

# New approach to sulfonated diphosphine complexes: synthesis and amphoteric behaviour of zwitterionic $[\text{Mn}^+(\text{CO})_4\{(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3^-\}]$

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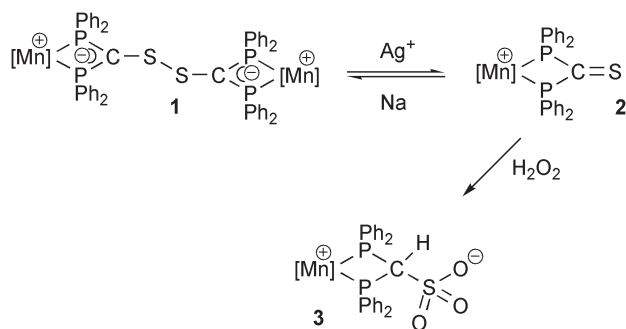
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Oxidation of the thioketone residue in the complex  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}=\text{S}\}]^+$  (**2**) with hydrogen peroxide affords the sulfonate derivative  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3^-\}]$  (**3**), which shows amphoteric behaviour in reversible acid–base processes, and is easily chlorinated to give  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}(\text{Cl})\text{SO}_3^-\}]$  (**8**).

We have recently reported that the disulfide complex  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}-\text{S}-\text{S}-\text{C}(\text{PPh}_2)_2\}\text{Mn}(\text{CO})_4]$  (**1**)<sup>1</sup> undergoes oxidative cleavage of the sulfur–sulfur bond to give the mono-nuclear thioketone derivative  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}=\text{S}\}]^+$  (**2**) (Scheme 1).<sup>2</sup> Compound **2** features interesting reactivity patterns toward reducing agents, being able to regenerate the sulfur–sulfur bond to give **1** after reaction with Na.<sup>2</sup> Beside this electron-acceptor behaviour, we have now found that the thione residue of **2** can be oxidized with hydrogen peroxide affording the zwitterionic complex  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3^-\}]$  (**3**), that incorporates a sulfonate functionality at the central carbon atom of the diphosphine (Scheme 1). Sulfonated diphosphines have attracted widespread interest in recent years as they greatly increase the solubility of their corresponding metal complexes in aqueous media;<sup>3</sup> in most cases sulfonation is carried out on the aryl substituents at phosphorus by severe treatment with  $\text{H}_2\text{SO}_4$ – $\text{SO}_3$  mixtures.<sup>3,4</sup> By contrast, the methodology provided herein allows sulfonation to take place at the carbon backbone of the diphosphine (dppm) and under very mild conditions.



**Scheme 1** Synthesis of the diphosphinothioketone complex **2** and its oxidation to the sulfonate derivative **3**;  $[\text{Mn}] = [\text{Mn}(\text{CO})_4]$ .

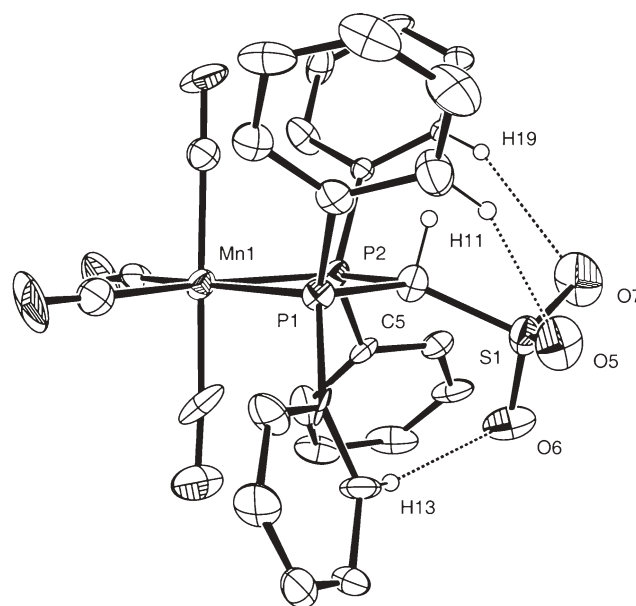
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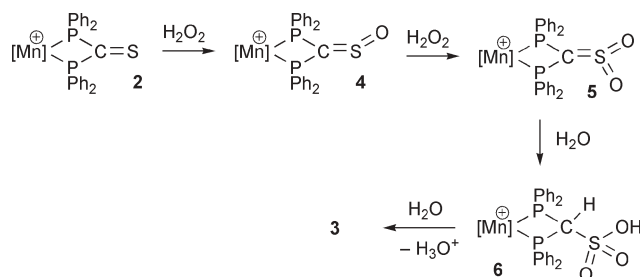
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Thus, the treatment of a dichloromethane solution of  $2.\text{ClO}_4$  with threefold excess of  $\text{H}_2\text{O}_2$  (30% solution in  $\text{H}_2\text{O}$ ) lead to the formation of **3** after 1 h of stirring at room temperature. Compound **3** was isolated in 70% yield after crystallization. The spectroscopic data of **3** reveal the presence of the new sulfonate functionalized diphosphine ligand. The IR spectrum in KBr shows bands at 1250, 1236 and  $1038\text{ cm}^{-1}$  for the S–O stretching modes;<sup>5</sup> the  $^1\text{H}$  NMR spectrum of a  $\text{CD}_2\text{Cl}_2$  solution of **3** shows a triplet at 6.50 ppm ( $^2J_{\text{PH}} = 13\text{ Hz}$ ) assigned to the  $\text{P}_2\text{CH}$  proton, and the  $^{13}\text{C}$  NMR spectrum presents a triplet at 75.6 ppm ( $^1J_{\text{PC}} = 13\text{ Hz}$ ) for the central carbon atom of the diphosphine.<sup>6</sup>

Colourless single crystals of **3** suitable for an X-ray analysis were obtained from slow diffusion of hexane into a dichloromethane solution of the compound.<sup>†</sup> The structure is shown in Fig. 1 together with selected bond distances and angles. The S1–O (1.44 Å on average) and S1–C5 (1.80 Å) bond lengths, as well as the different bond angles around the sulfur atom are typical for



**Fig. 1** A view of the crystal structure of **3**. For clarity most hydrogen atoms of phenyl groups are not shown. Selected bond lengths (Å) and angles (°): P1–C5 1.848(15), P2–C5 1.874(12), C5–S1 1.807(14), S1–O5 1.448(10), S1–O6 1.461(13), S1–O7 1.422(12), O5···H11 2.416(13), O6···H13 2.414(14), O7···H19 2.502(13); P1–C5–P2 96.2(7), C5–S1–O5 105.9(7), C5–S1–O6 104.5(8), C5–S1–O7 106.8(8), O5–S1–O6 112.9(7), O6–S1–O7 111.1(9), O7–S1–O5 114.7(8), C11–H11···O5 155.4(14), C13–H13···O6 150.6(10), C19–H19···O7 149.0(8).



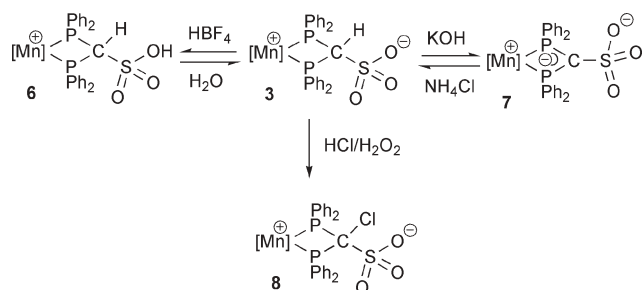
**Scheme 2** Proposed mechanism for the formation of **3**, involving sulfine (**4**), sulfene (**5**), and sulfonic acid (**6**) intermediates.

uncoordinated sulfonate groups, and can be compared with those usually found in organic aminosulfonic acids, which exist as zwitterions (ammoniosulfonate).<sup>7</sup> Owing to the presence of the sulfonate group the solubility of complex **3** in polar solvents is dramatically increased with respect to the analogous dpmm parent complex.<sup>8</sup>

Most sulfonate compounds of transition metals contain the sulfonate group either as an external anion of the corresponding cationic complex, or as a ligand coordinated to the metal through the oxygen atoms in a variety of coordination modes.<sup>9</sup> In this regard, complex **3** is a remarkable example of a neutral sulfonate complex lacking a metal–oxygen bond. This circumstance allows three of the phenyl groups to point towards the oxygen atoms of the sulfonate in order to establish three intramolecular C–H⋯O hydrogen bonds,<sup>10</sup> which stabilize the uncoordinated  $-\text{SO}_3^-$  residue (Fig. 1). To the best of our knowledge, diphosphino-methylsulfonates are unknown, although other phosphorus-substituted methylsulfonates have been described in the literature, remarkably the  $\alpha$ -phosphono methylsulfonates of general formula  $\{\text{P}(\text{O})(\text{OR}')_2\text{C}(\text{H})(\text{R})\text{SO}_3\text{K}\}$  that are potent squalene synthase inhibitors and so potential selective cholesterol lowering agents,<sup>11</sup> as well as the 1,1-bis(phosphono)methylsulfonate  $\{\text{P}(\text{O})(\text{OR})_2\text{C}(\text{H})\text{SO}_3\text{Na}\}$ , which is used in the preparation of supercharged analogues of nucleotides.<sup>12</sup>

It has been described that controlled oxidation of thioketones with  $\text{H}_2\text{O}_2$  can lead to the formation of sulfoxes.<sup>13</sup> Oxidation of certain thiones with oxygen to afford ketones appears to proceed through the formation of sulfene intermediates.<sup>14</sup> Considering all the above, a likely mechanism for the formation of **3** is proposed in Scheme 2; this implies the formation of the sulfine and sulfene intermediates **4** and **5**, respectively, followed by the hydrolysis of the last to afford the sulfonic acid functionality in complex **6**, as typically occurs with transient sulfoxes which are trapped by water.<sup>15</sup> Compound **6** would be finally deprotonated by water yielding **3**.

Complex **3** can be viewed as an  $\text{SO}_3$  adduct of the diphosphinomethanide complex  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}\}]$ . Nevertheless,



**Scheme 3** Amphoteric behaviour of complex **3**, and chlorination reaction at the central carbon atom of the diphosphine to yield **8**.

direct reaction of this complex with  $\text{SO}_3$  sources such as  $\text{SO}_3$ , DMF results in the instantaneous formation of the cationic complex  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}_2\}]^+$  instead of **3**.

The  $\text{P}_2\text{CH}$  group in the anionic ligand  $[(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3]^-$  in **3** is acidic enough as to be readily deprotonated by treatment with KOH in  $\text{CH}_2\text{Cl}_2$  (Scheme 3), yielding the potassium salts of complex **7** that formally contains the dianionic diphosphine  $[(\text{PPh}_2)_2\text{CSO}_3]^{2-}$ . The spectroscopic data of **7** (Table 1) show strong lowering in the frequencies of the IR bands of carbonyl and sulfonate groups with respect to those of **3**; similarly, the phosphorus signal in the  $^{31}\text{P}$  NMR spectrum is strongly shifted to higher field. Protonation of **7** with a weak acid ( $\text{NH}_4^+$ ) readily turns it into **3**, which can be further protonated with an strong acid ( $\text{HBF}_4$ ) affording the cationic complex **6** (Scheme 3), which contains the sulfonic acid-substituted diphosphine  $[(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3\text{H}]$ . Complex **6** is readily transformed to **3** in the presence of traces of water, thus precluding isolation of pure solid samples of this compound. Obviously, **6** features IR and  $^{31}\text{P}$  NMR bands at higher frequencies than those of **7** and **3** (Table 1).

The easy dissociation of the  $\text{P}_2\text{CH}$  proton in complex **3** allows the diphosphine to be doubly functionalized at the central carbon atom. A preliminary example is provided by the treatment of a dichloromethane solution of **3** with concentrated hydrochloric acid–30%  $\text{H}_2\text{O}_2$  system,<sup>16</sup> affording  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}(\text{Cl})\text{SO}_3\}]$  (**8**) (Scheme 3). The reduction of electronic density on the metal atom produced by chlorination of the diphosphine is reflected in the spectroscopic data of **8** (Table 1), especially in the very low-field signal at 68 ppm in the  $^{31}\text{P}$  NMR spectrum.

To summarize, we have reported herein that the thione residue in the complex  $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2)_2\text{C}=\text{S}\}]^+$  (**2**) can be oxidized with  $\text{H}_2\text{O}_2$  under mild conditions to yield a sulfonate functionality; which provides an unprecedented access to sulfonated diphosphines of dpmm-type. The method allows sulfonation of the diphosphine to take place at the carbon backbone, in opposition to most known experimental procedure to obtain sulfonated diphosphines based on severe treatment with oleum, that introduce the sulfonate group at the aryl substituents of the phosphorus atoms.

**Table 1** Selected spectroscopic data for the new compounds

Complex	Ligand	IR( $\nu\text{CO}$ ) <sup>a</sup>	IR( $\nu\text{SO}$ ) <sup>b</sup>	$^{31}\text{P}$ NMR <sup>c</sup>
<b>7</b>	$[(\text{PPh}_2)_2\text{CSO}_3]^{2-}$	2073, 1990, 1962	1180, 1161, 1016	0.8
<b>3</b>	$[(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3]^-$	2090, 2026, 2010, 1999	1250, 1238, 1038	28.0
<b>6</b>	$[(\text{PPh}_2)_2\text{C}(\text{H})\text{SO}_3\text{H}]$	2095, 2034, 2014	—	31.3
<b>8</b>	$[(\text{PPh}_2)_2\text{C}(\text{Cl})\text{SO}_3]^-$	2093, 2027, 2016, 1998	1263, 1247, 1046	68.0

<sup>a</sup>  $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ . <sup>b</sup> KBr,  $\text{cm}^{-1}$ . <sup>c</sup>  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ .

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## Notes and references

† Crystal data for **3**:  $\text{C}_{29}\text{H}_{21}\text{MnO}_7\text{P}_2\text{S}$ ,  $M = 630.40$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 10.714(4)$ ,  $b = 14.256(2)$ ,  $c = 18.824(7)$  Å,  $V = 2875(2)$  Å<sup>3</sup>,  $\rho_{\text{calc'd}} = 1.456$  g cm<sup>-3</sup>,  $T = 293$  K,  $Z = 4$ ,  $\lambda = 1.54184$  Å,  $\mu = 5.854$  mm<sup>-1</sup>, 11310 reflections measured, 2227 unique ( $R_{\text{int}} = 0.083$ ), 1478 observed [ $I > 2\sigma(I)$ ],  $R_1 = 0.077$ ,  $wR_2 = 0.177$  [ $I > 2\sigma(I)$ ], largest diff. peak and hole 0.757 and  $-0.497$  e Å<sup>-3</sup>. The structure showed a rather large disorder in the sulfonate and phenyl groups, and even in the carbonyl ligands. Modelling the disorder by means of 'rigid bond' and 'similarity' restraints for the components of the anisotropic displacement parameters solved most of the problems, but nevertheless three atoms (C2, C4, and C18) had to be isotropically refined in order to prevent them from going non-positive definite. CCDC 274156. See <http://dx.doi.org/10.1039/b507600e> for crystallographic data in CIF or other electronic format.

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