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Preliminary Communication

Co-ordination of copper and silver by $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$

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Abstract

The thiamacrocycle $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ reacts with $Ag[BF_4]$ and PPh_3 to afford the fluxional compound $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6(AgPPh_3)][BF_4]$, the structure of which has been established by X-ray crystallography, and with $[Cu(CH_3CN)_4][PF_6]$ to afford $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6(CuCH_3CN)][PF_6]$, which undergoes phosphine substitution.

There is currently considerable interest in crown thioether chemistry, especially the remarkable ligating ability of 1,4,7-trithiacyclononane [1], and applications in the areas of nuclear medicine [2] and organometallic chemistry [3] are being explored. Recently we reported the synthesis of the novel thiamacrocycle **1** *via* the acid catalysed reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with 2-mercaptoethyl sulfide [4]. The thiamacrocycle was found to adopt an exodentate conformation in the solid state, in a similar manner to 2,5,8-trithia[9]-*o*-benzenophane (TTOB) [5]. Although a large conformational change is required for **1** to coordinate facially with a metal ligand fragment this has been observed with TTOB, and we now present the first crystallographic evidence that such co-ordination is possible with the more encumbered 3,6,9-trithiacycloundecyne hexacarbonyldicobalt complex.

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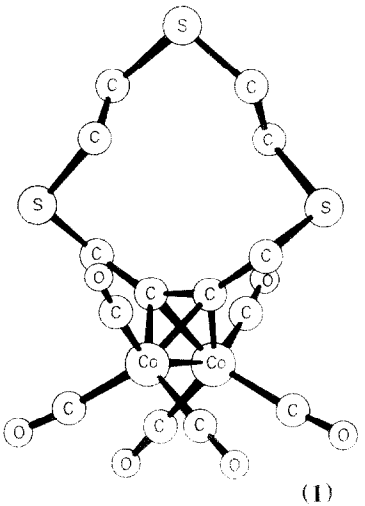

(1)

Reaction of a CH_3CN solution of **1** with equimolar amounts of $Ag[BF_4]$ and PPh_3 at room temperature affords $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6(AgPPh_3)][BF_4]$ (**2**) in good yield (*ca.* 69%) *. The X-ray crystal structure of **2** **, shown in Fig. 1, reveals that the $AgPPh_3^+$ fragment is co-ordinated by all three sulfur atoms of the ring, which now adopts an endodentate conformation. The structure can be compared with that of $[Ag(TTOB)PPh_3]^+$ with distortions caused by the steric bulk of the dicobalt unit, and the wider

* *Selected spectroscopic data:* Compound **2**: ν(CO) (CH_2Cl_2) 2098m, 2060vs and 2028s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.5–7.3 (m, 15H, Ph), 4.55 (s, 4H, CCH_2) and 3.3–3.1 (m, 8H, SCH_2); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 200.0 (CO), 135–130 (Ph), 90.4 (C_2), 37.1, 34.2 and 31.2 (CH_2). FAB mass spectrum: m/z 859 ($M^+ - BF_4$).

Compound **3**: ν(CO) (CH_2Cl_2) 2098m, 2061vs and 2038s cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.57, 3.37 [AB, 4H, CCH_2, J_{AB} 15], 3.3–2.9 (m, 8H, SCH_2) and 2.20 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 198.6, 197.7 (CO), 118.3 (CN), 87.1 (C_2), 37.7, 36.7, 33.1 (CH_2) and 2.3 (CH_3). FAB mass spectrum: m/z 553 ($M^+ - PF_6 - MeCN$).

Compound **4**: ν(CO) (CH_2Cl_2) 2097m, 2057vs and 2027s cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6–7.2 (m, 15H, Ph), 4.63, 4.56 [AB, 4H, CCH_2, J_{AB} 16] and 3.4–2.8 (m, 8H, SCH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 199.0, 198.2 (CO), 134–129 (Ph), 86.4 (C_2), 38.7, 37.0 and 33.6 (CH_2). FAB mass spectrum: m/z 815 ($M^+ - PF_6$).

Compound **5**: ν(CO) (CH_3CN) 2096m, 2057s and 2026vs cm^{-1}; ^1H NMR (CD_3CN) δ 7.6–7.1 (m, 20H, Ph), 4.47 (s, 8H, CCH_2) and 3.2–2.9 (m, 16H, SCH_2); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 199.8 (CO), 134–130 (Ph), 103.5 [d, PC≡CP, J(PC) 41], 89.1 (C_2), 38.0, 36.8 and 33.7 (CH_2). FAB mass spectrum: m/z 1647 ($M^+ - PF_6$).

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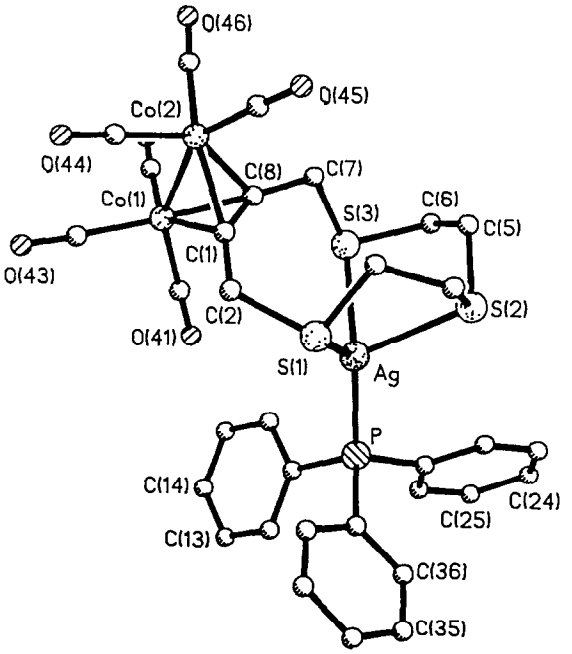

Fig. 1. The molecular structure of **2** with the BF_4^- counter ion omitted. Dimensions: Ag–S(1) 2.579(2), Ag–S(2) 2.688(2), Ag–S(3) 2.595(2), Ag–P 2.416(2), Co(1)–Co(2) 2.466(2) Å: angles: S(1)–Ag–S(2) 82.1(1), S(1)–Ag–S(3) 104.8(1), S(2)–Ag–S(3) 83.7(1), S(1)–Ag–P 126.8(1), S(2)–Ag–P 118.9(1), S(3)–Ag–P 124.5(1), C(2)–C(1)–C(8) 147.6(6), C(1)–C(8)–C(7) 147.8(5)°.

angles at the acetylenic carbons [C(2)–C(1)–C(8) 147.6(6) and C(1)–C(8)–C(7) 147.8(5)°] compared with those in the benzenophane (*ca.* 123°) [6]. All three silver–sulfur distances in **2** [2.579(2), 2.688(2), 2.595(2) Å] are longer than those in $[Ag(TTOB)PPh_3]^+$ [2.565(1), 2.600(1), 2.554(2) Å], and the silver–phosphorus distance in **2** [2.416(2) Å] is longer than the corresponding distance in $[Ag(TTOB)PPh_3]^+$ [2.382(1) Å].

The NMR spectra of **2** show that the molecule is fluxional at room temperature. For example, in the ^1H NMR spectrum the methylene protons adjacent to the alkyne carbons appear as a singlet, and in the $^{13}C\{^1H\}$ NMR spectrum the carbonyl ligands appear as a single resonance. Low temperature ^1H NMR spectra of **2** are in accord with the solid state structure; the methylene protons adjacent to the alkyne carbons appear as an AB pattern (δ 4.63, 4.56, $J_{AB} = 16$ Hz) at 212 K, indicating that at room temperature a fluxional process equivalences both sides of the macrocyclic ring. This could be achieved by the $Ag(PPh_3)^+$ fragment pivoting rapidly about the unique sulfur and hence migrating between the two faces or by intermolecular exchange of $Ag(PPh_3)^+$ fragments.

Reaction of equimolar quantities of **1** and $[Cu(CH_3CN)_4][PF_6]$ at room temperature affords $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6(CuCH_3CN)][PF_6]$ (**3**) in *ca.* 72% yield. The NMR spectra of **3** reveal that it is static on the NMR timescale at room temperature, and two resonances are observed in the $^{13}C\{^1H\}$ NMR for the carbonyl ligands. The acetonitrile ligand is very labile and FAB mass spectroscopy detects isotope envelopes due to $M^+ - PF_6 - CH_3CN - nCO$ ($n = 0$–6). Reaction of **3** with triphenylphosphine affords $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6(CuPPh_3)][PF_6]$ (**4**) (*ca.* 60% yield) in which the phosphine replaces the acetonitrile. Reaction of **3** with bis(diphenylphosphino)acetylene (dppa) which is incapable of chelation affords $[Co\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6(CuPPh_2\text{-}C{\equiv}CPPh_2Cu)Co_2\{\mu\text{-}C_2(CH_2SCH_2\text{-}CH_2)_2S\}(CO)_6][PF_6]_2$ (**5**) in which two copper centres are linked by the dppa. The chelating phosphine bis(diphenylphosphino)ethane (dppe) abstracts the copper ion from **3** to afford $[Cu(dppe)_2]^+$ and **1** is released. We are currently investigating the synthesis and co-ordination chemistry of a variety of related macrocycles containing sulfur, oxygen, nitrogen and phosphorus heteroatoms.

** *Crystal data:* Compound **2**: $C_{32}H_{27}AgBCo_2F_4O_6PS_3$, $M = 947.2$, triclinic, space group $P\bar{1}$, $a = 10.820(5)$, $b = 13.293(7)$, $c = 15.273(9)$ Å, $\alpha = 113.49(4)$, $\beta = 95.17(4)$, $\gamma = 107.24(4)°$, $U = 1869(2)$ Å^3, $Z = 2$, $D_c = 1.68$ g cm^{-3}, $F(000) = 944$, μ(Mo-K$_\alpha$) = 16.7 cm^{-1}, $R = 0.039$ ($R' = 0.045$) for 5131 unique absorption-corrected intensities [295 K, Wyckoff ω-scans, $2\Theta \leq 50°$, $F \geq 5\sigma(F)$, Mo-Kα radiation ($\bar{\lambda} = 0.71073$ Å)]. Data were collected using a Siemens R3m/V diffractometer and the structure was solved by Patterson and Fourier methods with full matrix least squares refinement. List of atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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