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A novel route to dithiolenes from 1,3-dithiole-2-thiones at a dicobalt centre

Harry Adams, Laurence V. Y. Guio, Michael J. Morris * and A. James Pratt

Department of Chemistry, University of Sheffield, Sheffield, UK S3 7HF
E-mail: M.Morris@sheffield.ac.uk

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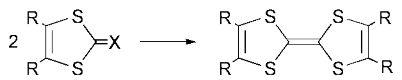
On reaction with $[Co_2(\mu\text{-dppm})(CO)_6]$ at room temperature, 4,5-bis(alkoxycarbonyl)-1,3-dithiole-2-thiones are dismantled into dithiolene and thiocarbonyl ligands by cleavage of two C–S bonds to give $[Co_2(\mu\text{-CS})(\mu\text{-}S_2C_2R_2)(CO)_3(\mu\text{-dppm})]$ (R = CO_2Me, CO_2Et).

The coupling of 1,3-dithiole-2-thiones **1** (or the corresponding ketones **2**) is an important step in many syntheses of tetrathiafulvalenes (TTF's), which are used in the production of charge transfer salts for investigation as organic metals (Scheme 1).[1,2]



1 X = S
2 X = O

Scheme 1

Conventionally this step is effected thermally by $P(OEt)_3$ or similar trivalent phosphorus compounds, though yields can be variable and some functional groups will not tolerate these conditions. Some years ago, it was reported that certain organometallic compounds, of which $[Co_2(CO)_8]$ was the most efficient, also promoted the coupling of **1** to TTF's, though in relatively poor yields (*ca.* 25%).[3] Since then this method has been applied occasionally, sometimes in cases where phosphites were ineffective.[4] In recent studies of this reaction we have isolated an unstable species, possibly an unknown Co/S/CO cluster, from the reaction of **1** with cobalt carbonyl, though as yet it has resisted our attempts at characterisation.[5] We therefore turned to the substituted derivative $[Co_2(\mu\text{-dppm})(CO)_6]$ **3** in the hope that more stable compounds would be produced. We now show that in fact the reaction takes a different and highly unusual course, involving conversion of the heterocycle into thiocarbonyl and dithiolene fragments at room temperature.

Treatment of orange dicobalt complex **3** with one equivalent of 4,5-bis(carbomethoxy)-1,3-dithiole-2-thione **1a** in toluene for 17 h at room temperature gave a deep green solution, from which crystals of $[Co_2(\mu\text{-CS})\{\mu\text{-}S_2C_2(CO_2Me)_2\}(\mu\text{-dppm})(CO)_3]$ (**4a**, 53%) were isolated either by removal of solvent and recrystallisation by diffusion of light petroleum (bp 60–80 °C) into a dichloromethane solution, or by column chromatography on silica (Scheme 2). The complex is stable in air for short periods as a solid, but solutions decompose rapidly to a brown species which contains no carbonyl ligands. The mass spectrum of **4a** showed a molecular ion corresponding to a complex in which three carbonyls had been lost and one molecule of heterocycle incorporated.† The ^1H NMR spectrum was broad and uninformative, but the ^{13}C NMR spectrum showed three carbonyl peaks, together with resonances for the dppm ligand and for two inequivalent CO_2Me groups. Moreover, a triplet was observed at extremely low field (δ 353.3, J = 14 Hz) which could not easily be assigned. Hence the molecular structure of **4a** was determined by X-ray diffraction and is shown in Fig. 1, with selected bond lengths and angles contained in the caption.‡

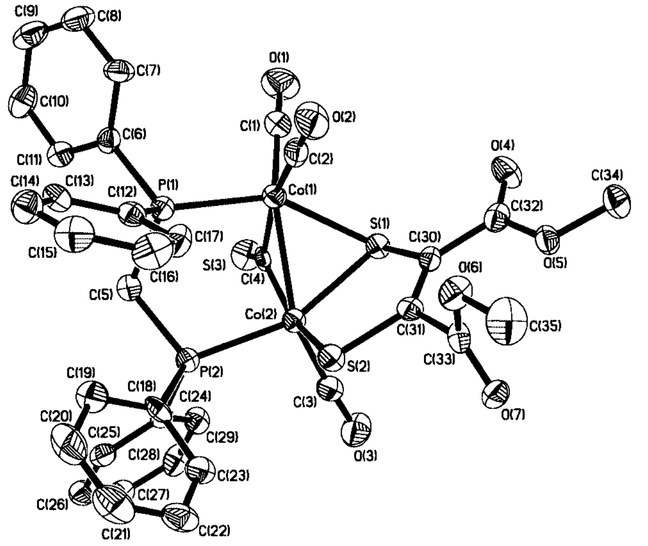
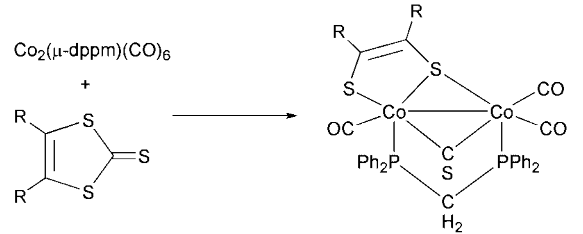


Fig. 1 Molecular structure of complex **4a** in the crystal. Selected bond lengths (Å) and angles (°): Co(1)–Co(2) 2.4498(11), Co(1)–C(4) 1.912(5), Co(2)–C(4) 1.883(5), Co(1)–S(1) 2.2670(16), Co(2)–S(1) 2.1995(16), Co(2)–S(2) 2.2897(16), S(3)–C(4) 1.609(5), C(30)–C(31) 1.352(7); Co(2)–C(4)–Co(1) 80.4(2), Co(2)–S(1)–Co(1) 66.51(4), S(1)–Co(2)–S(2) 89.81(5).



1a R = CO_2Me
1b R = CO_2Et

4a R = CO_2Me
4b R = CO_2Et

Scheme 2

The two cobalt atoms are joined by a single bond [Co(1)–Co(2) 2.4498(11) Å] which is bridged by the dppm ligand. A thiocarbonyl group C(4)–S(3), formed by cleavage of the thione functionality from the heterocycle, also bridges the two metals symmetrically. The identity of this ligand is confirmed by the presence of a peak at 1147 cm^{-1} in the IR spectrum in KBr similar to that observed for other dicobalt complexes containing a μ-CS ligand.[6] It is also clear that the μ-CS ligand is responsible for the low field signal in the ^{13}C NMR spectrum. The remaining portion of the organic ligand is bonded as an unsymmetrically bridging dithiolene, in which S(1) bridges the metal–metal bond whereas S(2) is bonded only to Co(2). This form of coordination is well known for dithiolene ligands; recent examples include two isomers of $[Mo_2(CO)_2\{\mu\text{-}S_2C_2\text{-}$

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$(CO_2Me)_2\}_2(\eta\text{-}C_5H_5)_2]$.[7] The C(30)–C(31) bond distance in this ligand is 1.352(7) Å, which is typical for dithiolenes.

Reaction of **3** with the carboethoxy-substituted thione **1b** afforded an analogous complex **4b** (34%), with almost identical spectroscopic properties.† However when attempts were made to extend the reaction to alkylthio-substituted species (*e.g.* R = SMe or SCOPh) the reactions did not appear to proceed to completion; although there was some evidence for the formation of similar compounds, they could not be isolated cleanly. The ketone derived from **1a**, 4,5-bis(carbomethoxy)-1,3-dithiole-2-one, did not react with **3** to give a complex with a bridging carbonyl. Efforts to prepare complexes with dppe in place of dppm were thwarted by the surprising fact that there is no known preparative route to $[Co_2(CO)_6(\mu\text{-dppe})]$.

In recent work we have demonstrated that the reaction of **1a** with the dimolybdenum alkyne complex $[Mo_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ proceeds by rupture of the C=S bond, ring opening of the heterocycle and coupling of the thione carbon to the alkyne to give $[Mo_2(\mu\text{-}S)\{\mu\text{-}SC(CO_2Me){=}C(CO_2Me)SCC(CO_2Me){=}C(CO_2Me)\}(\eta\text{-}C_5H_5)_2]$.[8] Clearly the mode of reactivity observed at the dppm-bridged dicobalt centre is completely different, involving as it does cleavage of the two C–S single bonds of the trithiocarbonate moiety. Given the structure of **4** it is easy to see why thermolysis of these complexes does not give rise to the corresponding TTF; possibly unproductive side reactions such as these are responsible for the low yields observed with cobalt carbonyl. Our efforts to tune this system to provide a mild, high-yield route for the coupling of thiones **1** are continuing.

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Notes and references

† Selected spectroscopic data: (NMR in $CDCl_3$, 250 MHz, $SiMe_4$ $\delta = 0$; ^{31}P relative to 85% $H_3PO_4 = 0.0$ ppm, all signals are singlets unless otherwise stated). **4a**: mp 268–271 °C. IR (CH_2Cl_2): 2047, 2011, 1729, 1693 cm^{-1}. IR (KBr): 1147 cm^{-1} (μ-CS). ^1H NMR: δ 7.65–7.10 (m, 20 H, Ph), 4.32 (m, 2 H, CH_2) 3.80 (br s, 6 H, Me); ^{13}C NMR: δ 353.3 (t, $J = 14$ Hz, μ-CS), 198.6 (CO), 197.9 (m, CO), 176.6 (d, $J = 14$ Hz, CO), 169.2, 162.6 (both $\mathit{C}O_2Me$), 136.0–128.1 (m, Ph + dithiolene carbons), 52.9, 52.4 (both Me), 40.3 (t, $J = 24$ Hz, CH_2); ^{31}P NMR: δ 36.9, 28.5 (both d, $J = 54$ Hz). MS *m*/*z* 837 ($M + H^+$), 809, 780, 752 ($M - nCO^+$, $n = 1$–3). Found: C, 46.68; H, 3.27; S, 11.09. Calc. for **4a**·CH_2Cl_2: C, 46.91; H, 3.26; S, 10.42%.

4b: mp 221–224 °C. IR (CH_2Cl_2): 2047, 2011, 1723, 1689 cm^{-1}. IR (KBr) 1148 cm^{-1} (μ-CS). ^1H NMR: δ 7.80–7.20 (m, 20 H, Ph), 4.26 (m, 4 H, $C\mathit{H}_2CH_3$), 3.80 (m, 2 H, CH_2), 1.35 (m, 6 H, $CH_2C\mathit{H}_3$); ^{13}C NMR: δ 354.2 (t, $J = 14$ Hz, μ-CS), 198.7 (m, CO), 198.1 (m, CO), 176.2 (d, $J = 15$ Hz, CO), 168.7, 162.1 (both $\mathit{C}O_2Et$), 136.1–128.3 (m, Ph + dithiolene carbons), 61.8, 61.1 (both $\mathit{C}H_2CH_3$), 40.3 (t, $J = 23$ Hz, CH_2), 14.3, 13.9 (both $CH_2C\mathit{H}_3$); ^{31}P NMR: δ 36.7, 28.2 (both d, $J = 59$ Hz). MS *m*/*z* 865 ($M + H^+$), 837, 808, 780 ($M - nCO^+$, $n = 1$–3). Found: C, 50.80; H, 3.81; S, 11.43. Calc.: C, 51.42; H, 3.73; S, 11.13%.

‡ Crystal data for **4a**·CH_2Cl_2: $C_{36}H_{30}Cl_2Co_2O_7P_2S_3$; $M = 921.48$, monoclinic, $a = 14.377(4)$, $b = 19.726(6)$, $c = 14.775(6)$ Å, $\beta = 111.669(9)°$, $U = 3894(2)$ Å^3, $Z = 4$, space group $P2_1/n$ (a non-standard setting of $P2_1/c$ C^5_{2h}, no. 14), $\mu(\text{Mo-K}_\alpha) = 1.279$ mm^{-1}, $T = 150(2)$ K, 25383 reflections measured, 9295 unique [$R(\text{int}) = 0.1285$]. The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Refinement converged at a final $R = 0.0605$ ($wR_2 = 0.1504$ for all data). Program: SHELXTL.[9] CCDC reference number 186/2174. See http://www.rsc.org/suppdata/dt/b0/b006052f/ for crystallographic files in .cif format.

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