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S_2CPR_3 adducts as bridging ligands in tricobalt clusters. X-Ray structure of $[Co_3(CO)_7(\mu_3-CH)(\mu_2-S_2CPCy_3)]$

Bernardo Alvarez, Daniel Miguel, Víctor Riera

Departamento de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo (Spain)

and Santiago García-Granda

Departamento de Química Física y Analítica, Universidad de Oviedo, E-33071 Oviedo (Spain)

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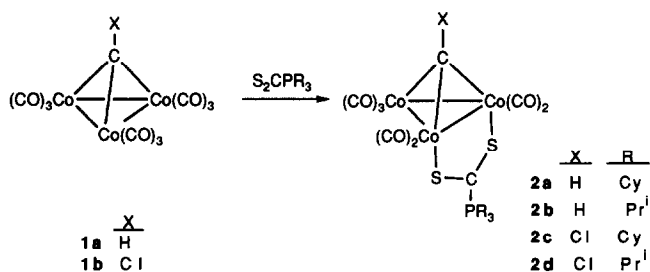
Abstract

$[Co_3(CO)_9(\mu_3-CX)]$ ($X = H, Cl$) react with S_2CPR_3 ($R =$ cyclohexyl, Cy or isopropyl, iPr) in CH_2Cl_2 to give heptacarbonyltricobalt clusters $[Co_3(CO)_7(\mu_3-CX)(\mu_2-S_2CPR_3)]$ in which the S_2CPR_3 act as four-electron ligands, bridging a Co–Co cluster edge in a $\sigma(S)$, $\sigma(S')$ fashion, as shown by an X-ray determination on a crystal of the derivative with $X = H$, $R = Cy$. The five-membered CoSCSCo ring is nearly perpendicular to the Co_3 triangle (*i.e.* axial), in contrast to the equatorial disposition usually found in related complexes with phosphorus ligands.

Alkyldynetricobalt clusters have been extensively studied for over twenty years. Apart from the chemistry centred at the μ_3 -alkylidyne carbon atom [1,2], there has been a continuing interest in the preparation of derivatives containing monodentate and bidentate ligands, mainly with donor atoms of Group 15 (phosphorus, arsenic), through carbonyl substitution on the parent compounds $[Co_3(\mu_3-CX)(CO)_9]$ [2,3]. However, as far as we know, there is no report of stable derivatives containing sulfur ligands. Here we present the preparation of some alkyldynetricobalt clusters containing S_2CPR_3 groups acting as $\sigma(S)$, $\sigma(S')$ bridging ligands along a cluster edge. This is also the first report of S_2CPR_3 groups acting as ligands in trimetallic clusters.

Compounds $[Co_3(CO)_9(\mu-CX)]$ ($X = H$, **1a** [4] or Cl , **1b** [5]) react with one molar equivalent of S_2CPR_3 in CH_2Cl_2 to give heptacarbonyl clusters $[Co_3(CO)_7(\mu_3-CX)(\mu_2-S_2CPR_3)]$ (**2a–d**, see Scheme 1) in moderate yields (30–50%). An X-ray structure determination was carried out on a single crystal of **2a** ($X = H$, $R =$ cyclohexyl) (Fig. 1). The phosphoniodithioformate S_2CPCy_3 acts as a 4e-donor towards a cluster edge [distances $Co(1)–S(1)$ 2.253(2), $Co(2)–S(2)$ 2.246(2) Å]. The five-membered $Co(1)–S(1)–C(1)–S(2)–Co(2)$ ring is fairly planar (the main

Correspondence to: Dr. D. Miguel, Departamento de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo, Spain.



Scheme 1.

deviation affects the atom S(1), at 0.055 Å from the best plane) and forms a dihedral angle of 80.24(4)° with the Co₃ triangle: *i.e.* the S₂CPR₃ ligand is axial. This is in contrast with the behaviour observed for P ligands, which usually adopt an equatorial disposition, as found in [Co₃(μ₃-CMe)(CO)₇(μ-dppm)] [6], [Co₃(μ₃-CMe)(CO)₈(PPh₃)] [7], and [Co₃(μ₃-CMe)(CO)₆{P(OMe)₃}₃] [8].

Additionally, in the structure of **2a**, the bridged edge of the cluster [Co(1)–Co(2) 2.452(1) Å] is significantly shorter than the non-bridged edges [Co(1)–Co(3) 2.507(1), Co(2)–Co(3) 2.516(1) Å]. This is in contrast with the other structures mentioned above, in which the substitution of CO groups by phosphines, phosphites, or diphosphines leads to an elongation of the metal–metal distance. This has been attributed to the increase of electron density on the cobalt atoms as CO

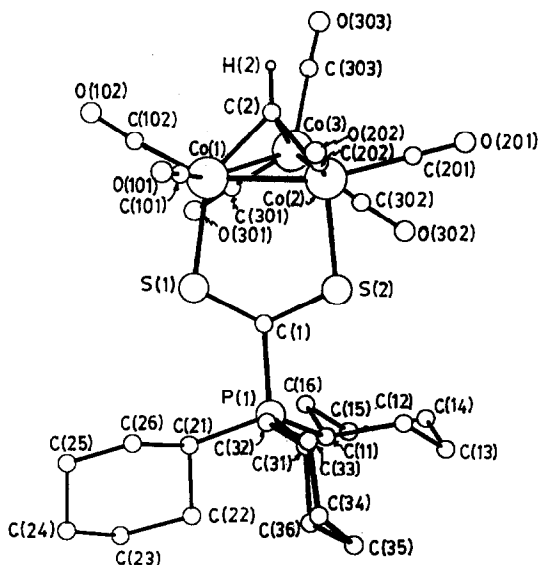


Fig. 1. Perspective view of the molecule of **2a**, showing the atom numbering. Hydrogen atoms of cyclohexyl rings have been omitted for clarity. Selected bond distances (Å) and angles (°): Co(1)–Co(2) 2.452(1), Co(1)–Co(3) 2.507(1), Co(2)–Co(3) 2.516(1), Co(1)–S(1) 2.253(2), Co(2)–S(2) 2.246(2), Co(1)–C(2) 1.870(8), Co(2)–C(2) 1.875(7), Co(3)–C(2) 1.894(8), C(1)–S(1) 1.672(6), C(1)–S(2) 1.670(6), S(2)–C(1)–S(1) 128.2(4), Co(1)–C(2)–Co(2) 81.8(3), Co(1)–C(2)–Co(3) 83.5(3), Co(2)–C(2)–Co(3) 83.8(3).

groups are replaced by poorer π -acceptors. This cannot apply to **2a**: the IR frequencies in a variety of compounds suggest that S_2CPR_3 is clearly a less good π -acceptor than dppm. On the other hand, the shortening of the bridged Co–Co bond in **2a** cannot be considered to be a consequence of geometrical restrictions imposed by the S_2CPCy_3 ligand, since in the structure of $[Re_2(CO)_8(\mu-S_2CPCy_3)]$ [9] there is a stable S_2CPCy_3 bridge spanning a Re–Re bonding distance of 2.987(1) Å. This suggests that a detailed study of the electronic structures of tricobalt alkylidyne clusters is needed.

Selected spectroscopic data. IR, $\nu(CO)$ (CH_2Cl_2 solutions, cm^{-1}), **2a**: 2049w, 2001s, 1982(sh). **2b**: 2050m, 2003s, 1982(sh). **2c**: 2062w, 2009s, 1989(sh). **2d**: 2062w, 2011s, 1991(sh). $^{31}P\{^1H\}$ NMR ($CDCl_3$ solutions, 121.5 MHz, δ , ppm to high frequencies from external 85% H_3PO_4), **2a**: 30.57; **2b**: 37.94; **2c**: 32.40; **2d**: 41.68.

Crystal and refinement data for compound 2a. $C_{28}H_{34}Co_3O_7PS_2$, $M = 742.46$, monoclinic, space group $P2_1/n$, $a = 17.651(4)$, $b = 13.421(7)$, $c = 13.270(2)$ Å, $\beta = 90.73(2)^\circ$, $V = 3143(2)$ Å³, $Z = 4$, $D_c = 1.56$ g cm^{-3} , $F(000)$ 1520, $\lambda(Mo)-(K\alpha)$ 0.71073 Å, $\mu = 17.69$ cm^{-1} , 293 K. Dark brown prismatic crystal (0.3 × 0.2 × 0.05 mm) grown by slow diffusion of hexane into a concentrated solution of the compound in CH_2Cl_2 . Intensities were collected on an Enraf–Nonius CAD4 diffractometer, using the ω – 2θ scan technique. 5510 reflections were measured in the range $0 \leq \theta \leq 25^\circ$; 2338 with $I \geq 3\sigma(I)$ were used in the refinement. An empirical (psi-scan based) absorption correction was applied [10]. Co, S, and P atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms from DIRDIF [11]. Full-matrix least-squares refinement was made with SHELX76 [12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atom of the methylidyne ligand was found in a difference Fourier map, and was isotropically refined. The remaining hydrogen atoms (in the cyclohexyl groups) were geometrically positioned, and were given an overall isotropic temperature factor which was refined. Final $R = 0.037$ ($R_w = 0.036$). Total number of parameters 366. Full lists of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters are available from the Cambridge Crystallographic Data Centre.

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