Reversible S–S Bond Breaking and Bond Formation in Disulfide-Containing Dinuclear Complexes of Mn**

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

Disulfide-containing compounds are of considerable biological and technological relevance, 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. We have recently reported that nucleophilic degradation of cyclooctasulfur by the diphosphanyl methane complex of manganese(0) [(CO)ₓMn{(PPh₂)₂C–S–S–C(PPh₂)}₂Mn(CO)ᵧ] allows the formation of the hexasulfur-bridged bis(diphosphanyl methane) dinuclear derivative [(CO)ₓMn{(PPh₂)₂C–S–S–C(PPh₂)}₂Mn(CO)ᵧ]²⁻. In this complex the polysulfur chain can be progressively shortened by treatment with PPh₃ leading finally to the disulfide complex 1, which does not undergo further sulfur extrusion processes. 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 diphosphanylthioketone, sulfenyl iodide, and thioxophosphorane ylide, as parts of the corresponding carbonyl complex of manganese(0). [(CO)ₓMn{(PPh₂)₂C–S–S–C(PPh₂)}₂Mn(CO)ᵧ] ¹

The treatment of 1 with one equivalent of I₂ 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)ₓ{(PPh₂)₂C–S–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⁻¹ which corresponds to the disulfide moiety in the starting complex 1. Reduction of 2 with Na in THF quantitatively 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)]. 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 methane ligand [(PPh₂)₂C–S–S–I]⁻ in which the sulfenyl iodide functionality is included. In fact, when 2 was protonated at the methanide carbon atom (using HBF₄), the opposite reaction was immediately observed (even at low temperature) yielding the dication 4 and I₂, 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 AgBF₄. 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 TIP₃F or an excess of I₂, which abstract iodide as TII and I⁻, respectively. To the best of our knowledge, diphosphanylthioketones are unknown, although the related carbodiphosphorane thiolate and selenolate zwitterions PPh₂(C(X)P)₂ (X = S, Se) have been described, as has the coupling of two selenolate functions upon oxidation to afford the cation [(PPh₂)₂C–Se–Se–C(PPh₂)]²⁺. Notably,

![Scheme 1. Reversible scission and formation of the S–S bond in 1, and synthesis of the ylide derivative 6. [Mn] = Mn(CO)ₓ; R = Ph.](image)
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,[9] whereas in our case oxidation of 1 (either with I$_2$ or Ag$^+$) results in the scission of the S–S bond.

The thione in 5 undergoes thioφilic addition by treatment with phosphines, such as PCy$_3$, to afford 6, a complex in which the diphosphane ligand contains a unique thiosphosphorane ylide functionality (Scheme 1). The same behavior is shown by complex 2, which readily reacts with PCy$_3$ by nucleophilic substitution of I$^-$ to give 6. Similar types of 1,3-dipolar reactions of thiones by trialkylphosphites, which led to tetraethafulvalene derivatives (constituents of organic conductors, Scheme 2),[10] as well as in the formation of phosphorus ylides from thiones.[11] However, this is the first time that such a derivative has been isolated and fully structurally characterized. 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 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$_3$ 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$_3$, thus completing the sulfur extrusion process from 5. However, the transient diphosphanylcarbene complex [Mn(CO)$_4$-([PPh$_2$)$_2$C]++]$^+$ which should remain in the reaction mixture was not detected; instead a complex mixture of mangan(0) 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 diphosphine moiety. Preliminary results show that 2 and 5 undergo nucleophilic attack on the sulfur atom not only with tertiary phosphines, 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·(0.022 g, 0.0877 mmol) was added to a solution of 1 (0.1 g, 0.086 mmol) in CH$_2$Cl$_2$. 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$_2$Cl$_2$/hexane to afford a red solid; yield 91% (0.11 g). Elemental analysis (%) calcd for C$_{29}$H$_{20}$IMnO$_4$P$_2$S: C 48.87, H 2.82; found: C 48.87, H 2.82; IR (CH$_2$Cl$_2$): ð = 4400 (s) cm$^{-1}$ (CO); $^3$P[H] NMR (121.5 MHz, CD$_2$Cl$_2$): $\delta$ = 4.00 (br); FAB-MS (positive-ion): m/z: 708 [M$^+$], 652 [M$^-$ – CO].

4: IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2094 (s), 2036 (m), 2011 (vs) cm$^{-1}$ (CO); Raman (KBr): $\tilde{\nu}$ = 451 (s) cm$^{-1}$ (S–S); $^3$P[H] NMR (121.3 MHz, CD$_2$Cl$_2$): $\delta$ = 34.0 (br); $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 6.98 (t, J$_{P,P}$ = 7 Hz). $^3$P{$_1^H$} NMR (121.5 MHz, CD$_2$Cl$_2$): $\delta$ = 44.0 (br); FAB-MS (positive-ion): m/z: 381 [M$^+$ – BF$_2$].

5: BF$_2$: AgBF$_4$ (0.35 g, 0.18 mmol) was added to a solution of 1 (0.1 g, 0.086 mmol) in CH$_2$Cl$_2$. 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$_2$Cl$_2$/hexane at –20°C to afford white crystals; yield 40% (0.054 g). Elemental analysis (%) calcd for C$_{29}$H$_{20}$BF$_4$MnO$_4$P$_2$S: C 52.13, H 3.02; found: C 52.03, H 2.96; IR (CH$_2$Cl$_2$): ð = 451 (s) cm$^{-1}$ (CO); $^3$P[H] NMR (121.5 MHz, CD$_2$Cl$_2$): $\delta$ = 44.0 (br); FAB-MS (positive-ion): m/z: 381 [M$^+$ – BF$_2$].

6: BF$_2$: PCy$_3$ (0.025 g, 0.09 mmol) was added to a solution of 5·BF$_2$ (0.06 g, 0.09 mmol) in CH$_2$Cl$_2$. After the mixture had been stirred for 20 min at room temperature, the solvent was evaporated to dryness. The residue was washed with Et$_2$O (20 mL) and recrystallized from CH$_2$Cl$_2$/Et$_2$O to obtain white crystals; yield 70% (0.06 g). Elemental analysis (%) calcd for C$_{29}$H$_{20}$BF$_4$MnO$_4$P$_2$S: C 50.51, H 5.63; found: C 50.9, H 5.88; IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2079 (s), 2014 (s), 1988 (vs) cm$^{-1}$ (CO); $^3$P[H] NMR (121.5 MHz, CD$_2$Cl$_2$): $\delta$ = 32.4 (br); 53.5 (t, J$_{P,P}$ = 7 Hz).

Received: July 31, 2000 [Z15557]
Efficient Catalytic Alkane Nitrination with NO₂ under Air Assisted by N-Hydroxyphthalimide**

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

In contrast to the nitrination of aromatic hydrocarbons, which is easily performed using nitric acid in the presence of sulfuric acid, the selective nitrination 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 reactions involving C–H bond homolysis.[1, 2] 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 nitrination of alkanes has been limited to lower alkanes such as methane and ethane.[3] For instance, the nitrination of propane produces all of the possible nitroparaffins, namely, nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane.[1, 3] The development of selective nitrination 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.[4, 5]

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.[5] The phthalimide N-oxyl (PINO) radical generated in situ from NHPI and O₂, 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 O₂ under aerobic conditions to give oxygen-containing compounds such as alcohols, ketones, and carboxylic acids. These results led us to become interested in the nitrination of alkanes with NO₂ 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 NO₂. The ESR measurement of the solution indicated a triplet signal, which is assigned to the PINO radical.[6] This is believed to be due to the fact that NO₂ is a stronger oxidant than O₂. Thus, the nitrination of cyclohexane (1) was examined using NO₂ in the presence of a catalytic amount of NHPI under several reaction conditions ([Eq. (1)], Table 1).

![Diagram](attachment:image.png)

The nitrination of 1 with NO₂ by NHPI proceeded smoothly at 70 °C to give nitrocyclohexane (2, 70% based on NO₂ 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 nitrination of 1 with NO₂ under selected conditions[a]

| Run | NHPI [mmol] | T [°C] | Yield of 2 [%][b] |
|-----|-------------|--------|-----------------|
| 1   | 0.6         | 70     | 70              |
| 2[c] | 0.6         | 70     | 43              |
| 3   | 0.6         | <2     |                 |
| 4   | 0.6         | 60     | 58              |
| 5   | 0.6         | 50     | 39              |
| 6   | 0.3         | 70     | 56              |
| 7[d] | 0.6        | 70     | 63              |
| 8[e] | 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 NO₂ used. [c] Under argon. [d] Recovered catalyst from run 1 was used. [e] The reaction was carried out using 1 (50 mL) and NO₂ (33 mmol). The yield of 2 is based on isolated product.

---

[1] This work was supported by the Research for the Future program, JSPS.

[5] Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.