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[Bis(diphenylphosphino)methane][μ,η^2-bis(trimethylstannyl)acetylene]tetracarbonyldicobalt

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Key indicators

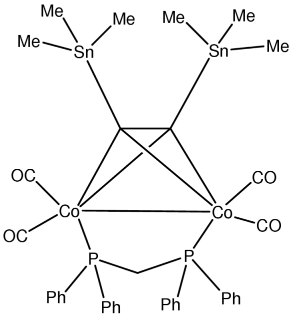
Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.008 Å
R factor = 0.036
wR factor = 0.105
Data-to-parameter ratio = 19.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Co_2(C_{25}H_{22}P_2)(C_8H_{18}Sn_2)(CO)_4]$, was prepared by displacement of two molecules of carbon monoxide in hexacarbonyldicobalt[μ,η^2-bis-(trimethylstannyl)]acetylene with a bidentate bis(diphenylphosphino)methane ligand. The displacement of carbon monoxide yields the product with substantially increased thermal stability and brings about noticeable changes in the geometry of the dicobaltatetrahedrane moiety, *viz*. lengthening of the carbon–carbon bond and shortening of the cobalt–cobalt and cobalt–carbon bonds.

Comment

The transformation of bis(trimethylstannyl)ethyne into a stannyl-substituted dicobaltatetrahedrane by treating it with dicobalt octacarbonyl ‘protects’ the carbon–carbon triple bond and thus, as expected, also stabilizes the bond between tin and the tetrahedrane moiety. Nevertheless, Stille-type palladium-catalysed carbon–carbon coupling reactions are still possible using activated organyl halides (Zavgorodnii *et al.*, 2000). However, unactivated organyl halides require more rigorous reaction conditions, under which the dicobaltatetrahedrane decomposes.



(I)

The title compound, (I), was thus prepared by displacing two molecules of carbon monoxide in hexacarbonyldicobalt[μ,η^2-bis-(trimethylstannyl)]acetylene (Seyferth & White, 1971; Zachwieja *et al.*, 2001) with bis(diphenylphosphino)methane, a procedure, which, according to literature precedent (Iwasawa & Hiroishi, 1999), should increase the thermal stability of the dicobaltatetrahedrane.

This prediction was correct, the decomposition temperature being increased by 80 K. The differences between the structures of the title compound (Fig. 1) and its carbonyl precursor are subtle: the carbon–carbon bond in the dicobaltatetrahedrane moiety increased in length from 1.309 (5) to 1.335 (5) Å, while the cobalt–cobalt bond contracted slightly

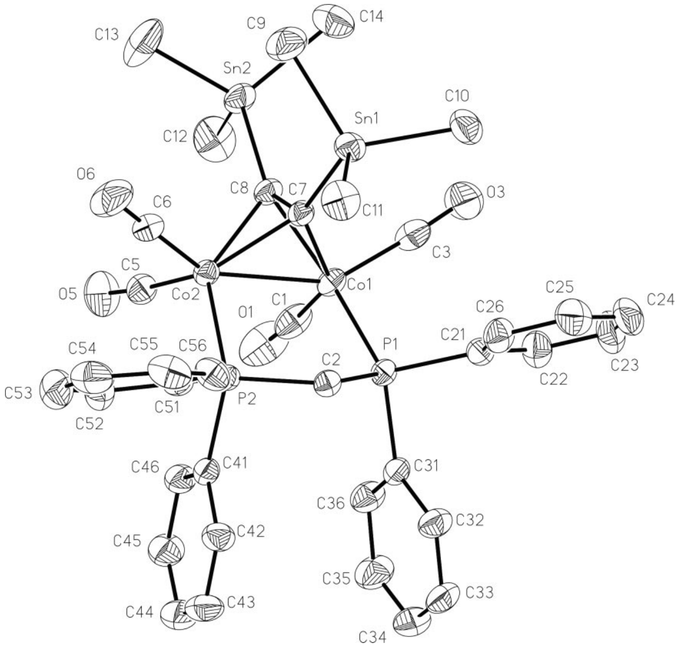


Figure 1
View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 30% probability level. H atoms are omitted for clarity.

from 2.5043 (9) to 2.4972 (8) Å. The cobalt–carbon bonds in the tetrahedrane moiety decreased in length quite considerably, lying between 1.968 (4) and 1.990 (4) Å, compared with 2.000 to 2.007 Å in the starting material.

These bond length changes also affect the bond angles in the dicobaltatetrahedrane moiety, particularly at the C(7) atom, where the Sn(1)—C(7)—C(8) angle decreases from 144.7 to 130.3 (3)°, while the Sn(2)—C(8)—C(7) angle remains almost unchanged at 145.3 (3) °. At the same time the angle Sn(1)—C(7)—Co(2) increases from 132.3° to 137.8 (2)°, while Sn(2)—C(8)—Co(1) decreases somewhat from 133.3 to 131.2 (2)°. This asymmetry in bond angles between C(7) and C(8) is reflected in the slightly asymmetric position of the diphosphinomethane moiety, the Co—P bond lengths being 2.2208 (12) and 2.2100 (12) Å respectively.

It is also noteworthy that the bonds between the Co atoms and the carbonyl-C atoms in the title compound are considerably shortened compared to the analogous bonds in the starting carbonyl complex (the corresponding average values are 1.770 Å and 1.798 Å).

Experimental

The compound was prepared by stirring hexacarbonyldicobalt[μ,η^2-bis-(trimethylstannyl)]acetylene (126 mg, 0.2 mmol) with 79 mg (0.2 mmol) of bis(diphenylphosphino)methane in 10 ml of dry hexane for 5 h under reflux in an inert atmosphere. It was separated by column chromatography (silica gel, hexane/benzene) as a black solid, m.p. 446 K, yield 116 mg (60%).

Crystal data

$C_{37}H_{40}Co_2O_4P_2Sn_2$
$M_r = 965.87$
Monoclinic, $P2_1/n$
$a = 16.012$ (3) Å
$b = 13.761$ (2) Å
$c = 18.126$ (4) Å
$\beta = 98.49$ (2)°
$V = 3950.1$ (13) Å^3
$Z = 4$

$D_x = 1.624$ Mg m^{-3}
Ag $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.8$–12.6°
$\mu = 1.15$ mm^{-1}
$T = 291$ (1) K
Plate, red-brown
0.35 × 0.35 × 0.10 mm

Data collection

Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (*WinGX*; Farrugia, 1999; North *et al.*, 1968)
$T_{\min} = 0.819$, $T_{\max} = 1.000$
8838 measured reflections
8572 independent reflections
5353 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.053$
$\theta_{\max} = 21.0°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.105$
$S = 0.99$
8572 reflections
430 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.054P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.10$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}

H atoms were placed in calculated positions with $U_{\rm iso}$ constrained to be 1.5 times $U_{\rm eq}$ of the carrier atom for the methyl–H and 1.2 times $U_{\rm eq}$ for the remaining H atoms. The highest peak in the final difference map is at a distance of 0.86 Å from Sn2.

Data collection: *CAD*-4 *Software* (Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms, 1996); program(s) used to solve structure: *SHELXS*-97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97, *PARST*95 (Nardelli, 1995).

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m534 Uwe Zachwieja *et al.* • $C_{37}H_{40}Co_2O_4P_2Sn_2$ *Acta Cryst.* (2001). E**57**, m533–m534