solvent was then evaporated to dryness and the residue was washed three times with diethyl ether (3 × 5 mL). The product was recrystallized from CH$_2$Cl$_2$/hexane (80% yield). Elemental analysis calcd (%) for C$_{58}$H$_{42}$B$_2$F$_8$Mn$_2$O$_8$P$_4$S$_6$ (1466.7): C 47.50, H 2.89; found: C 47.28, H 2.71.

Compound 9-(BF$_4$)$_2$: The compound was prepared from **4** by following the same method described for **8**-(BF$_4$)$_2$ (92% yield). Crystals of **9**-(ClO$_4$)$_2$ suitable for X-ray analysis were obtained by protonation of **4** with aqueous HClO$_4$ (70%) followed by crystallization of the reaction mixture from CH$_2$Cl$_2$/hexane. Elemental analysis calcd (%) for C$_{58}$H$_{42}$B$_2$F$_8$Mn$_2$O$_8$P$_4$S$_2$ (1338.5): C 52.05, H 3.16; found: C 51.87, H 2.97.

Compound 10-(BF$_4$)$_2$: The compound was prepared from **7** by following the same method described for **8**-(BF$_4$)$_2$ (82% yield). Elemental analysis calcd (%) for C$_{58}$H$_{42}$B$_2$F$_8$Mn$_2$O$_8$P$_4$S (1306.4): C 53.3, H 3.24; found: C 52.97, H 3.20.

Compound 11-BF$_4$: A solution of tetrafluoroboric acid/diethyl ether complex in CH$_2$Cl$_2$ (1.9 mL, 0.019 mmol, 0.01 M) was added dropwise to a solution of **4** (25 mg, 0.019 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature with continuous stirring. After 10 min the solution was filtered and the solvent evaporated to dryness to obtain a pale yellow solid (93% yield). Elemental analysis calcd (%) for C$_{58}$H$_{41}$BF$_4$Mn$_2$O$_8$P$_4$S$_2$ (1250.6): C 55.70, H 3.30; found: C 55.35, H 3.22.

Compound 6-BF$_4$: The compound was prepared similarly to **11**-BF$_4$ starting from **7** (91% yield). Elemental analysis calcd (%) for C$_{58}$H$_{41}$BF$_4$Mn$_2$O$_8$P$_4$S (1218.6): C 57.17, H 3.39; found: C 56.88, H 3.27.

Table 7. Crystallographic data for compounds **4**, **7**, and **9**-$(ClO_4)_2$.

	4	**7**	**9**-$(ClO_4)_2$
formula	$C_{58}H_{40}Mn_2O_8P_4S_2$	$C_{58}H_{40}Mn_2O_8P_4S.0.5CH_2Cl_2$	$C_{58}H_{42}Cl_2Mn_2O_{16}P_4S_2.CH_2Cl_2.5H_2O.HClO_4$
formula weight	1162.78	1173.18	1639.16
temperature [K]	293	293	200
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1$	$P2_1/n$
a [Å]	28.428(6)	12.153(9)	10.074(5)
b [Å]	11.953(4)	37.61(5)	17.779(6)
c [Å]	16.215(5)	12.487(9)	23.568(6)
α [°]	90	90	90
β [°]	98.48(2)	107.85(5)	93.068(17)
γ [°]	90	90	90
V [Å^3]	5450(3)	5431(9)	7144(4)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	1.417	1.435	1.524
μ[cm^{-1}]	7.12	7.25	66.52
θ range [°]	3–20	1.08–25.98	3.12–68.33
reflections collected	3663	11343	10195
independent reflections	804	10814	6797
goodness-of-fit on F^2	1.199	0.994	0.981
final R indices [$I > 2\sigma(I)$]; $R1$, $wR2$	0.0682, 0.1423	0.0594, 0.1278	0.0871, 0.2220
R indices (all data); $R1$, $wR2$	0.2240, 0.2321	0.2406, 0.1811	0.1349, 0.2420

Compound 12-$(PF_6)_2$: [AuCl(PPh_3)] (26 mg, 0.053 mmol) and an excess of $TlPF_6$ (91 mg, 0.26 mmol) were added to a solution of **4** (30 mg, 0.026 mmol) in CH_2Cl_2 (8 mL). The mixture was stirred for 12 h. The solution was then filtered through diatomaceous earth and the solvent evaporated to dryness under vacuum to afford a yellow solid which was washed with diethyl ether (90% yield). Elemental analysis calcd (%) for $C_{94}H_{70}Au_2F_{12}Mn_2O_8P_8S_2$ (2371.3): C 47.61, H 2.98; found: C 47.05, H 3.09.

Compound 13-$(PF_6)_2$: This compound was prepared similarly to **12**-$(PF_6)_2$ by treating **11**-BF_4 with one equivalent of [AuCl(PPh_3)] and an excess of $TlPF_6$. The compound was recrystallized from CH_2Cl_2/hexane (70% yield). Elemental analysis calcd (%) for $C_{76}H_{56}AuF_{12}Mn_2O_8P_7S_2$ (1913.1): C 47.72, H 2.95; found: C 47.90, H 3.08.

X-ray crystallographic study: The preparation of single crystals is described above for the individual compounds. Crystallographic data of the complex **3** were previously reported.[8] Data collection was carried out on a Siemens AED diffractometer for **4**, an Enraf–Nonius CAD4 diffractometer for **7** and an Enraf–Nonius Kappa CCD diffractometer for **9**-$(ClO_4)_2$. Graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used for **4** and **7**, and graphite-monochromated $Cu_{K\alpha}$ ($\lambda = 1.54184$ Å) for **9**-$(ClO_4)_2$. The structures were solved by direct and Paterson methods, and refined by full-matrix least-squares methods with the following program packages: SIR92[19] and SHELXL-97[20] for **4** and DIRDIF92[21] and SHELXL-97[20] for **7** and **9**-$(ClO_4)_2$. The presence of disordered CH_2Cl_2 was detected in complex **7** as well as rather disordered solvent molecules (five water molecules, a CH_2Cl_2, and a perchloric acid molecule) in compound **9**-$(ClO_4)_2$. Relevant crystallographic data and details of the refinement for the three structures are given in Table 7. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-160354 (**4**), CCDC-160715 (**7**), and CCDC-160716 (**9**-$(ClO_4)_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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