

Bis{1,4-bis(trimethylsilyl)buta-1,3-diene}cobalt: synthesis and molecular structure

F. Geoffrey N. Cloke ^{a,*}, Michael G. Gardiner ^b, Colin L. Raston ^b, Steven J. Simpson ^c

^a School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

^b Faculty of Science and Technology, Griffith University, Nathan, Brisbane, Queensland 4111, Australia

^c Department of Chemistry and Applied Chemistry, University of Salford, Salford M54 4WT, UK

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Abstract

Co-condensation of cobalt atoms with an excess of (*E,E*)-1,4-bis(trimethylsilyl)buta-1,3-diene in hexane at -196°C yields the homoleptic bis(butadiene) complex $[\text{Co}(\eta\text{-C}_4\text{H}_4(\text{SiMe}_3)_2)_2]$ (**1**) as the sole volatile product. Compound **1** was characterized by ^1H NMR and EPR spectroscopy, mass spectrometry and a single-crystal X-ray structure determination.

Keywords: Cobalt; Butadiene; Metal vapour synthesis; Crystal structure

1. Introduction

The strategy of using ligands with bulky substituents to impart stability to coordinatively and/or electronically unsaturated organometallic and coordination compounds is well established, and the role of the trimethylsilyl group in this regard is particularly noteworthy. Extension of this general approach to the synthesis of homoleptic butadiene complexes has recently been established in our report of stable “sandwich” compounds derived from 1,4-di-*tert*-butylbuta-1,3-diene, of the type $[\text{M}(\eta\text{-C}_4\text{H}_4^t\text{Bu}_2)_2]$, $\text{M} = \text{Ti}, \text{V}, \text{Co}$ [1,2]. Reports of the synthesis of substituted butadienes bearing $-\text{SiMe}_3$ substituents include, for example, 1,4- and 2,3-bis(trimethylsilyl)buta-1,3-diene [3] and 1,1,4,4-tetrakis(trimethylsilyl)buta-1,3-diene [4], but their low yield and irreproducible syntheses have precluded examination of their potential as ligands to date.

We recently described the facile, reliable synthesis of (*E,E*)-1,4-bis(trimethylsilyl)buta-1,3-diene [5] and a number of Main Group 1, 2 and 13 metal derivatives of this ligand [5,6], (*E,E*)-1,4-Bis(trimethylsilyl)buta-1,3-diene should also have good potential for stabilizing novel complexes in d-block chemistry, given the effect

that bis(trimethylsilyl) substitution of the related dimethylated *o*-xylene ligand has had on developing the transition metal chemistry [7] of that system and the parallel between the two systems.

Herein we describe some transition metal chemistry of (*E,E*)-1,4-bis(trimethylsilyl)buta-1,3-diene as an extension to our investigations into the behaviour of 1,4-di-*tert*-butylbuta-1,3-diene complexes of the first-row transition metals [1,2]. Reported is the synthesis and molecular structure of the homoleptic bis(butadiene) cobalt complex $[\text{Co}(\eta\text{-C}_4\text{H}_4(\text{SiMe}_3)_2)_2]$ (**1**), obtained as the sole volatile product from the co-condensation of cobalt atoms with an excess of (*E,E*)-1,4-bis(trimethylsilyl)buta-1,3-diene at -196°C .

2. Experimental section

2.1. General procedures

All manipulations were carried out using standard Schlenk and glove-box techniques under high-purity argon or nitrogen. Solvents were dried, distilled and degassed prior to use by conventional procedures. Celite 545 filter aid was dried in an oven at 200°C . (*E,E*)-1,4-Bis(trimethylsilyl)buta-1,3-diene was prepared as described previously [5]. The metal vapour synthesis apparatus was of a previously described design [8]. ^1H NMR

* Corresponding author.

spectra were recorded on a Bruker WM-360 spectrometer in deuterated benzene and referenced to the residual ^1H resonance of the solvent. Elemental analyses were performed by Canadian Microanalytical Services (Vancouver, Canada). Melting points were determined in sealed glass capillaries under nitrogen. EPR spectra were recorded on a Varian E104A spectrometer. Polycrystalline 2,2'-diphenylpicrylhydrazine (DPPH) was used as an external standard for the calibration of g_{av} values. Mass spectra were recorded on a Kratos MS80RF spectrometer using electron impact (EI) ionization operating at 70 eV.

2.2. Synthesis of $[\text{Co}\{\eta\text{-C}_4\text{H}_4(\text{SiMe}_3)_2\}_2]$ (1)

Electron-beam vaporized cobalt (1.55 g, 26.3 mmol) was co-condensed with an excess of the ligand (16.0 g, 80.6 mmol) in hexane (30 cm³) at 77 K, over a period of 3 h. The liquid nitrogen was drained off and, after warming to room temperature under dinitrogen, the products were extracted from the reactor by washing with pentane (750 cm³). The resultant solution was then filtered through a Celite bed supported on a frit and the solvent was removed under reduced pressure to leave a thick brown oil. The excess of the ligand was removed by sublimation (50°C/10⁻⁵ mbar). The residue was then transferred to a horizontal sublimation tube and deep-brown crystals of the product (1.23 g, 10.2% based on cobalt) sublimed out at 80°C/10⁻⁵ mbar. The sublimed product may be recrystallized from concentrated pentane solutions at -30°C with difficulty; m.p. 119–120°C. ^1H NMR (360 MHz, C₆D₆): δ 0.83, 0.34 (2 × 18 H, broad, $w_{1/2} \approx 100$ Hz, Me); EPR (297 K, C₆H₆): $g_{\text{av}} = 2.171$, $w_{1/2} \approx 200$ G; MS: m/z 456 (M⁺, 18%). Anal. Found C 52.59, H 9.96%; Calc. C 52.70, H 9.73%.

2.3. Structure determination for compound 1

C₂₀H₄₄Si₄Co, $M = 455.84$, monoclinic, space group C2/c (No. 15), $a = 18.438(3)$ Å, $b = 15.804(9)$ Å, $c = 13.556(3)$ Å, $\beta = 134.49(1)^\circ$, $U = 2818(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.074$ g cm⁻³, $F(000) = 988$. Monochromated Cu K α radiation, $\lambda = 1.54178$ Å, $\mu = 66.76$ cm⁻¹.

A crystal of 1, 0.30 × 0.12 × 0.30 mm, suitable for X-ray structure determination, was grown by sublimation at 80°C (10⁻⁵ mbar) and mounted in a sealed capillary under argon. Data were collected on a Rigaku AFC5R diffractometer at 295 K in the $\omega/2\theta$ mode ($2\theta_{\text{max}} = 120.2^\circ$) with a scan width of (0.84 + 0.30 tan θ)° and a scan rate of 8.0° min⁻¹. A total of 2194 unique reflections ($R_{\text{int}} = 0.068$) were measured, and 1164 reflections with $I > 3.0\sigma(I)$ were used in the full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$. Data were corrected for Lorentz

polarization, decay (-5%) and absorption (ψ scans) effects. The structure was solved by direct methods using the TEXSAN package of the Molecular Structure Corp. [9]. Neutral-atom complex scattering factors were employed [10]. The ORTEP-II program was used for the molecular projection diagram [11]. Anisotropic thermal parameters were refined for all non-hydrogen atoms in the structure determination. Hydrogen atom positions were calculated and constrained at estimated values (C-H 0.95 Å). Temperature factors for hydrogen atoms were estimated at $1.2 \times U_{ii}$ (average) of the attached carbon atom. A packing disorder of one of the trimethylsilyl substituents was apparent in Fourier maps, and was modelled as a population-constrained 50:50 site occupancy disorder with both methyl orientations refined anisotropically. The final residuals were $R = 0.060$ and $R_w = 0.062$, and a final difference map had extreme values of +0.38 and -0.31 e Å⁻³. Non-hydrogen atom coordinates and isotropic thermal parameters are presented in Table 1 and selected structural parameters are given in Table 2. Tables of hydrogen atom coordinates and thermal parameters, and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Synthesis and characterization

Co-condensation of cobalt atoms with an excess of (*E,E*)-1,4-bis(trimethylsilyl)buta-1,3-diene in hexane at -196°C yielded a black-brown solution, which, after removal of solvent and excess of the ligand, afforded brown-black crystals of the title compound as the only

Table 1
Non-hydrogen atom coordinates and isotropic thermal parameters for $[\text{Co}\{\eta\text{-C}_4\text{H}_4(\text{SiMe}_3)_2\}_2]$ (1)

Atom	x	y	z	B_{eq} (Å ²) ^a
Co(1)	0.5	0.0922(1)	0.25	3.99(7)
Si(1)	0.5586(2)	0.2548(2)	0.1324(2)	6.0(1)
Si(2)	0.2773(2)	-0.0473(2)	0.0724(2)	6.5(1)
C(1)	0.3497(5)	0.0363(5)	0.0768(7)	5.0(3)
C(2)	0.4229(6)	0.0204(5)	0.0746(7)	5.1(3)
C(3)	0.4835(5)	0.0871(5)	0.0880(6)	5.0(3)
C(4)	0.4726(5)	0.1721(5)	0.1002(7)	4.9(3)
C(5)	0.3539(8)	-0.1442(7)	0.163(1)	11.7(7)
C(6)	0.1647(7)	-0.0728(7)	-0.110(1)	10.0(5)
C(7)	0.2354(9)	-0.0103(8)	0.155(1)	12.9(8)
C(8a)	0.616(2)	0.217(2)	0.067(3)	11(1)
C(8b)	0.683(2)	0.210(2)	0.220(4)	15(2)
C(9a)	0.481(2)	0.349(2)	0.032(3)	12(2)
C(9b)	0.502(2)	0.303(2)	-0.028(3)	12(2)
C(10a)	0.664(2)	0.284(2)	0.311(2)	8(1)
C(10b)	0.584(3)	0.341(2)	0.250(4)	15(2)

^a Isotropic equivalent thermal parameters.

Table 2
Selected structural parameters for $[\text{Co}(\eta\text{-C}_4\text{H}_4(\text{SiMe}_3)_2)]$ (**1**)

<i>Bond distances (Å)</i>					
Co(1)–C(1)	2.203(7)	C(3)–C(4)	1.385(9)	Si(1)–C(10a)	1.80(2)
Co(1)–C(2)	2.056(6)	Si(1)–C(4)	1.855(7)	Si(1)–C(10b)	1.89(2)
Co(1)–C(3)	1.997(6)	Si(1)–C(8a)	1.88(2)	Si(2)–C(1)	1.849(7)
Co(1)–C(4)	2.130(7)	Si(1)–C(8b)	1.83(2)	Si(2)–C(5)	1.85(1)
C(1)–C(2)	1.394(9)	Si(1)–C(9a)	1.84(3)	Si(2)–C(6)	1.849(9)
C(2)–C(3)	1.453(9)	Si(1)–C(9b)	1.80(3)	Si(2)–C(7)	1.838(1)
<i>Bond angles (°)</i>					
C(1)–Co(1)–C(4)		86.6(3)	Si(2)–C(1)–C(2)		123.9(6)
C(1)–Co(1)–C(1) ^a		132.7(4)	C(1)–C(2)–C(3)		122.5(7)
C(1)–Co(1)–C(4) ^a		122.3(3)	C(2)–C(3)–C(4)		123.8(7)
C(4)–Co(1)–C(4) ^a		107.3(4)	Si(1)–C(4)–C(3)		122.7(6)

^a Denotes symmetry operator (1 – x, y, 1/2 – z).

volatile product on sublimation (see Scheme 1). The formulation of the homoleptic bis(butadiene) complex was confirmed by microanalysis and an X-ray structure determination, which revealed a monomeric open sandwich structure in the solid state (see below). The complex exhibits a molecular ion peak in its EI mass spectrum in addition to mass fragments corresponding to the loss of Me, SiMe₃ and (Me₃Si)₂C₄H₄ from the molecular ion.

The ¹H NMR spectrum of the paramagnetic complex **1** in the spectral range –200 to 200 ppm exhibits two broad resonances of equal intensity at 0.83 and 0.34 ppm ($w_{1/2} \approx 100$ Hz) assigned to the trimethylsilyl protons of the complex. This is consistent with the pseudo-tetrahedral coordination of the open sandwich structure found in the solid state (see below) being retained in solution. Similar behaviour has been seen for the diamagnetic titanium analogue, $[\text{Ti}(\eta\text{-C}_4\text{H}_4^t\text{Bu}_2)_2]$, whose ¹H NMR spectrum exhibits two chemically distinct tert-butyl proton resonances, the vinylic protons displaying an AA'XX' spin system [2]. For **1**, presumably the proximity of the paramagnetic metal centre to the vinylic protons further broadens those resonances, making them indistinguishable from the baseline. The room-temperature solution EPR spectrum of **1** exhibits a single, broad, featureless singlet ($g_{\text{av}} = 2.171$, $w_{1/2} \approx 200$ G).

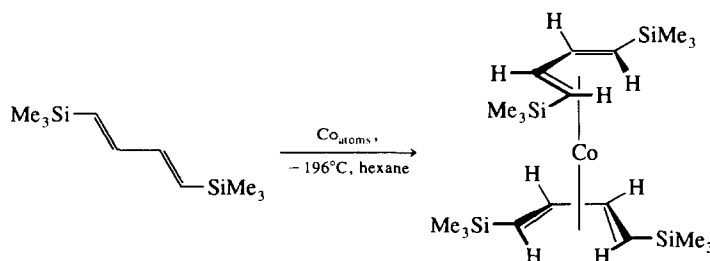
Compound **1** is stable in the solid state for several months under argon and displays only moderate air sensitivity in the solid state or in solution. In benzene solution, **1** decomposes only slowly. Sealed C₆D₆ NMR

solutions free of oxygen/water show only traces of free (*E,E*)-1,4-bis(trimethylsilyl)buta-1,3-diene after several weeks. The tert-butyl analogue of **1**, $[\text{Co}(\eta\text{-C}_4\text{H}_4^t\text{Bu}_2)_2]$, readily undergoes ligand substitution reactions, effectively acting as a source of Co(0) in its reactions [1]. The reactivity of **1** has not yet been investigated.

3.2. Structure determination for compound **1**

The crystal structure determination showed the compound to be monomeric, the structure having been solved by direct method routines. The complex crystallizes as prismatic crystals in the monoclinic space group *C*2/*c* (No. 15) with four molecules in the unit cell, the asymmetric unit containing one half of the molecule of *C*₂ symmetry (see Fig. 1). Selected bond distances and angles are listed in Table 2. The compound is the first neutral homoleptic butadiene complex of a the first-row transition metal.

The structure of **1** can be described as bis- π^2 open metallocene, or butadiene sandwich structure with a pseudo-tetrahedral coordination environment for the cobalt centre (considering the metal–ligand interaction to be through the double bonds of the 1,3-diene). The presence of this rotamer is presumably the result of lower steric repulsion between the trimethylsilyl substituents in this conformation, and this can also account for the small tilt angle between the two diene ligand planes (defined by C1, C2, C3 and C4) of 11.3°. In the related anionic complex $[\text{Co}(\eta\text{-C}_4\text{H}_4^t\text{Bu}_2)_2]^-$ [1], the



Scheme 1.

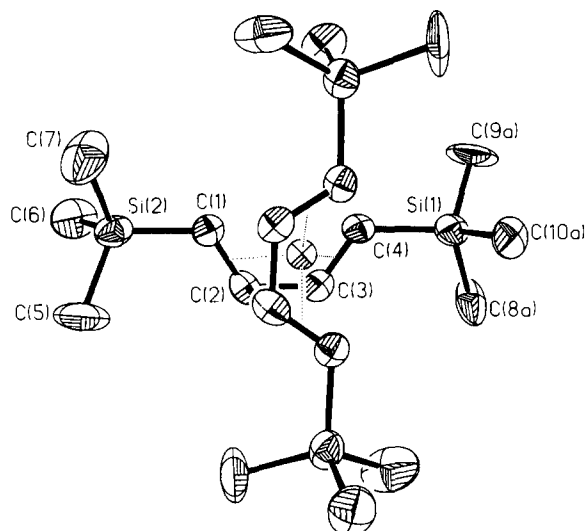


Fig. 1. ORTEP [11] diagram of $[\text{Co}(\eta\text{-C}_4\text{H}_4(\text{SiMe}_3)_2)_2]$ (**1**) showing atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level. For clarity the hydrogens are shown as spheres of arbitrary radii and one orientation of the disordered trimethylsilyl group is shown.

bulky substituents are similarly disposed about the metal centre in a tetrahedral arrangement, although the tilting of the ligand planes differs somewhat in those cases, and is unaccounted for at present. The C–C bond distances for **1** are typical for late transition metal–diene complexes, varying in the order short–long–short for C1–C2 (1.394(9) Å), C2–C3 (1.453(9) Å) and C3–C4 (1.385(9) Å). The trimethylsilyl substituents lie close to the plane defined by atoms C1–C4. The Co–C distances to the 2 and 3 positions are significantly shorter (average 2.03 Å) than those to the terminal 1 and 4 positions (average 2.17 Å). The difference between these Co–C distances 0.14 Å, compares with that in the closely related anionic complex $[\text{Co}(\eta\text{-C}_4\text{H}_4^t\text{Bu}_2)_2]^-$, 0.15 Å [1]. The Co–C distances in $[\text{Co}(\eta\text{-C}_4\text{H}_4^t\text{Bu}_2)_2]^-$ are not significantly different from those observed for **1** (Co–C_{1,4}(average) = 2.15 Å; Co–C_{2,3}(average) = 2.00 Å). The ligand bite angle θ_1 (the angle subtended at the metal centre by the mid-

points of the ligand double bonds) of 67.9° in **1** is comparable to those in other late transition metal–butadiene complexes [12].

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