Thiocyanogen Insertion

Insertion of Thiocyanogen into a P–C Bond and Subsequent Formation of Polysulfide Derivatives[**]

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Classical reactivity of thiocyanogen ($(SCN)_2$) involves the breaking of the sulfur–sulfur bond to give thiocyanate derivatives, and this pseudohalogen behavior has been widely applied in organic synthesis,[1] and in the field of coordination chemistry as well.[2] In contrast, to our knowledge the only example of a thiocyanogen reaction occurring

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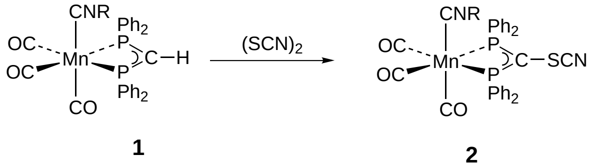
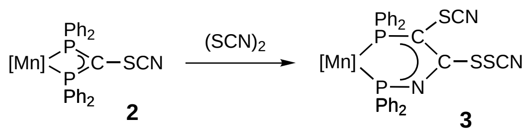
without cleavage of the S–S bond that has been described in the literature is the cycloaddition of $(SCN)_2$ with hexafluoroacetone, which leads to the formation of a 4H-dioxazine derivative.[3] Herein we describe a rare example of insertion of thiocyanogen into a P–C bond of a diphosphanylmethanide ligand, which initially proceeded without breaking the S–S bond leading later to the formation of a unique class of dimetallic polysulfides.

We have recently reported that the addition of $(SCN)_2$ to the diphosphanylmethanide complex *fac*-[Mn(CN*t*Bu)$(CO)_3\{(PPh_2)_2CH\}$] (**1**) allows the isolation of *fac*-[Mn(CN*t*Bu)$(CO)_3\{(PPh_2)_2CSCN\}$] (**2**) (Scheme 1). This reaction can be rationalized assuming a heterolytic cleavage of the S–S bond in the thiocyanogen molecule by the methanide carbon atom.[4] We have now found that a further treatment of **2** with $(SCN)_2$ leads to the insertion of this molecule into a P–C bond of the diphosphanylmethanide ligand yielding *fac*-[Mn(CN*t*Bu)$(CO)_3\{(PPh_2)C(SCN)C(SSCN)N(PPh_2)\}$] (**3**) (Scheme 2), which was isolated as a white solid. Noteworthy, the reaction takes place instantaneously at room temperature, although the insertion implies the breaking of a rather strong P–C bond.[5] Insertion reactions of molecules into P–C bonds are very rarely encountered in the literature; examples are the insertion of nitriles either into the P–C bond of a phosphinidene complex,[6] or into a P–C bond of strained three-membered rings of 2H-azaphosphirene complexes,[7] and the insertion of electron-poor alkynes into a P–C bond of a coordinated phosphane ligand.[8]

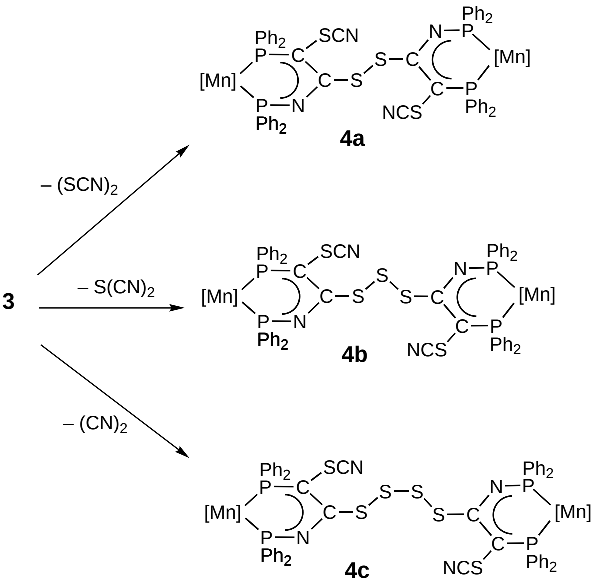


Scheme 1. Reaction of complex **1** with thiocyanogen to afford **2**. R = *t*Bu.



Scheme 2. Insertion reaction of thiocyanogen into a P–C bond of **2** to yield **3**. [Mn] = [Mn(CN*t*Bu)$(CO)_3$].

Compound **3** was characterized spectroscopically, by elemental analysis, and by FAB mass spectrometry (see Experimental Section). Compound **3** slowly decomposes when left to stand in solution, thus precluding the preparation of single crystals for X-ray analysis. However, the elution of **3** through an alumina column in CH_2Cl_2/Hexane leads to the formation of the dimetallic complexes **4a, 4b**, and **4c**, in an approximate ratio of 6:4:1, respectively (Scheme 3). Compounds **4a–c** are unique polysulfide derivatives that contain a bridging chain of two to four sulfur atoms, and are formally made from the coupling of two molecules of **3** with elimination of the pseudohalogen molecules $(SCN)_2$, $S(CN)_2$, and $(CN)_2$, respectively. This result can be compared with the S–S coupling process which allows the formation of the dimetallic disulfide [$(CO)_4Mn\{(PPh_2)_2C\text{-}S\text{-}S\text{-}C(PPh_2)_2\}Mn(CO)_4$] on passing the complex [$Mn(CO)_4\{(PPh_2)_2C\text{-}S\text{-}I\}$] through an alumina column, with elimination of I_2.[9] Since the formation of **4a, 4b**, and **4c** from **3** requires the scission of two S–S bonds, one S–S bond and one S–C bond, and two S–C bonds, respectively, the relative amount of each compound in the reaction mixture could be explained by considering the weakness of the S–S bond versus the S–C bond in the inserted thiocyanogen molecule. Complexes **4a–c** are all colorless and have very similar spectroscopic features and solubility, and therefore are difficult to characterize and separate. Thus, the IR spectra in the region where the CO and CN stretches are found are practically identical for the three species, and from the $^{31}P\{^1H\}$ NMR spectra the complexes can only be distinguished by slight differences in the chemical shift of one of the two nonequivalent phosphorus atoms (see Experimental Section). Nevertheless, the major species, **4a** and **4b**, could be separated by chromatography and were fully characterized, including the elucidation of their solid-state structures by X-ray crystallography.[10] The minor product **4c** could not be totally purified as it always contains some amount of **4b**, so its characterization is based mainly on the FAB mass spectrum.



Scheme 3. Formation of the polysulfide dimetallic derivatives **4a, 4b** and **4c** from complex **3**. [Mn] = [Mn(CN*t*Bu)$(CO)_3$].

The structure of **4a** (Figure 1) formally contains a thiocyanogen molecule inserted into two P–C (methanide) bonds of two diphosphanylmethanide complexes **2**, although, as stated above, its formation implies a process of S–S bonds breaking and forming. The structural features of the two related halves of the molecule are very similar. The octahedral coordination around each Mn atom involves three carbonyl groups, an isocyanide ligand and two chelating P atoms from the modified diphosphanylmethanide ligand.

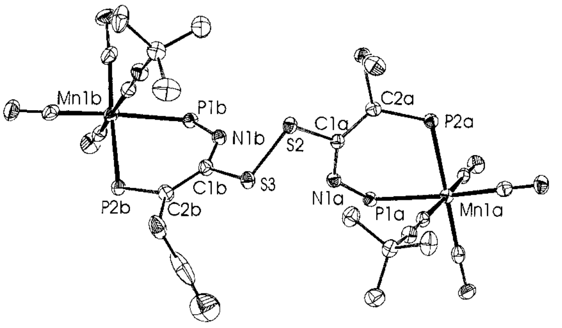


Figure 1. Molecular structure of **4a**. Hydrogen atoms and phenyl groups are omitted for clarity (ellipsoids set at the 30% probability level). Selected bond lengths [Å] and angles [°]: N1a-P1a 1.648(3), N1a-C1a 1.298(5), C1a-C2a 1.411(5), P2a-C2a 1.782(4), C1a-S2 1.824(4), P1b-N1b 1.645(3), N1b-C1b 1.301(5), C1b-C2b 1.398(5), P2b-C2b 1.785(4), C1b-S3 1.833(4), S2-S3 2.023(14), P1a-Mn1a-P2a 85.98(4), C1a-N1a-P1a 125.1(3), N1a-C1a-C2a 130.8(4), N1a-C1a-S2 116.7(3), C2a-C1a-S2 112.5(3), C1a-C2a-P2a 124.7(3), C1a-S2-S3 105.28(13), C1b-S3-S2 103.94(14), P1b-Mn1b-P2b 83.70(4), C1b-N1b-P1b, 126.4(3), N1b-C1b-C2b 131.8(4), N1b-C1b-S3 114.9(3), C2b-C1b-S3 113.3(2). Torsion angles [°]: N1a-C1a-S2-S3 5.9(3), C1a-S2-S3-C1b −93.70(18), S2-S3-C1b-N1b 19.9(3).

The bond lengths within the skeleton P1-N1-C1-C2-P2 of the expanded chelating ligand are shorter than single bonds, especially P1−N1 (1.646(3) Å on average) and N1−C1 (1.299(5) Å on average), as a result of the delocalization of the formal negative charge throughout the skeleton. The S2−S3 bond length (2.023(14) Å) is slightly shorter than that found in the cyclo-octasulfur molecule (2.06 Å), whereas the C1−S bond lengths (1.828(4) Å on average) are typical for a single bond. The structure of the trisulfide derivative **4b** (Figure 2) is closely related to **4a** with a more sulfur atom, the different bond distances and angles being very similar to those found for **4a**.

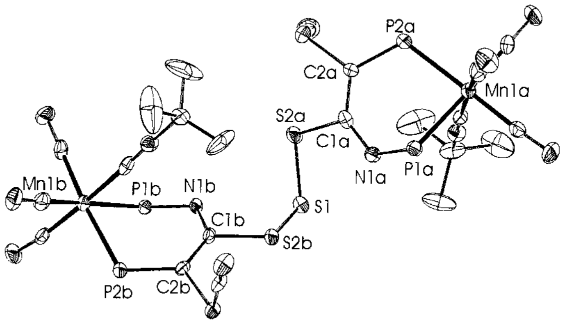


Figure 2. Molecular structure of **4b**. Hydrogen atoms and phenyl groups are omitted for clarity (ellipsoids set at the 20% probability level). Selected bond lengths [Å] and angles [°]: N1a-P1a 1.623(8), N1a-C1a 1.324(11), C1a-C2a 1.434(13), P2a-C2a 1.763(10), C1a-S2a 1.817(10), S2a-S1 2.020(4), S1-S2b 2.025(4), P1b-N1b 1.629(7), N1b-C1b 1.300(11), C1b-C2b 1.427(13), P2b-C2b 1.791(10), C1b-S2b 1.829(9), P1a-Mn1a-P2a 86.92(11), C1a-N1a-P1a 123.4(7), N1a-C1a-C2a 129.8(9), N1a-C1a-S2a 116.8(8), C2a-C1a-S2a 113.4(8), C1a-S2a-S1 103.2(4), C1a-C2a-P2a 125.1(7), S2a-S1-S2b 108.72(18), P1b-Mn1b-P2b 83.15(11), C1b-N1b-P1b, 123.6(7), N1b-C1b-C2b 130.4(8), N1b-C1b-S2b 117.0(7), C2b-C1b-S2b 112.6(7), C1b-C2b-P2b 123.5(3), C1b-S2b-S1 102.2(4). Torsion angles [°]: N1b-C1b-S2b-S1 −18.6(8), C1b-S2b-S1-S2a 80.6(4), S2b-S1-S2a-C1a 86.1(4), S1-S2a-C1a-N1a −3.7(9).

The length of the sulfur chains in compounds **4a–c** is essentially maintained when they are dissolved in organic solvents and left to stand for several days. When a mixture of **4b–c** is heated to reflux in toluene, some quantity of **4a** is formed, but mainly the starting materials decompose.

Preliminary results show that protonation of **3** with HBF_4 at the imino-nitrogen atom also produces the instantaneous scission of the inserted thiocyanogen molecule, thus giving a mixture of cationic dimetallic intermediates, which were converted to the same mixture of neutral compounds **4a–c** as above by deprotonation with KOH. It can be deduced that the interaction of **3** with alumina produces the same effect as that of a combined acid-base treatment with this complex.

In summary, we have found that thiocyanogen can be inserted into a P−C bond of a coordinated diphosphanylmethanide ligand under mild conditions, without breaking of the S−S bond, thus affording a new highly functionalized and very reactive diphosphanylmethanide ligand. The activation of S−S or S−C bonds in this ligand, with parallel S−S coupling processes, produces a number of unprecedented polysulfide derivatives that contain pendant carbonyl complexes of manganese(I). Experiments with the aim of inserting other unsaturated molecules into the P−C bonds of **3** are currently in progress.

Experimental Section

3: A solution containing $(SCN)_2$ (0.027 g, 0.230 mmol) was added dropwise to a solution of **2** (0.15 g, 0.226 mmol) with continuous stirring over five minutes at room temperature. The solution was then concentrated to 2 mL under vacuum. The addition of hexane (10 mL) produced the precipitation of a white solid; yield 85% (0.15 g). Elemental analysis (%) calcd for $C_{36}H_{29}MnN_4O_3P_2S_3$: C 55.53, H 3.75, N 7.19; found: C 54.58, H 3.97, N 6.92; IR (CH_2Cl_2): $\tilde{\nu}$ = 2172 (m) (CN*t*Bu), 2147 w (SCN), 2030 vs, 1967 cm^{-1} s (CO); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.96–7.04 (20H, Ph), 1.50 ppm (s, 9H, *t*Bu); ^{31}P{^{1}H} NMR (121.5 MHz, CH_2Cl_2/D_2O): δ = 70.8 (s, br), 47.1 ppm (s, br); FAB-MS (positive ion): *m*/*z*: 779 [M^+], 753 [M^+−CN], 721 [M^+−SCN], 689 [M^+−SSCN].

4a–c: Compound **3** (0.1 g, 0.128 mmol) was passed through an alumina column (activity degree III). Elution with CH_2Cl_2/hexane (1:1) afforded **4b** along with small amounts of **4c**, further elution with CH_2Cl_2/hexane (3:2) afforded **4a**. Both fractions were recrystallized in CH_2Cl_2/hexane to obtain **4a** and **4b** as colorless crystals. A second recrystallization of the first fraction provided **4c** as the major product in the mother liquor. **4a**: yield 30% (0.028 g). Elemental analysis (%) calcd for $C_{70}H_{58}Mn_2N_6O_6P_4S_4$: C 58.33, H 4.06, N 5.83; found: C 58.61, H 4.17, N 6.01; IR (CH_2Cl_2): $\tilde{\nu}$ = 2173 m (CN*t*Bu), 2142 w (SCN), 2025 vs, 1961 cm^{-1} s (CO); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.70–5.70 (40H, Ph), 1.60 ppm (s, 18H, *t*Bu); ^{31}P{^{1}H} NMR (121.5 MHz, CH_2Cl_2/D_2O): δ = 61.1 (s, br), 47.2 ppm (s, br); FAB-MS (positive ion): *m*/*z*: 1441 [M^+]. **4b**: yield 20% (0.019 g). Elemental analysis (%) calcd for $C_{70}H_{58}Mn_2N_6O_6P_4S_5$: C 57.06, H 3.97, N 5.70; found: C 56.85, H 4.05, N 5.98; IR (CH_2Cl_2): $\tilde{\nu}$ = 2174 (m) (CN*t*Bu), 2142 w (SCN), 2026 vs, 1963 cm^{-1} s (CO); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.19–6.97 (40H, Ph), 1.57 ppm (s, 18H, *t*Bu); ^{31}P{^{1}H} NMR (121.5 MHz, CH_2Cl_2/D_2O): δ = 64.6 (s, br), 47.4 ppm (s, br); FAB-MS (positive ion): *m*/*z*: 1473 [M^+].**4c**: IR (CH_2Cl_2): $\tilde{\nu}$ = 2174 m (CN*t*Bu), 2142 w (SCN), 2026 vs, 1963 cm^{-1} s (CO); ^{31}P{^{1}H} NMR (121.5 MHz, CH_2Cl_2/D_2O): δ = 67.6 (s, br), 47.5 ppm (s, br); FAB-MS (positive-ion): *m*/*z*: 1505 [M^+].

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[10] Diffraction data were collected on an Enraf–Nonius diffractometer at 293 K. The structures were solved by direct methods and refined by using full-matrix least squares on F^2 with all non-hydrogen atoms anisotropically defined. Crystal data for **4a** ($C_{70}H_{58}Mn_2N_6O_6P_4S_4$): $M_r = 1441.27$, triclinic, space group $P\bar{1}$, $a = 11.1915(7)$, $b = 17.3864(7)$, $c = 18.9243(9)$ Å, $\alpha = 104.540(3)$, $\beta = 94.546(5)$, $\gamma = 90.072(5)°$, $V = 3552.3(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.347$ g cm^{-1-3}, $F(000) = 1484$, $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). For 13309 independent reflections and 947 parameters, final R indices [$I > 2\sigma I$]: $R1 = 0.0510$ and $wR_2 = 0.1315$. Crystal data for **4b** ($C_{70}H_{58}Mn_2N_6O_6P_4S_5$): $M_r = 1473.28$, triclinic, space group $P\bar{1}$, $a = 11.2755(4)$, $b = 16.4423(6)$, $c = 21.9661(11)$ Å, $\alpha = 72.807(2)$, $\beta = 77.227(2)$, $\gamma = 72.190(3)°$, $V = 3665.6(3$ Å^3, $Z = 2$, $\rho_{calcd} = 1.335$ g cm^{-1-3}, $F(000) = 1516$, $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). For 10418 independent reflections and 838 parameters, final R indices [$I > 2\sigma I$]: $R1 = 0.0663$ and $wR_2 = 0.1609$. CCDC-197197 and CCDC-197198 (**4a** and **4b**, respectively) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).