Cleavage of C=S Multiple Bonds by Unsaturated Cobalt Centres: Crystal Structure of $[(C_5H_5)\overline{Co\{C(NPh)NPhC(S)S}\}(CNPh)]$

Ian R. Beaumont, Michael J. Begley, Simon Harrison and Anthony H. Wright*

Chemistry Department, University of Nottingham, Nottingham NG7 2RD, UK

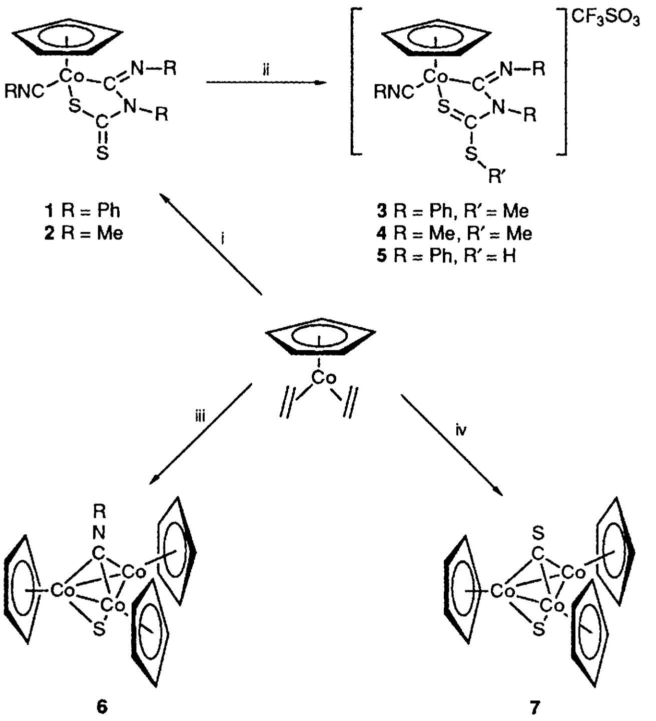
Multiple C=S bond cleavage takes place at ambient temperatures when isothiocyanates react with $[(C_5H_5)Co(C_2H_4)_2]$ giving five-membered metallacyclic complexes such as the structurally characterised complex $[(C_5H_5)Co\{C(NPh)NPhC(S)S\}(CNPh)]$.

The ability of transition metals to interact with multiple bonds is one of the cornerstones of modern inorganic chemistry. Some of these interactions lead to cleavage of the bond, providing access to dramatic molecular reorganisations. The scission of carbon–carbon multiple bonds has been widely studied and exploited,[1] but the cleavage of multiple bonds involving heteroatoms has been much less explored.

While examining new synthetic routes to electron-rich metal clusters,[2] we have discovered novel C=S bond cleavage reactions. The key feature of the reactions appears to be the substrate $[CpCo(C_2H_4)_2]^3$ (Cp = C_5H_5) that can be used to generate the CpCo fragment under very mild conditions. Small changes in the proportions of substrates lead to different products; mononuclear complexes or trimetallic clusters. In both cases C=S bond cleavage is involved, but in the former case multiple C=S cleavage is effected. A subsequent report of the use of $[CpCo(PPh_3)_2]$ in a very similar reaction gives a different set of mononuclear products, but related trimetallic clusters.[4] This demonstrates the subtle balance of factors involved in creating the right ligand environment at the metal centre to direct the reaction in a particular direction.

When $[CpCo(C_2H_4)_2]$ is treated with an excess of isothiocyanate (phenyl or methyl) at room temperature, vigorous evolution of ethylene is observed, and two products can be separated from the reaction mixture; the known cluster $[Cp_3Co_3S_2]^5$ and the new compounds $[CpCo\{C(NR)NRC(S)S\}(CNR)]$ (R = Ph, **1** and R = Me, **2**) (Scheme 1).† The multiple C=S bond-breaking processes that lead to **1** and **2** were only revealed following an X-ray crystal structure determination of **1** (Fig. 1).‡ The structure shows that three isothiocyanate ligands have been combined and one sulphur atom extruded. However only one of the original C=S links remains intact. The five-membered metallacyclic ring formed in the reaction is planar (the largest deviation from the best fit plane being less than 0.13 Å). All the bond lengths in the ring are close to those of typical single X–Y bonds,[6] indicating only a small degree of unsaturation.

The exocyclic sulphur is nucleophilic and is readily methylated or protonated to generate the complexes **3**, **4** and **5**. The site of electrophilic addition can be easily inferred from the IR spectra. The ν_{CN} stretches for both the isocyanide ligand and the exocyclic C=N bond, C(3)–N(3), are only slightly affected by the addition.



Scheme 1 R = Ph or Me, R′ = Me or H. *Reagents and conditions*: i, SCNR (excess), 20 °C, Et_2O; ii, MeI (R′ = Me), or CF_3SO_3H (R′ = H), 20 °C, CH_2Cl_2; iii, SCNR (0.33 equiv.), 20 °C, Et_2O, iv, CS_2 (0.33 equiv.), 20 °C, tetrahydrofuran (THF)

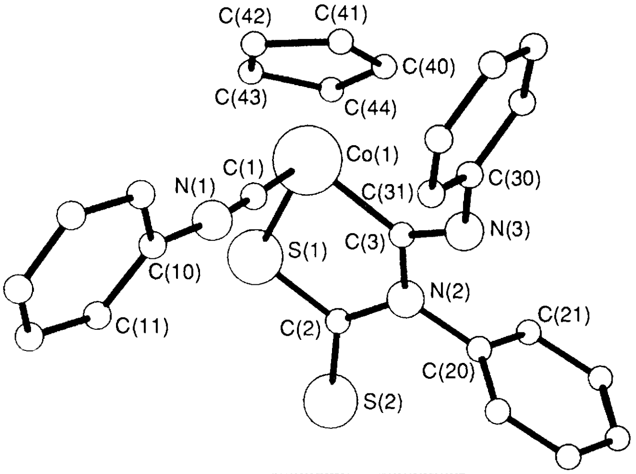


Fig. 1 Structure of $[(C_5H_5)Co\{C(NPh)NPhC(S)S\}(CNPh)]$ **1**. Distances and angles include: Co–C(1) 1.79(1), Co–C(3) 1.94(1), Co–S(1) 2.18(3), C(1)–N(1) 1.17(1), C(2)–N(2) 1.36(1), C(3)–N(2) 1.41(1), C(3)–N(3) 1.28(1), C(2)–S(1) 1.73(1), C(2)–S(2) 1.65(1) Å; C(1)–Co–S(1) 92.3(3), C(1)–Co–C(3) 92.1(3), S(1)–Co–C(3) 85.9(3), Co–C(1)–N(1) 175.7(8), C(1)–N(1)–C(10) 174.0(9), Co–S(1)–C(2) 100.9(3), Co–C(3)–N(2) 115.4(6), S(1)–C(2)–N(2) 114.0(6), C(2)–N(2)–C(3) 120.6(6), S(1)–C(2)–S(2) 120.7, S(2)–C(2)–N(2) 125.2(6), C(2)–N(2)–C(20) 119.1(7), C(3)–N(2)–C(20) 119.6(6), Co–C(3)–N(3) 129.4(6), N(2)–C(3)–N(3) 115.2(7)°.

An entirely different mechanism must operate when the reaction forming **1** is carried out with a deficiency of isothiocyanate. In this case a tricobalt cluster **6** is formed, the same product that can be isolated using other sources of the CpCo moiety.[4]

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† *Spectroscopic data* for selected compounds: (satisfactory C, H and N analyses have been obtained for **1** and **2**). **1** $[(C_5H_5)Co\{C(NPh)NPhC(S)S\}(CNPh)]$: ^1H NMR ($CDCl_3$) δ 7.47–6.67 (m, 15H, 3Ph) and 4.94 (s, 5H, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 213.3, 175.6, 152.4, 146.5 (quaternary C), 129.9–120.3 × Ph(3) and 88.8 (s, C_5H_5); IR (Nujol) ν(CN)/cm^{-1} 2154s, 1604s and 1587s; *m/z* (EI) 497 (M^+).

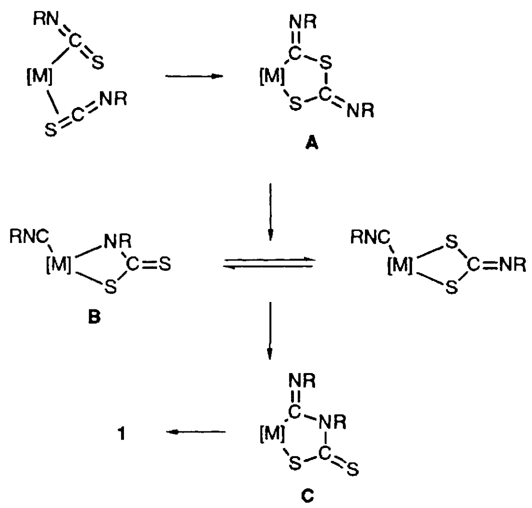
2 $[(C_5H_5)Co\{C(NMe)NMeC(S)S\}(CNMe)]$: ^1H NMR ($CDCl_3$) δ 5.14 (s, 5H, C_5H_5), 3.66 (s, 3H, Me), 3.39, and 3.36 (s, 6H, 2 × Me); IR (Nujol) ν(CN)/cm^{-1} 2205 and 1609 br; *m/z* (EI) 311 (M^+).

3 $[(C_5H_5)Co\{C(NPh)NPhC(SMe)S\}(CNPh)]I$: ^1H NMR ($CDCl_3$) δ 7.7–6.7 (m, 15H, 3Ph), 5.42 (s, 5H, C_5H_5) and 2.89 (s, 3H, Me); ^{13}C NMR ($CDCl_3$) δ 205.7, 174.8, 150.7, 139.8 (quaternary C), 130.9–119.4 × Ph(3), 90.6 (s, C_5H_5) and 19.7 (s, Me); IR (Nujol) ν(CN)/cm^{-1} 2170, 1613 and 1589; *m/z* (FAB) 512 (M^+).

4 $[(C_5H_5)Co\{C(NMe)NMeC(SMe)S\}(CNMe)]I$: ^1H NMR ($CDCl_3$) δ 5.5 (s, 5H, C_5H_5), 3.58, 3.55 (s, 6H, 2 × Me) and 3.43 (s, 3H, Me); IR (Nujol) ν(CN)/cm^{-1} 2237, 1647 and 1580 cm^{-1}.

5 $[(C_5H_5)Co\{C(NPh)NPhC(SH)S\{(CNPh)](CF_3SO_3)$: ^1H NMR (CD_3COCD_3) δ 7.74–7.31 (15H, m, 3 × Ph) and m, 5.44 (5H, s, C_5H_5); IR (Me_2CO) ν(CN)/cm^{-1} 2197, 1614 and 1593 cm^{-1}.

‡ *Crystal Data*: $C_{26}H_{20}CoN_3S_2$, M = 497.4, space group $P2_1/n$, a = 9.921(1), b = 14.179(3), c = 17.684(2) Å, β = 94.45(2)°, U = 2480.11 Å^3, D_c = 1.33 g cm^{-3}, $F(000)$ = 1024 for Z = 4. The intensity data were collected on a Hilger and Watts Y290 diffractometer, using Mo-Kα radiation, within the limits $1 < \theta < 20°$, μ(Mo-Kα) = 16.7 cm^{-1}; no absorption correction was considered necessary. The structure was solved by Patterson and Fourier methods on the basis of 1615 significant $[I > 3\sigma(I)]$ reflections from a total of 2328. Refinement by full-matrix least squares led to final R and R_w values of 0.048 and 0.052 respectively, where the weighting scheme was based on a Chebyshev polynomial and including anomalous scattering for the cobalt atom. Hydrogen atoms were located in a difference Fourier synthesis and refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2 Possible mechanism for the formation of **1**

The reaction can be compared with that involving carbon disulphide. In this case the analogous tricobalt complex **7**[7] is formed in highest yield when the stoichiometry of the reaction $CpCo(C_2H_4)_2 : CS_2$ is 3 : 1. As the proportion of CS_2 is increased the yield of the cluster **7** decreases and increasing amounts of $Cp_3Co_3S_2$ are formed. However, in this case no mononuclear products could be isolated.

The mechanism of the reaction forming **1** and **2** differs significantly from that observed with the isoelectronic d^8 ruthenium and rhodium complexes.[8] However, it is possible to piece together a reasonable mechanism (Scheme 2). The key feature of the mechanism lies in the different possible coordination modes of the dithiocarbamate ligand, a ligand that has received little study.[9]

When $[CpCo(PMe_3)_2]$ is treated with isothiocyanates a metallocycle **A** may be isolated.[10] The analogous reaction with $[RhCl(PPh_3)_3]$ produces a complex with an extra vacant coordination site and the metallocycle collapses to give an isocyanide–dithiocarbamate complex.[8] This same extra site is available when $[CpCo(C_2H_4)_2]$ is used as a substrate but the harder cobalt centre would be expected to favour the *S,N*-bound isomer **B** rather than the *S,S'*-bound isomer. On simple thermodynamic grounds the former isomer would be expected to undergo more facile insertion by isocyanide to give the observed metallocycle **C** in a process comparable to that occurring on tungsten in the formation of a related ligand.[11] The resulting vacant coordination site would then provide access for the final isothiocyanate addition and sulphur extrusion comparable to that observed in the formation of $[Fe(CO)_4CNPh]$.[12]

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