Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis[1,3-bis(trimethylsilyl)allyl]cobalt(II), a stable electron-deficient allyl complex

J. Dominic Smith,[a] Keith T. Quisenberry,[a] Timothy P. Hanusa[a]* and William W. Brennessel[b]

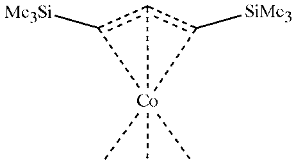
[a]Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA, and [b]Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA
Correspondence e-mail: t.hanusa@vanderbilt.edu

Received 10 August 2004
Accepted 16 August 2004
Online 18 September 2004

The title compound, bis[(1,2,3-η)-(2E)-1,3-bis(trimethylsilyl)prop-2-enyl]cobalt(II), [Co($C_9H_{21}Si_2$)$_2$], is a homoleptic allyl complex with η^3-bound ligands. The Co—C distances range from 1.996 (3) to 2.096 (3) Å and the allyl ligands adopt staggered, nearly parallel, arrangements around the Co atom. The trimethylsilyl groups are in *syn–anti* conformations; the steric shielding they provide to the metal is probably responsible for the thermal stability of the compound.

Comment

The only homoleptic allyl compound of cobalt to be characterized to date is the tris(allyl) species (C_3H_5)$_3$Co (Wilke *et al.*, 1966), which decomposes at 233 K and of which the structure is unknown. It is possible to increase the thermal stability of allyl compounds by using substituted ligands, and several bis(η^3-allyl)metal complexes of the first-row transition metals have been prepared with the bulky bis(1,3-trimethylsilyl)allyl ligand which have no counterparts with unsubstituted ligands, such as [η^3-1,3-($SiMe_3$)$_2C_3H_3$]$_2$Cr and [η^3-1,3-($SiMe_3$)$_2C_3H_3$]$_2$Fe (Smith *et al.*, 2001). We have found that this ligand also effectively stabilizes a compound with cobalt. Specifically, the title compound, (I), a formally 15-electron species, [1,3-($SiMe_3$)$_2C_3H_3$]$_2$Co, can be isolated as an air- and moisture-sensitive solid (m.p. 346 K) which is far more thermally robust than (C_3H_5)$_3$Co. We present here the structure of (I).



(I)

Compound (I) forms yellow–orange crystals and the complex crystallizes as a monomer with approximate C_2 symmetry. The two substituted allyl ligands are arranged about the metal in a staggered configuration (Fig. 1), with an angle between the C_3 allyl planes of 5.5 (5)°. The ligands are bound in a η^3 manner to the Co center, with Co—C bond lengths varying from 1.996 (3) to 2.096 (3) Å (Table 1). The $SiMe_3$ groups are in a *syn–anti* arrangement on each allyl ligand, similar to the situation in [η^3-1,3-($SiMe_3$)$_2C_3H_3$]$_2$Cr and [η^3-1,3-($SiMe_3$)$_2C_3H_3$]$_2$Fe (Smith *et al.*, 2001). The *anti* Si atoms display large displacements out of the C_3 allyl plane, with torsion angles of 39.2 (4) (C1—C2—C3—Si3) and 41.8 (4)° (Si3—C4—C5—C6). The *syn* Si atoms, in contrast, lie much closer to the allyl planes [Si1—C1—C2—C3 = 175.3 (2)° and C4—C5—C6—Si4 = 178.2 (2)°]. There is a slight lateral shift of the allyl ligands, with the C atoms bearing the *syn* $SiMe_3$ groups (atoms C1 and C6) further from the metal [2.091 (3) and 2.096 (3) Å, respectively] than those with the *anti* $SiMe_3$ groups [atoms C3 and C4 at 2.046 (3) and 2.050 (3) Å, respectively]. This slippage pattern also exists in the Cr and Fe counterparts.

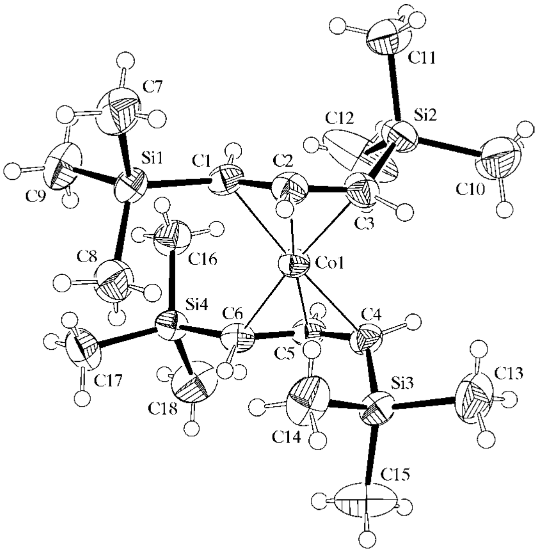


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The range of bond distances in (I) is somewhat larger than the range of 1.918–1.948 Å observed in the cobalt(II) compound (η^3-C_3H_5)(η^5-Me_5C_5)Co (Nehl, 1993), for example, which suggests that steric encumbrance from the allyl ligands may be contributing to bond lengthening. Nevertheless, there is no evidence for agostic interactions (Brookhart & Green, 1983) with the H atoms of the ligand $SiMe_3$ groups and the metal. There are also no intramolecular Me$\cdots$Me contacts closer than the sum of their van der Waals radii (4.0 Å; Pauling, 1960).

Experimental

Under a nitrogen atmosphere, $CoCl_2$ (0.500 g) was dissolved in tetrahydrofuran (THF; 10 ml) and cooled to 195 K. A solution of

DOI: 10.1107/S0108270104020293

K[1,3-$(SiMe_3)_2C_3H_3$] (1.725 g; Harvey *et al.*, 1999) dissolved in THF (15 ml) was added dropwise with stirring over 30 min. The dark-red mixture was then allowed to warm slowly to room temperature with stirring. The THF was removed under vacuum and the residue extracted with small portions (5 ml) of hexanes. The extract was filtered and the solvent removed from the filtrate under vacuum. The resulting nearly black oil crystallized over several days to yield yellow–orange crystals of (I) (1.23 g, 75% yield, m.p. 346 K). Analysis calculated for $C_{18}H_{42}CoSi_4$: C 50.30, H 9.85%; found: C 50.30, H 9.81%. Principle IR bands (KBr, ν, cm^{-1}): 2955 (*s*), 2899 (*m*), 2366 (*w*), 1698 (*w*), 1449 (*m*), 1400 (*w*), 1248 (*s*), 1028 (*s*), 1009 (*s*), 843 (*s*), 800 (*s*), 715 (*w*), 549 (*w*), 478 (*br*, *w*). Magnetic moment (toluene-d_8): $\mu = 1.7 \times 10^{-23}$ A m^2 at 298 K. The compound sublimes at 323 K under reduced pressure (10^{-2} Torr; 1 Torr = 133.322 Pa) and is soluble in ethers and hydrocarbons.

Crystal data

$[Co(C_9H_{21}Si_2)_2]$
$M_r = 429.81$
Monoclinic, $P2_1/c$
$a = 12.341$ (1) Å
$b = 10.3381$ (9) Å
$c = 21.024$ (2) Å
$\beta = 99.371$ (2)°
$V = 2646.5$ (4) $Å^3$
$Z = 4$
$D_x = 1.079$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3337 reflections
$\theta = 1.7$–25.1°
$\mu = 0.83$ mm^{-1}
$T = 173$ (2) K
Block, orange
0.31 × 0.24 × 0.16 mm

Data collection

Siemens SMART Platform CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{min} = 0.767$, $T_{max} = 0.876$
25 453 measured reflections
4688 independent reflections
4033 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 25.1°$
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.111$
$S = 1.02$
4688 reflections
244 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 1.7528P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.11$ e $Å^{-3}$
$\Delta\rho_{min} = -0.30$ e $Å^{-3}$

Methyl H atoms were placed in ideal positions and further refined as rigid groups allowed to rotate but not tip. The H atoms on atoms C1–C6 were found from a difference electron-density map and allowed to refine freely. A residual peak of 1.1 e $Å^{-3}$ was found at slightly less than 1 Å from the Co atom, possibly because of residual absorption errors or Fourier termination errors. Atoms C10 and C12 show somewhat high U_{eq} values, but the use of a disorder model did not significantly improve the refinement.

Table 1
Selected geometric parameters (Å, °).

Co1—C1	2.091 (3)	Co1—C6	2.096 (3)
Co1—C2	1.996 (3)	C1—C2	1.421 (4)
Co1—C3	2.046 (3)	C2—C3	1.407 (4)
Co1—C4	2.050 (3)	C4—C5	1.419 (4)
Co1—C5	2.006 (3)	C5—C6	1.407 (4)
C3—C2—C1	124.5 (3)	C6—C5—C4	123.3 (2)

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

The Petroleum Research Fund of the American Chemical Society is thanked for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1658). Services for accessing these data are described at the back of the journal.

References

Blessing, R. (1995). *Acta Cryst.* A**51**, 33–38.
Brookhart, M. & Green, M. L. H. (1983). *J. Organomet. Chem.* **250**, 395–408.
Bruker (1998). *SHELXTL-Plus.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT.* Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SMART.* Version 5.618. Bruker AXS Inc., Madison, Wisconsin, USA.
Harvey, M. H., Hanusa, T. P. & Young, V. G. Jr (1999). *Angew. Chem. Int. Ed.* **38**, 217–219.
Nehl, H. (1993). *Chem. Ber.* **126**, 1519–1527.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 261. Ithaca: Cornell University Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Smith, J. D., Hanusa, T. P. & Young, V. G. Jr (2001). *J. Am. Chem. Soc.* **123**, 6455–6456.
Wilke, G., Bogdanovic, B., Hardt, P., Heimbach, P., Keim, W., Kroner, M., Oberkirch, W., Tanaka, K. & Walter, D. (1966). *Angew. Chem. Int. Ed. Engl.* **5**, 151–164.