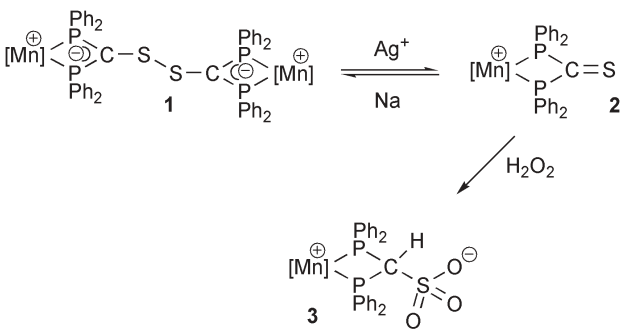
New approach to sulfonated diphosphine complexes: synthesis and amphoteric behaviour of zwitterionic $[Mn^{+}(CO_4\{(PPh_2)_2C(H)SO_3^{-}\}]$

Javier Ruiz,*[a] Mario Ceroni,[a] Marilín Vivanco,[a] Marta P. Gonzalo,[a] Santiago García-Granda[b] and Francisco van der Maelen[b]

Received (in Cambridge, UK) 1st June 2005, Accepted 26th July 2005
First published as an Advance Article on the web 5th September 2005
DOI: 10.1039/b507600e

Oxidation of the thioketone residue in the complex $[Mn(CO)_4\{(PPh_2)_2C{=}S\}]^+$ (2) with hydrogen peroxide affords the sulfonate derivative $[Mn(CO)_4\{(PPh_2)_2C(H)SO_3\}]$ (3), which shows amphoteric behaviour in reversible acid–base processes, and is easily chlorinated to give $[Mn(CO)_4\{(PPh_2)_2C(Cl)SO_3\}]$ (8).

We have recently reported that the disulfide complex $[Mn(CO)_4\{(PPh_2)_2C{-}S{-}S{-}C(PPh_2)_2\}Mn(CO)_4)]$ (**1**)[1] undergoes oxidative cleavage of the sulfur–sulfur bond to give the mononuclear thioketone derivative $[Mn(CO)_4\{(PPh_2)_2C{=}S\}]^+$ (**2**) (Scheme 1).[2] Compound **2** features interesting reactivity patterns toward reducing agents, being able to regenerate the sulfur–sulfur bond to give **1** after reaction with Na.[2] 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 $[Mn(CO)_4\{(PPh_2)_2C(H)SO_3\}]$ (**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;[3] in most cases sulfonation is carried out on the aryl substituents at phosphorus by severe treatment with H_2SO_4–SO_3 mixtures.[3,4] 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**; [Mn] = $[Mn(CO)_4]$.

[a]*Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Oviedo, 33071, Spain. E-mail: jruiz@fq.uniovi.es; Fax: +34 98510 3446; Tel: +34 985102977*
[b]*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Oviedo, 33071, Spain*

Thus, the treatment of a dichloromethane solution of **2**.ClO_4 with threefold excess of H_2O_2 (30% solution in H_2O) 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 cm^{-1} for the S–O stretching modes;[5] the ^1H NMR spectrum of a CD_2Cl_2 solution of **3** shows a triplet at 6.50 ppm ($^2J_{PH}$ = 13 Hz) assigned to the P_2CH proton, and the ^{13}C NMR spectrum presents a triplet at 75.6 ppm ($^1J_{PC}$ = 13 Hz) for the central carbon atom of the diphosphine.[6]

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.† 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

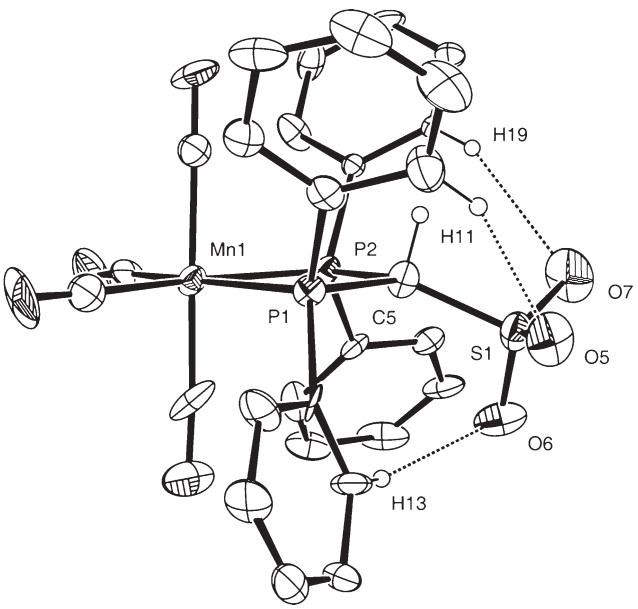
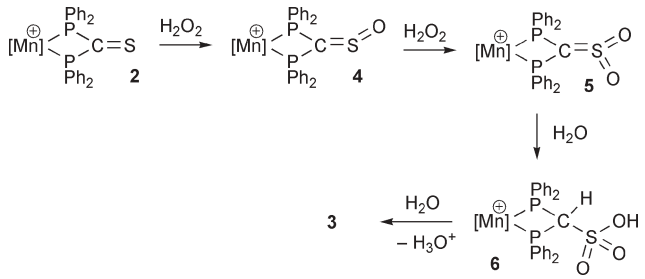
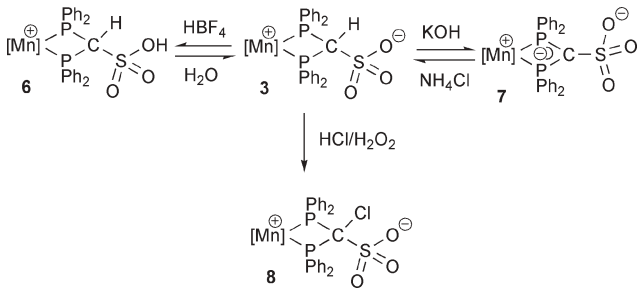


Fig. 1 A view of the crystal structure of **3**. For clarity most hydrogen atoms of phenyl groups are not shown. Selected bond lengths (Å) and angles (°): P1–C5 1.848(15), P2–C5 1.874(12), C5–S1 1.807(14), S1–O5 1.448(10), S1–O6 1.461(13), S1–O7 1.422(12), O5···H11 2.416(13), O6···H13 2.414(14), O7···H19 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.



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

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

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.[9] In this regard, complex **3** is a remarkable example of a neutral sulfonato 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,[10] which stabilize the uncoordinated $–SO_3^-$ residue (Fig. 1). To the best of our knowledge, diphosphinomethylsulfonates are unknown, although other phosphorus-substituted methylsulfonates have been described in the literature, remarkably the α-phosphono methylsulfonates of general formula $\{P(O)(OR')_2C(H)(R)SO_3K\}$ that are potent squalene synthase inhibitors and so potential selective cholesterol lowering agents,[11] as well as the 1,1-bis(phosphono)methylsulfonate $\{(P(O)(OR)_2)_2C(H)SO_3Na\}$, which is used in the preparation of supercharged analogues of nucleotides.[12]

It has been described that controlled oxidation of thioketones with H_2O_2 can lead to the formation of sulfines.[13] Oxidation of certain thiones with oxygen to afford ketones appears to proceed through the formation of sulfene intermediates.[14] 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 sulfenes which are trapped by water.[15] Compound **6** would be finally deprotonated by water yielding **3**.

Complex **3** can be viewed as an SO_3 adduct of the diphosphinomethanide complex $[Mn(CO)_4\{(PPh_2)_2CH\}]$. Nevertheless, direct reaction of this complex with SO_3 sources such as SO_3.DMF results in the instantaneous formation of the cationic complex $[Mn(CO)_4\{(PPh_2)_2CH_2\}]^+$ instead of **3**.

The P_2CH group in the anionic ligand $[(PPh_2)_2C(H)SO_3]^-$ in **3** is acidic enough as to be readily deprotonated by treatment with KOH in CH_2Cl_2 (Scheme 3), yielding the potassium salts of complex **7** that formally contains the dianionic diphosphine $[(PPh_2)_2CSO_3]^{2-}$. 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}P NMR spectrum is strongly shifted to higher field. Protonation of **7** with a weak acid (NH_4^+) readily turns it into **3**, which can be further protonated with an strong acid (HBF_4) affording the cationic complex **6** (Scheme 3), which contains the sulfonic acid–substituted diphosphine $[(PPh_2)_2C(H)SO_3H]$. 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}P NMR bands at higher frequencies than those of **7** and **3** (Table 1).

The easy dissociation of the P_2CH 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% H_2O_2 system,[16] affording $[Mn(CO)_4\{(PPh_2)_2C(Cl)SO_3\}]$ (**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}P NMR spectrum.

To summarize, we have reported herein that the thione residue in the complex $[Mn(CO)_4\{(PPh_2)_2C=S\}]^+$ (**2**) can be oxidized with H_2O_2 under mild conditions to yield a sulfonate functionality; which provides an unprecedented access to sulfonated diphosphines of dppm-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(νCO)[a]	IR(νSO)[b]	^{31}P NMR[c]
7	$[(PPh_2)_2CSO_3]^{2-}$	2073, 1990, 1962	1180, 1161, 1016	0.8
3	$[(PPh_2)_2C(H)SO_3]^-$	2090, 2026, 2010, 1999	1250, 1238, 1038	28.0
6	$[(PPh_2)_2C(H)SO_3H]$	2095, 2034, 2014	—	31.3
8	$[(PPh_2)_2C(Cl)SO_3]^-$	2093, 2027, 2016, 1998	1263, 1247, 1046	68.0

[a] CH_2Cl_2, cm^{-1}. [b] KBr, cm^{-1}. [c] CD_2Cl_2, δ.

We thank the Spanish Ministerio de Ciencia y Tecnología (PGE and FEDER funding, Project BQU2003-01011) for financial support.

Notes and references

† Crystal data for **3**: $C_{29}H_{21}MnO_7P_2S$, $M = 630.40$, orthorhombic, space group $P2_12_12_1$, $a = 10.714(4)$, $b = 14.256(2)$, $c = 18.824(7)$ Å, $V = 2875(2)$ Å^3, $\rho_{calcd} = 1.456$ g cm^{-3}, $T = 293$ K, $Z = 4$, $\lambda = 1.54184$ Å, $\mu = 5.854$ mm^{-1}, 11310 reflections measured, 2227 unique ($R_{int} = 0.083$), 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^{-3}. 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.

1 J. Ruiz, M. Ceroni, O. V. Quinzani, V. Riera, M. Vivanco, S. García-Granda, F. Van der Maelen, M. Lanfranchi and A. Tiripicchio, *Chem. Eur. J.*, 2001, **7**, 4422.

2 J. Ruiz, M. Ceroni, O. V. Quinzani, V. Riera and O. E. Piro, *Angew. Chem., Int. Ed.*, 2001, **40**, 220.

3 (*a*) W. A. Hermann and C. W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1524; (*b*) G. Verspui, F. Schanssema and R. A. Sheldon, *Angew. Chem., Int. Ed.*, 2000, **39**, 804; (*c*) J. Bakos, Á. Orosz, B. Heil, M. Laghmari, P. Lhoste and D. Sinou, *J. Chem. Soc., Chem. Commun.*, 1991, 1684; (*d*) Y. Amrani, L. Lecomte, D. Sinou, J. Bakos, I. Toth and B. Heil, *Organometallics*, 1989, **8**, 542; (*e*) C. Lensink and J. G. de Vries, *Tetrahedron: Asymmetry*, 1992, **3**, 235; (*f*) M. D. Miquel-Serrano, A. Aghmiz, M. Diéguez, A. M. Masdeu-Bultó, C. Claver and D. Sinou, *Tetrahedron: Asymmetry*, 1999, **10**, 4463.

4 H. Ding, B. B. Bunn and B. E. Hanson, *Inorg. Synth.*, 1998, **32**, 29.

5 The *ν*S–O bands in the IR spectra of the sulfonate groups usually appears in the range 1300–1000 cm^{-1}; see for instance: G. A. Lawrance, *Chem. Rev.*, 1986, **86**, 17.

6 The NMR data of compound **3** are similar to those of other tetracarbonylmanganese(I) complexes containing C-functionalized dppm: J. Ruiz, V. Riera, M. Vivanco, S. García-Granda and M. R. Díaz, *Organometallics*, 1998, **17**, 4562.

7 (*a*) M. A. Leonard and P. J. Squattrito, *Acta Crystallogr., Sect. C*, 1997, **53**, 648; (*b*) L. Skrzypek and K. Suwinska, *Heterocycles*, 2002, **57**, 2035; (*c*) M. Canagaratna, J. A. Phillips, H. Goodfriend and K. R. Leopold, *J. Am. Chem. Soc.*, 1996, **118**, 5290.

8 The compound $[Mn(CO)_4(dppm)]ClO_4$ is only very slightly soluble in acetone, whereas complex **3** is extremely soluble in this solvent. **3** is also very soluble in 1 : 2 acetone–water mixtures, although it is not soluble in pure water.

9 (*a*) J. Cai, *Coord. Chem. Rev.*, 2004, **248**, 1061; (*b*) N. W. Alcock, T. J. Kemp and J. Leciejewicz, *Inorg. Chim. Acta*, 1993, **203**, 81; (*c*) H. Werner, M. Bosch, M. E. Schneider, C. Hahn, F. Kukla, M. Manger, B. Weberndörfer and M. Laubender, *J. Chem. Soc., Dalton Trans.*, 1998, 3549.

10 The C–H···O distances in **3** (average value 2.44 Å) is even shorter than the mean distance of 2.55 Å found in similar hydrogen bonds (Csp^2–H···O); for a review see: T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48.

11 R. M. Lawrence, S. A. Biller, J. K. Dickson, Jr., J. V. H. Logan, D. R. Magnin, R. B. Sulsky, J. D. DiMarco, J. Z. Gougoutas, B. D. Beyer, S. C. Taylor, S. Lan, C. P. Ciosek, Jr., T. W. Harrity, K. G. Jolibois, L. K. Kunselman and D. A. Slusarchyk, *J. Am. Chem. Soc.*, 1996, **118**, 11668.

12 X. Liu, X. Zhang and G. M. Blackburn, *Chem. Commun.*, 1997, 87.

13 (*a*) R. Huang and J. H. Espenson, *J. Org. Chem.*, 1999, **64**, 6935; (*b*) R. Huang and J. H. Espenson, *J. Org. Chem.*, 1999, **64**, 6374.

14 L. Carlsen, *J. Org. Chem.*, 1976, **41**, 1976.

15 (*a*) J. F. King, J. Y. L. Lam and S. Skonieczny, *J. Am. Chem. Soc.*, 1992, **114**, 1743; (*b*) J. F. King and J. Y. L. Lam, *J. Org. Chem.*, 1993, **58**, 3429.

16 For the use of HCl/H_2O_2 system for the halogenation of organic compounds see: (*a*) A. O. Terent'ev, S. V. Khodykin, N. A. Troitskii, Y. N. Ogibin and G. I. Nikishin, *Synthesis*, 2004, **17**, 2845; (*b*) P. V. Vyas, A. K. Bhatt, G. Ramachandraiah and A. V. Bedekar, *Tetrahedron Lett.*, 2003, **44**, 4085.

