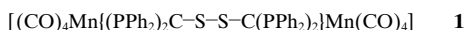


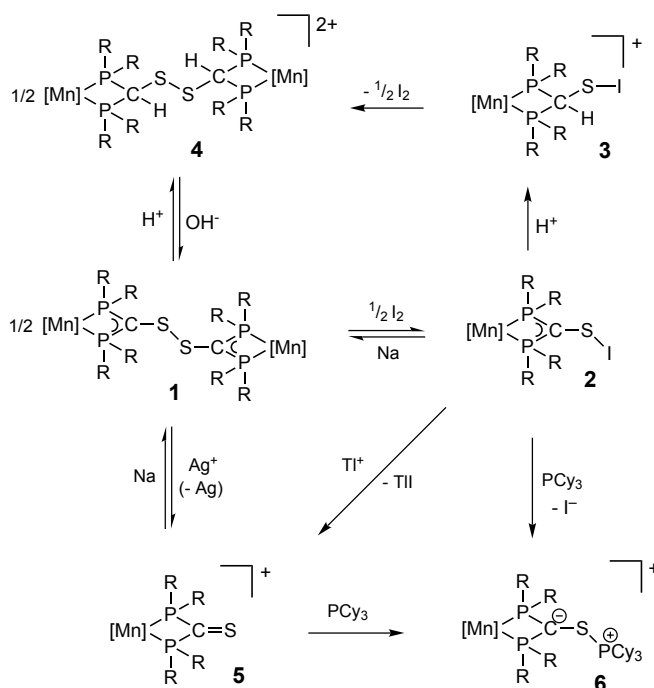
Reversible S–S Bond Breaking and Bond Formation in Disulfide-Containing Dinuclear Complexes of Mn<sup>I</sup>\*\*

Javier Ruiz,\* Mario Ceroni, Oscar V. Quinzani, Víctor Riera, and Oscar E. Piro

Disulfide-containing compounds are of considerable biological<sup>[1]</sup> and technological relevance,<sup>[2]</sup> and the mechanisms by which the sulfur–sulfur bond in these compounds can be reversibly broken and formed has attracted a great deal of interest.<sup>[3]</sup> We have recently reported that nucleophilic degradation of cyclooctasulfur by the diphosphanymethanide complex of manganese(I) [Mn(CO)<sub>4</sub>{(PPh<sub>2</sub>)<sub>2</sub>CH}] allows the formation of the hexasulfur-bridged bis(diphosphanymethanide) dimetallic derivative [(CO)<sub>4</sub>Mn{(PPh<sub>2</sub>)<sub>2</sub>C–S<sub>6</sub>–C(PPh<sub>2</sub>)<sub>2</sub>–Mn(CO)<sub>4</sub>].<sup>[4]</sup> In this complex the polysulfur chain can be progressively shortened by treatment with PPh<sub>3</sub> leading finally to the disulfide compound **1**, which does not undergo further sulfur extrusion processes.<sup>[5]</sup> We have now explored the chemistry of this disulfide derivative with regard to the controlled scission and formation of the sulfur–sulfur bond, promoted either by redox processes or by combined redox and acid–base treatments. This has led to a number of scarce functionalities such as diphosphanylthioetone, sulfenyl iodide, and thioxophosphorane ylide, as parts of the corresponding carbonyl complex of manganese(I).



The treatment of **1** with one equivalent of I<sub>2</sub> in dichloromethane led instantaneously to the formation of **2** (Scheme 1), which was isolated as a red solid. The spectroscopic and analytical data for **2** (see Experimental Section), as well as further reactivity studies (see below), strongly support the proposed formulation for this complex as the sulfenyl iodide derivative [Mn(CO)<sub>4</sub>{(PPh<sub>2</sub>)<sub>2</sub>C–S–I}]. The Raman spectrum of **2** is in agreement with the scission of the S–S bond upon oxidation with iodine, since it shows the complete disappearance of the strong S–S stretching band at 321 cm<sup>-1</sup> which corresponds to the disulfide moiety in the starting complex **1**. Reduction of **2** with Na in THF quantitatively



Scheme 1. Reversible scission and formation of the S–S bond in **1**, and synthesis of the ylide derivative **6**. [Mn] = Mn(CO)<sub>4</sub><sup>+</sup>. R = Ph.

regenerates the disulfide **1**. The sulfur–sulfur bond formation to give **1** is also accomplished by passing **2** through an alumina column and, partially, by heating a solid sample of **2** under vacuum at about 200 °C. In spite of their biochemical interest (e.g., as intermediates in the iodination of tyrosine), thermally stable sulfenyl iodides are scarce owing to their very favored disproportionation [Eq. (1)].<sup>[6]</sup> For this reason, they had never



been prepared by direct reaction of a disulfide with iodine. In our case, the noteworthy stability of **2** could be due to the anionic character of the diphosphanyl methanide ligand {(PPh<sub>2</sub>)<sub>2</sub>C–S–I}<sup>-</sup> in which the sulfenyl iodide functionality is included. In fact, when **2** was protonated at the methanide carbon atom (using HBF<sub>4</sub>), the opposite reaction was immediately observed (even at low temperature) yielding the dication **4** and I<sub>2</sub>, instead of the mononuclear species **3** (Scheme 1). This means that the sulfur–sulfur bond is once again easily regenerated by treatment with acids. Naturally, the cationic derivative **4** is transformed into **1** by simple reaction with KOH.

The sulfur–sulfur bond in **1** can also be broken by oxidation by using two equivalents of AgBF<sub>4</sub>. This led to **5**, which, on reduction with Na in THF, readily regenerated **1**. The cationic complex **5** can also be prepared through iodide abstraction from **2**, by using either TIPF<sub>6</sub> or an excess of I<sub>2</sub>, which abstract iodide as TII and I<sub>3</sub><sup>-</sup>, respectively. To the best of our knowledge, diphosphanylthioetones are unknown, although the related carbodiphosphorane thiolate and selenolate zwitterions PPh<sub>3</sub>C(X)PPh<sub>3</sub> (X = S, Se) have been described,<sup>[7]</sup> as has the coupling of two selenolate functions upon oxidation to afford the cation [(PPh<sub>3</sub>)<sub>2</sub>C–Se–Se–C(PPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>.<sup>[8]</sup> Notably,

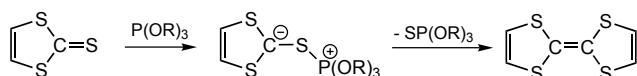
[\*] Dr. J. Ruiz, M. Ceroni, Prof. Dr. V. Riera  
Departamento de Química Orgánica e Inorgánica  
Facultad de Química, Universidad de Oviedo  
33071 Oviedo (Spain)  
Fax: (+34)98-510-3446  
E-mail: jruiz@sauron.quimica.uniovi.es

Dr. O. V. Quinzani  
Departamento de Química e Ingeniería Química  
Universidad Nacional del Sur  
8000 Bahía Blanca (Argentina)  
Dr. O. E. Piro  
Departamento de Física  
Facultad de Ciencias Exactas  
Universidad Nacional de La Plata and IFLP (CONICET)  
C.C. 67. 1900 La Plata (Argentina)

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the well-known processes of S–S bond formation from thiol functionalities, which stabilize the tertiary structure of many proteins, take place by oxidative coupling,<sup>[9]</sup> whereas in our case oxidation of **1** (either with I<sub>2</sub> or Ag<sup>+</sup>) results in the scission of the S–S bond.

The thione in **5** undergoes thiophilic addition by treatment with phosphanes, such as PCy<sub>3</sub>, to afford **6**, a complex in which the diphosphane ligand contains a unique thioxophosphorane ylide functionality (Scheme 1). The same behavior is shown by complex **2**, which readily reacts with PCy<sub>3</sub> by nucleophilic substitution of I<sup>−</sup> to give **6**. Similar types of 1,3-dipolar molecules are assumed to be reaction intermediates in the well-known desulfurization and coupling reactions of 1,3-dithiole-2-thiones by trialkylphosphites, which led to tetra-thiafulvalene derivatives (constituents of organic conductors, Scheme 2),<sup>[10]</sup> as well as in the formation of phosphorus ylides



Scheme 2. Schematic representation of the desulfurization of 1,3-dithiole-2-thiones by thiophilic addition of phosphites to give tetra-thiafulvalene derivatives.

from thiones.<sup>[11]</sup> However, this is the first time that such a derivative has been isolated and fully structurally characterized. The structure of **6**·BF<sub>4</sub>, which has been elucidated by X-ray crystallography (Figure 1),<sup>[12]</sup> clearly shows the presence of the modified diphosphane ligand [((PPh<sub>2</sub>)<sub>2</sub>CSPCy<sub>3</sub>)<sub>2</sub>η<sup>2</sup>(P, P')] coordinated to the Mn(CO)<sub>4</sub> moiety. The P1–P2–C5–S skeleton departs appreciably from the expected planar conformation (the sulfur atom is at 0.644(2) Å from the P1–P2–C5 plane), probably due to the

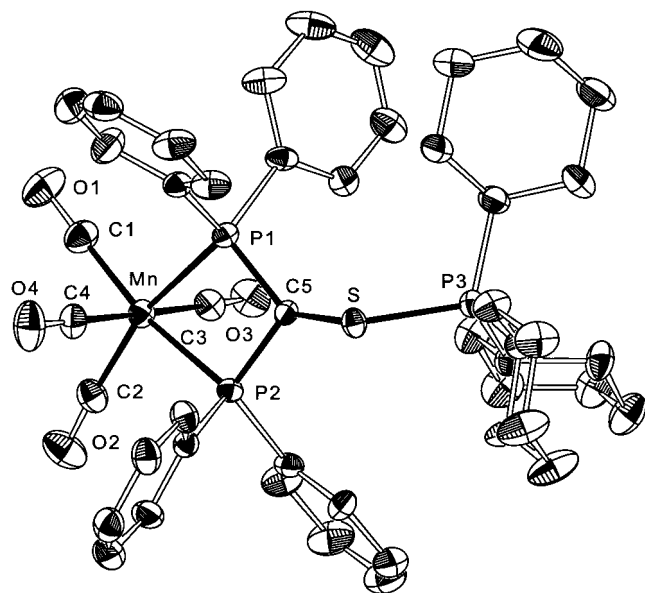


Figure 1. Structure of the cationic complex **6** in the crystal (30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Mn–P1 2.342(2), Mn–P2 2.318(2), P1–C5 1.756(7), P2–C5 1.744(7), C5–S 1.760(7), S–P3 2.107(3); P1–Mn–P2 70.39(7), Mn–P1–C5 93.4(2), Mn–P2–C5 94.5(2), P1–C5–P2 100.3(3), P1–C5–S 131.2(4), P2–C5–S 121.9(4), C5–S–P3 116.0(2).

steric hindrance of the cyclohexyl groups. The three bond lengths around the ylide carbon atom are slightly shorter than expected for single bonds (P1–C5 1.756(7), P2–C5 1.744(7), C5–S 1.760(7) Å). The P1–P2–C5 and C5–S–P3 planes are almost mutually perpendicular (dihedral angle 79.0(3)°), which minimizes the steric repulsions between the cyclohexyl and phenyl rings. In the S–PCy<sub>3</sub> moiety the phosphorus atom has a distorted tetrahedral coordination geometry, and the P–S distance (2.107(3) Å) is typical of a single bond.

The gentle warming of **6** in THF readily liberates SPCy<sub>3</sub>, thus completing the sulfur extrusion process from **5**. However, the transient diphosphanycarbene complex [Mn(CO)<sub>4</sub>–{(PPh<sub>2</sub>)<sub>2</sub>C:}]<sup>+</sup> which should remain in the reaction mixture was not detected; instead a complex mixture of manganese(I) derivatives is found that still requires characterization.

In summary, the approach presented allows the reversible scission and formation of the S–S bond in the dinuclear complex **1**, which, in parallel, enables the generation of unusual functionalities at the central carbon atom of the diphosphane moiety. Preliminary results show that **2** and **5** undergo nucleophilic attack on the sulfur atom not only with tertiary phosphanes, but also with a wide variety of nucleophilic reagents such as KCN, MgRCl, and NaSR. Thus these complexes show great promise for synthetic applications.

#### Experimental Section

**2**: I<sub>2</sub> (0.022 g, 0.087 mmol) was added to a solution of **1** (0.1 g, 0.086 mmol) in CH<sub>2</sub>Cl<sub>2</sub>. After the mixture had been stirred for 5 min at room temperature, the solvent was evaporated to dryness, and the brown residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to afford a red solid; yield 91% (0.11 g). Elemental analysis (%) calcd for C<sub>29</sub>H<sub>20</sub>IMnO<sub>4</sub>P<sub>2</sub>S: C 49.18, H 2.85; found: C 48.87, H 2.82; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}$  = 2081 (s), 2011 (sh), 2001 (vs), 1982 (m) cm<sup>−1</sup> (CO); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 36.5 (br); FAB-MS (positive-ion): *m/z*: 708 [*M*<sup>+</sup>], 652 [*M*<sup>+</sup> – 2 CO].

**4**: IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}$  = 2094 (s), 2036 (m), 2011 (vs) cm<sup>−1</sup> (CO); Raman (KBr):  $\tilde{\nu}$  = 451 (s) cm<sup>−1</sup> (S–S); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 34.0 (br); <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 6.98 (t, <sup>2</sup>J<sub>PH</sub> = 7 Hz, 2H; P<sub>2</sub>CH).

**5**·BF<sub>4</sub>: AgBF<sub>4</sub> (0.35 g, 0.18 mmol) was added to a solution of **1** (0.1 g, 0.086 mmol) in CH<sub>2</sub>Cl<sub>2</sub>. The resulting suspension, protected from light, was stirred for 1 h. Then the solution was filtered off and evaporated to dryness. The residue was recrystallized twice in CH<sub>2</sub>Cl<sub>2</sub>/hexane at −20 °C to afford white crystals; yield 40% (0.054 g). Elemental analysis (%) calcd for C<sub>29</sub>H<sub>20</sub>BF<sub>4</sub>MnO<sub>4</sub>P<sub>2</sub>S: C 52.13, H 3.02; found: C 52.03, H 2.96; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}$  = 2093 (s), 2033 (m), 2011 (vs) cm<sup>−1</sup> (CO); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 44.0 (br); FAB-MS (positive-ion): *m/z*: 581 [*M*<sup>+</sup> – BF<sub>4</sub>].

**6**·BF<sub>4</sub>: PCy<sub>3</sub> (0.025 g, 0.09 mmol) was added to a solution of **5**·BF<sub>4</sub> (0.06 g, 0.09 mmol) in CH<sub>2</sub>Cl<sub>2</sub>. After the mixture had been stirred for 20 min at room temperature, the solvent was evaporated to dryness. The residue was washed with Et<sub>2</sub>O (20 mL) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to obtain white crystals; yield 70% (0.06 g). Elemental analysis (%) calcd for C<sub>47</sub>H<sub>55</sub>BF<sub>4</sub>MnO<sub>4</sub>P<sub>3</sub>S: C 59.51, H 5.63; found: C 59.10, H 5.88; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}$  = 2079 (s), 2014 (s), 1988 (vs) cm<sup>−1</sup> (CO); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 32.4 (br), 53.5 (t, <sup>3</sup>J<sub>PP</sub> = 7 Hz).

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- [12] Crystal data for **6**·BF<sub>4</sub> (C<sub>47</sub>H<sub>53</sub>BF<sub>4</sub>MnO<sub>4</sub>P<sub>3</sub>S): *M*<sub>r</sub> = 948.61, triclinic, space group *P*1, *a* = 11.771(2), *b* = 13.909(2), *c* = 16.416(4) Å, *α* = 67.69(1), *β* = 82.86(2), *γ* = 81.43(1)°, *V* = 2452.8(8) Å<sup>3</sup>, *Z* = 2, *ρ*<sub>calcd</sub> = 1.285 g cm<sup>-3</sup>, *F*(000) = 988, MoK<sub>α</sub> radiation (*λ* = 0.71073 Å), *μ*(MoK<sub>α</sub>) = 0.191 mm<sup>-1</sup>; crystal dimensions 0.10 × 0.28 × 0.40. Diffraction data were collected on an Enraf-Nonius diffractometer at 293 K. The structure was solved by direct methods and refined using full-matrix least-squares on *F*<sup>2</sup> with all non-hydrogen atoms anisotropically defined. The hydrogen atoms were placed in calculated positions, isotropically refined with common thermal parameters and allowed to ride on their parent carbon atoms. For 4866 observed reflections with *I* > 2σ(*I*) and 551 parameters, the conventional *R* is 0.081 and *wR*2 = 0.252. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145733. 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).

## Efficient Catalytic Alkane Nitration with NO<sub>2</sub> under Air Assisted by *N*-Hydroxyphthalimide\*\*

Satoshi Sakaguchi, Yoshiki Nishiwaki, Takaaki Kitamura, and Yasutaka Ishii\*

In contrast to the nitration of aromatic hydrocarbons, which is easily performed using nitric acid in the presence of sulfuric acid, the selective nitration of aliphatic hydrocarbons is very difficult because of the exceedingly low reactivity of the latter. Currently, nitrations of aliphatic hydrocarbons are carried out at fairly high temperatures (250–400 °C) using nitrogen dioxide or nitric acid, and they proceed by free radical chain

[\*] Prof. Y. Ishii, S. Sakaguchi, Y. Nishiwaki, T. Kitamura  
Department of Applied Chemistry  
Faculty of Engineering and High Technology Research Center  
Kansai University, Suita, Osaka 564-8680 (Japan)  
Fax: (+81)6-6339-4026  
E-mail: ishii@ipcku.kansai-u.ac.jp

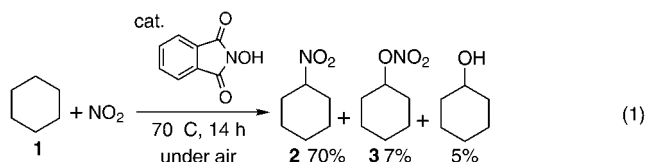
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reactions involving C–H bond homolysis.<sup>[1, 2]</sup> Under such high temperatures, higher alkanes undergo not only homolysis of C–H bonds but also cleavage of the C–C skeleton. Therefore, large-scale nitration of alkanes has been limited to lower alkanes such as methane and ethane.<sup>[2]</sup> For instance, the nitration of propane produces all of the possible nitroparaffins, namely, nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane.<sup>[1, 3]</sup> The development of selective nitration of cyclohexane is very attractive, since nitrocyclohexane is easily converted into cyclohexanone oxime, the raw material of *ε*-caprolactam, which in turn leads to nylon-6.<sup>[4–6]</sup>

Recently we developed a catalytic method for the generation of alkyl radicals from saturated hydrocarbons using *N*-hydroxyphthalimide (NHPI), which serves as the radical catalyst.<sup>[7]</sup> The phthalimide *N*-oxyl (PINO) radical generated in situ from NHPI and O<sub>2</sub>, which lies in a triplet state, abstracts the hydrogen atom from the saturated hydrocarbons, forming the corresponding alkyl radicals. These radicals are readily trapped by O<sub>2</sub> under aerobic conditions to give oxygen-containing compounds such as alcohols, ketones, and carboxylic acids. These results led us to become interested in the nitration of alkanes with NO<sub>2</sub> by the use of NHPI as a catalyst.

In the first trial, NHPI was added at room temperature to a stirred benzene solution containing dissolved NO<sub>2</sub>. The ESR measurement of the solution indicated a triplet signal, which is assigned to the PINO radical.<sup>[8]</sup> This is believed to be due to the fact that NO<sub>2</sub> is a stronger oxidant than O<sub>2</sub>. Thus, the nitration of cyclohexane (**1**) was examined using NO<sub>2</sub> in the presence of a catalytic amount of NHPI under several reaction conditions ([Eq. (1)], Table 1).



The nitration of **1** with NO<sub>2</sub> by NHPI proceeded smoothly at 70 °C to give nitrocyclohexane (**2**, 70% based on NO<sub>2</sub> used; Table 1, run 1) and cyclohexyl nitrite (**3**, 7%) along with a small amount of an oxygenated product, cyclohexanol (5%).

Table 1. NHPI-catalyzed nitration of **1** with NO<sub>2</sub> under selected conditions.<sup>[a]</sup>

Run	NHPI [mmol]	<i>T</i> [°C]	Yield of <b>2</b> [%] <sup>[b]</sup>
1	0.6	70	70
2 <sup>[c]</sup>	0.6	70	43
3	–	70	< 2
4	0.6	60	58
5	0.6	50	39
6	0.3	70	56
7 <sup>[d]</sup>	0.6	70	63
8 <sup>[e]</sup>	9	70	53

[a] Reactions were run as described in the Experimental Section. [b] Yields are average values obtained from several runs and are based on NO<sub>2</sub> used. [c] Under argon. [d] Recovered catalyst from run 1 was used. [e] The reaction was carried out using **1** (50 mL) and NO<sub>2</sub> (33 mmol). The yield of **2** is based on isolated product.