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Formation of Novel Bidentate and Crown Thioether Ligands *via* Dicobalt Alkyne Complexes

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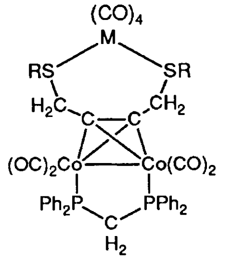
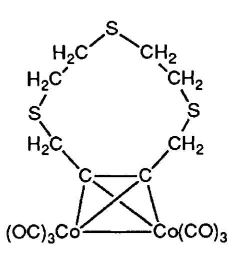
Open chain and cyclic thioalkyne complexes capable of ligating metal–carbonyl moieties are prepared by the reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with mono- and di-thiols in the presence of HBF_4 and the structures of $[Co_2(CO)_4(\mu\text{-dppm})\{\mu\text{-}C_2(CH_2SMe)_2\}Mo(CO)_4]$ and $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ have been established by X-ray crystallography; dppm = bis(diphenylphosphino)methane.

The relatively weak π back-acceptor and σ-donor abilities of thioether ligands have resulted in their coordination chemistry being dominated by multidentate systems.[1] Recent interest has focused on crown thioethers, which typically bind metal ions more strongly than simple mono- or bi-dentate thioethers.[2] We have shown that alkyne complexes can be used in the formation of chelates[3] and macrocycles[4] and in this communication we report how the chemistry of dicobalt hexacarbonyl stabilised propynyl cations[5] can be used to synthesise new bidentate- and crown-thioether ligands.



4a M = Cr, R = Me
4b M = Cr, R = Et
5a M = Mo, R = Me
5b M = Mo, R = Et
6a M = W, R = Me
6b M = W, R = Et



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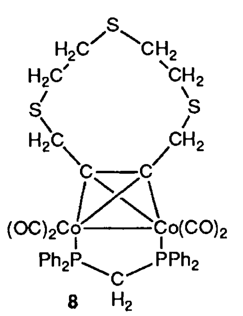

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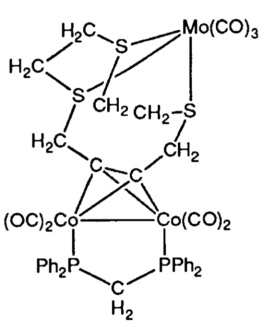

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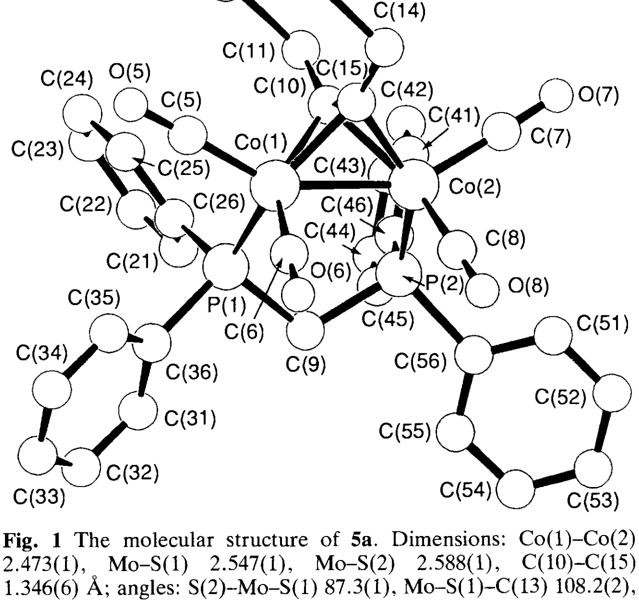

Fig. 1 The molecular structure of **5a**. Dimensions: Co(1)–Co(2) 2.473(1), Mo–S(1) 2.547(1), Mo–S(2) 2.588(1), C(10)–C(15) 1.346(6) Å; angles: S(2)–Mo–S(1) 87.3(1), Mo–S(1)–C(13) 108.2(2), C(13)–S(1)–C(14) 97.5(2), Mo–S(2)–C(12) 107.4(2), C(12)–S(2)–C(11) 98.3(3), C(11)–C(10)–C(15) 140.0(4), C(10)–C(15)–C(14) 143.8(4)°.

Reaction of $[Co_2(\mu\text{-}HC{\equiv}CCH_2)(CO)_6]^+$ with EtSH in CH_2Cl_2 affords $[Co_2(\mu\text{-}HC{\equiv}CCH_2SEt)(CO)_6]$ **1**;† however, the HBF_4 catalysed reaction of $[Co_2(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_6]$ with EtSH in CH_2Cl_2 affords **1** more conveniently in *ca.* 84% yield. Similarly, reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with RSH in the presence of HBF_4 affords $[Co_2(\mu\text{-}RSCH_2C{\equiv}CCH_2SR)(CO)_6]$ **2b** (R = Et), **2c** (R = Ph), which have analogous spectroscopic properties to **2a** (R = Me) prepared by the reaction of octacarbonyldicobalt with 2,7-dithiaoct-4-yne. In order to test the ability of the coordinated dithiaalkynes to act as chelating ligands it was found to be necessary to substitute two carbonyl ligands in compounds **2** with bis(diphenylphosphino)methane (dppm) to afford the compounds $[Co_2(\mu\text{-}RSCH_2C{\equiv}CCH_2SR)(\mu\text{-}dppm)(CO)_4]$ **3**, in which the cobalt–cobalt bonds are stabilised by a bridging dppm and the remaining four carbonyl ligands are less prone to undergo substitution.[6]

Reaction of **3a** and **3b** with $[M(CO)_4(norbornadiene)]$ (M = Cr, Mo, W) affords compounds **4–6**, the IR and NMR spectra of which can be interpreted by comparison with compounds **3** and other *cis*-$[M(CO)_4(RS\frown SR)]$ complexes.[7] The structure of **5a** has been established by a single crystal X-ray diffraction study‡ and is shown in Fig. 1. The chelate ring adopts a conformation with *cis* orientation of the methyl groups as opposed to the *trans* alkyl orientation observed in the solid-state structures of *cis*-$[M(CO)_4(RSCH_2CH_2SR)]$ (M = Cr, R = Me[8] or Bu^t;[9] M = W, R = Bu^t[10]) where the controlling factor is alkyl–alkyl non-bonded interactions.[7] However, when unsaturated ligand backbones constrain the chelate ring to be planar as in *cis*-$[Cr(CO)_4(Bu^tSCH{=}CHSBu^t)]$[11] the controlling factor is alkyl group–carbonyl group nonbonded interactions and a *cis* conformation is adopted.[7] Inspection of the geometry of **5a** suggests that a *trans* conformation would result in a significant methyl-axial cobalt carbonyl steric interaction. The room temperature NMR spectra of **4–6** indicate that sulphur inversion[9] and alkyne rocking[10] produce effective mirror planes both perpendicular and parallel to the cobalt–cobalt bond on the NMR timescale, while the $^{13}C\{^1H\}$ spectrum of **5a** at −90 °C indicates that only the *cis* invertomer is present in accord with the solid-state structure.[13]

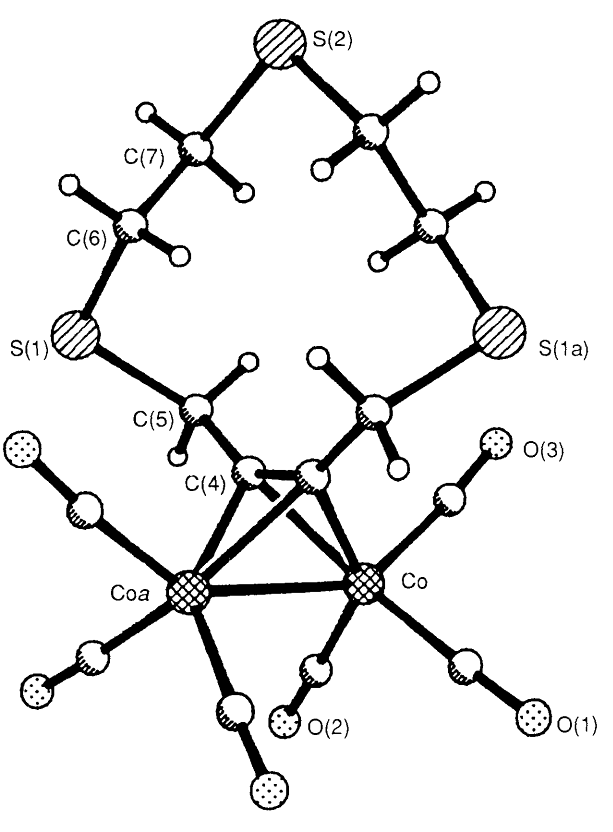

Fig. 2 The molecular structure of **7**. S(2) and the midpoint of the Co–Co*a* vector lie on a crystallographically imposed twofold axis and atoms with a suffix "*a*" are generated by symmetry. Dimensions: Co–Co*a* 2.498(2), Co–C(4) 1.962(4), Co–C(4*a*) 1.964(4), C(4)–C(4*a*) 1.346(8) Å: angles: C(5)–S(1)–C(6) 101.0(2), C(7)–S(2)–C(7*a*) 101.1(3), C(5)–C(4)–C(4*a*) 149.1(2)°.

Treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with bis(2-mercaptoethyl) sulphide in the presence of HBF_4 exploits both the geometric and electronic influences of the hexacarbonyldicobalt fragment on the coordinated butynediol and affords the cyclic compound **7** in *ca.* 38% yield. The X-ray

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† *Selected spectroscopic data*: Compound **1**: ν_{co} (light petroleum, 40–60 °C) 2095w, 2057s, 2032s, 2027m and 2013w cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.09 (s, 1H, CH), 3.95 (s, 2H, CH_2), 2.68 (q, 2H, CH_2Me, J_{HH} 7 Hz) and 1.31 (t, 3H, CH_3, J_{HH} 7 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 199.6 (CO), 93.5 (CCH_2), 73.3 (CH), 35.8 (CH_2), 26.7 (CH_2Me), and 14.4 (CH_3).

Compound **2a**: ν_{co} (light petroleum) 2092m, 2059s, 2055s and 2033s cm^{-1}; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 198.3 (CO), 95.0 (C_2), 37.3 (CH_2) and 15.4 (CH_3).

Compound **3a**: ν_{co} (light petroleum) 2025m, 1998s and 1974s cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.64–7.08 (m, 20H, Ph), 4.00 (t, 4H, SCH_2, J_{PH} 3 Hz), 3.48 (t, 2H, PCH_2P, J_{PH} 11 Hz) and 2.20 (s, 6H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 203.9 (CO), 137–128 (m, Ph), 95.5 (C_2), 41.5 (t, PCH_2P, J_{PC} 20 Hz), 40.4 (SCH_2) and 17.3 (CH_3).

Compound **5a**: ν_{co} (light petroleum) 2032m, 2023m, 2003s, 1979m, 1913s and 1866m cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.24 (m, 20H, Ph), 4.17 (s, 4H, SCH_2), 3.45 (t, 2H, PCH_2P, J_{PH} 10 Hz) and 2.51 (s, 6H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 217.1 [*eq*-$Mo(CO)_2$], 206.6 [*ax*-$Mo(CO)_2$], 203.9 [$Co_2(CO)_4$], 137–128 (m, Ph), 89.0 (C_2), 50.2 (SCH_2), 43.4 (t, PCH_2P, J_{PC} 19 Hz) and 27.5 (CH_3).

Compound **6b**: $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 208.1 [*eq*-$W(CO)_2$, J_{wc} 166 Hz], 203.9 [$Co_2(CO)_4$], 202.7 [*ax*-$W(CO)_2$, J_{wc} 136 Hz], 137–128 (m, Ph), 88.0 (C_2), 48.6 (SCH_2), 43.5 (t, PCH_2P, J_{PC} 20 Hz), 38.9 (CH_2Me) and 13.6 (CH_3).

Compound **7**: ν_{co} (light petroleum) 2093m, 2056vs, 2031s, 2026m and 2013w cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.16 (s, 4H, CH_2) and 3.09–2.85 (m, 8H, CH_2CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 199.1 (CO), 93.9 (C_2), 35.0, 30.4 and 28.5 (CH_2).

Compound **8**: ν_{co}(CH_2Cl_2) 2023m, 1993s and 1965m cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.41–7.22 (m, 20H, Ph) 4.15 (s, 4H, CH_2), 3.50 (t, 2H, PCH_2P, J_{PH} 10 Hz) and 3.14–2.87 (m, 8H, CH_2CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 205.6 (CO), 137–128 (m, Ph), 95.3 (C_2), 42.5 (t, PCH_2P, J_{PC} 20 Hz), 36.3, 32.6 and 29.9 (CH_2).

Compound **9**: ν_{co} (toluene) 2024m, 1998s, 1970m, 1941s and 1838s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.44–7.27 (m, 20H, Ph) 4.53 (d, 2H, CH_2, J_{HH} 15 Hz), 4.33 (d of t, 2H, CH_2, J_{HH} 15 and J_{PH} 4 Hz), 3.46 (t, 2H, PCH_2P, J_{PH} 10 Hz) and 3.01–2.68 (m, 8H, CH_2CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 221.9 [Mo(CO)], 219.9 [$Mo(CO)_2$], 205.0 [$Co(CO)_2$], 204.3 [$Co(CO)_2$], 137–128 (m, Ph), 88.1 (C_2), 44.1 (CH_2), 41.3 (t, PCH_2P, J_{PC} 20 Hz), 35.2 and 33.5 (CH_2).

‡ *Crystal data* for **5a**: $C_{39}H_{32}Co_2MoO_8P_2S_2$, $M = 968.6$, monoclinic, space group $P2_1/n$, $a = 11.930(3)$, $b = 16.181(4)$, $c = 21.595(4)$ Å $\beta = 95.08(2)°$, $U = 4152.2$ Å^3, $Z = 4$, $D_c = 1.55$ g cm^{-3}, $F(000) = 1052$, μ(Mo-Kα) = 12.3 cm^{-1}, $R = 0.034$ ($R_w = 0.037$) for 4506 unique absorption-corrected intensities [293 K, $\omega/2\theta$ scans $2\theta \le 50°$, $F \ge 5\sigma(F)$, Mo-Kα radiation ($\bar{\lambda} = 0.710\,69$ Å)]. Data were collected using an Enraf-Nonius CAD4 diffractometer and the structure was solved by Patterson and Fourier methods with full-matrix least-squares refinement.

Crystal data for **7**: $C_{14}H_{12}Co_2O_6S_3$, $M = 490.3$, orthorhombic, space group *Pbcn*, $a = 13.458(4)$, $b = 18.195(5)$, $c = 7.996(2)$ Å, $U = 1958.1(9)$ Å^3, $Z = 4$, $D_c = 1.66$ g cm^{-3}, $F(000) = 984$, μ(Mo-Kα) = 20.2 cm^{-1}, $R = 0.038$ ($R_w = 0.042$) for 1192 unique absorption-corrected intensities [293K, Wyckoff ω-scans $2\theta \le 50°$, $F \ge 5\sigma(F)$, Mo-Kα radiation ($\bar{\lambda} = 0.710\,69$ Å)]. Data were collected using a Nicolet P3 diffractometer and the structure was solved by Patterson and Fourier methods with full-matrix least-squares refinement. Atom coordinates, bond distances and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1. Structure factors are available from the authors.

crystal structure of **7**, shown in Fig. 2, reveals that all three sulphur atoms are exodentate to the ring due to the *gauche* placement of the C–S linkages[2] and can be compared with the structure of 2,5,8-trithia[9]-*o*-benzenophane (TTOB).[14] Exodentate conformations do not preclude the possibility of macrocyclic thioether complexation as substantial conformational changes are possible as demonstrated by the coordination of TTOB to $Mo(CO)_3$.[14] Similarly, after substitution with dppm to afford **8**, reaction with $[Mo(CO)_3(\eta\text{-}C_6H_3Me_3)]$ in refluxing THF affords the $Mo(CO)_3$ complexed derivative **9** in *ca.* 95% yield.

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