Crystal structure of bis(η^3 -2-*tert*-butyl-3-*N,N*-dimethyl-1-*o*-tolyl-1-trimethylsilyl-1-azaallyl)cobalt(II), $\text{Co}[\text{CH}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)(\text{CCMe}_3)\text{N}(\text{SiMe}_3)]_2$

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Abstract

$\text{C}_{36}\text{H}_{62}\text{CoN}_4\text{Si}_2$, monoclinic, $P12_1/n1$ (no. 14), $a = 9.339(3)$ Å, $b = 18.914(7)$ Å, $c = 11.394(5)$ Å, $\beta = 95.976(4)^\circ$, $V = 2001.7$ Å³, $Z = 2$, $R_g(F) = 0.047$, $wR_{\text{ref}}(F^2) = 0.125$, $T = 273$ K.

Source of material

$t\text{-BuCN}$ (0.66 ml, 6.00 mmol) was added *via* a syringe to a yellow clear solution of $[\text{LiL}(\text{TMEDA})]$ ($\text{L} = \text{Me}_2\text{NCH}_2\text{-}o\text{-C}_6\text{H}_4\text{CH-SiMe}_3$, 2.07 g, 6.00 mmol) in diethyl ether (ca. 30 cm³) at 0 °C. The resulting mixture was stirred for 6 h at room temperature. Then CoCl_2 (0.39 g, 3.00 mmol) was added to a yellow solution at -78 °C. The resulting mixture was warmed up slowly to room temperature and stirred for 14 h. The white precipitate was filtered off. The filtrate was concentrated to 10 cm³ in vacuo and stored at room temperature yielding block-like red crystals of the title compound (0.98 g, 49 %).

Discussion

1-Azaallyl ligands can play the role of spectator ligands by virtue of their strong binding ability to metals, their exceptional and tunable steric demands, and their diverse bonding modes [1]. The crystal structure of the title compound revealed that it is a homoleptic metal- η^3 -azaallyl complex, which has a center of symmetry. It contains two azaallyl ligands bound in an $\eta^3\text{-N,C,C}$ mode to the Co atom which lies on an inversion center. The 1-

azaallyl group is bonded to Co atom in an $\eta^3\text{-N,C,C}$ mode, not in the κ^1 -enamido fashion [1–3], which contains an enlarged π -conjugation formed by an aryl ring and an η^3 -azaallyl group [4]. A significant feature of the title compound is that the central Co—C9 bond [2.038(2) Å] in the $\eta^3\text{-N,C,C}$ mode is slightly shorter than the terminal Co—C8 bond [2.099(3) Å], which can be explained as a steric hindrance effect. The ligand forms a non-planar four-membered ring (N1—C8—C9—Co). The dihedral angle between the N1—C8—Co and C8—C9—Co planes is $47.9(6)^\circ$. Although the C and N atoms of the azaallyl group are sp^2 hybridized and involved in a conjugated system, the N1—C9 bond (1.363(4) Å) has double-bond character.

Table 1. Data collection and handling.

Crystal:	red block, size $0.40 \times 0.40 \times 0.50$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	5.16 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{\text{max}}$:	50.02°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8132, 3534
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2704
$N(\text{param})_{\text{refined}}$:	208
Programs:	SHELXS-97 [5], SHELXL-97 [6], ORTEP [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	4e	0.3919	0.2797	−0.0956	0.069
H(1B)	4e	0.3333	0.2024	−0.0887	0.069
H(3)	4e	0.6315	0.2928	−0.1089	0.073
H(4)	4e	0.8706	0.2599	−0.0795	0.085
H(5)	4e	0.9315	0.1581	0.0247	0.084
H(6)	4e	0.7564	0.0862	0.0868	0.067
H(11A)	4e	0.1546	0.0784	0.2568	0.141
H(11B)	4e	0.1751	0.0593	0.1257	0.141
H(11C)	4e	0.2441	0.1284	0.1825	0.141
H(12A)	4e	0.3401	0.0664	0.4096	0.180
H(12B)	4e	0.4429	0.1166	0.3479	0.180
H(12C)	4e	0.4949	0.0407	0.3884	0.180
H(13A)	4e	0.3949	−0.0642	0.2816	0.169
H(13B)	4e	0.2822	−0.0552	0.1707	0.169
H(13C)	4e	0.2366	−0.0413	0.2973	0.169
H(14A)	4e	0.1503	0.2876	0.1151	0.151
H(14B)	4e	0.1316	0.2404	0.0014	0.151
H(14C)	4e	0.1825	0.3191	−0.0066	0.151
H(15A)	4e	0.4202	0.3512	0.0828	0.123
H(15B)	4e	0.5180	0.2929	0.1478	0.123
H(15C)	4e	0.3793	0.3188	0.2014	0.123
H(16A)	4e	0.8301	0.0638	0.3233	0.129
H(16B)	4e	0.8869	−0.0006	0.4014	0.129

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(16C)	4e	0.7350	0.0317	0.4156	0.129
H(17A)	4e	0.8236	-0.1008	0.0919	0.083
H(17B)	4e	0.9412	-0.0887	0.1985	0.083
H(17C)	4e	0.8955	-0.0263	0.1121	0.083

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(18A)	4e	0.5983	-0.1091	0.3801	0.116
H(18B)	4e	0.7364	-0.1498	0.3506	0.116
H(18C)	4e	0.5972	-0.1506	0.2609	0.116
H(8)	4e	0.383(3)	0.122(1)	0.062(2)	0.033(7)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co	2c	½	0	0	0.0314(3)	0.0285(3)	0.0311(3)	0.0010(2)	0.0046(2)	-0.0012(2)
N(1)	4e	0.5891(2)	0.0032(1)	0.1553(2)	0.036(1)	0.039(1)	0.033(1)	0.0001(9)	0.0003(9)	-0.005(1)
N(2)	4e	0.3371(2)	0.2546(1)	0.0641(3)	0.037(1)	0.042(2)	0.103(2)	0.005(1)	0.013(1)	-0.004(2)
Si	4e	0.71887(8)	-0.04148(5)	0.24528(7)	0.0445(4)	0.0575(5)	0.0383(4)	0.0042(4)	-0.0055(3)	0.0003(4)
C(1)	4e	0.3946(3)	0.2376(2)	-0.0470(3)	0.049(2)	0.043(2)	0.077(2)	-0.008(1)	-0.008(2)	0.017(2)
C(2)	4e	0.5481(3)	0.2097(2)	-0.0304(2)	0.047(2)	0.038(2)	0.049(2)	-0.007(1)	0.008(1)	-0.001(1)
C(3)	4e	0.6563(3)	0.2509(2)	-0.0693(3)	0.064(2)	0.044(2)	0.076(2)	-0.011(2)	0.015(2)	0.010(2)
C(4)	4e	0.7999(3)	0.2318(2)	-0.0513(3)	0.058(2)	0.059(2)	0.100(3)	-0.017(2)	0.033(2)	0.002(2)
C(5)	4e	0.8353(3)	0.1709(2)	0.0091(3)	0.042(2)	0.053(2)	0.120(3)	-0.004(2)	0.027(2)	-0.003(2)
C(6)	4e	0.7296(3)	0.1279(2)	0.0472(3)	0.041(2)	0.039(2)	0.090(2)	-0.002(1)	0.017(2)	0.002(2)
C(7)	4e	0.5830(3)	0.1455(1)	0.0278(2)	0.039(1)	0.034(1)	0.046(2)	-0.004(1)	0.012(1)	-0.010(1)
C(8)	4e	0.4668(3)	0.1012(1)	0.0679(2)	0.033(1)	0.030(1)	0.044(2)	0.000(1)	0.009(1)	-0.003(1)
C(9)	4e	0.4759(3)	0.0486(1)	0.1564(2)	0.040(1)	0.036(1)	0.034(1)	-0.005(1)	0.007(1)	-0.009(1)
C(10)	4e	0.3559(3)	0.0394(2)	0.2389(2)	0.046(2)	0.047(2)	0.042(2)	-0.002(1)	0.015(1)	-0.000(1)
C(11)	4e	0.2199(3)	0.0801(3)	0.1971(3)	0.054(2)	0.148(4)	0.085(3)	0.023(2)	0.038(2)	0.038(3)
C(12)	4e	0.4136(5)	0.0684(3)	0.3568(3)	0.098(3)	0.209(6)	0.060(2)	-0.036(3)	0.037(2)	-0.057(3)
C(13)	4e	0.3135(5)	-0.0373(2)	0.2480(5)	0.124(4)	0.058(2)	0.174(5)	-0.002(2)	0.107(4)	0.016(3)
C(14)	4e	0.1876(3)	0.2774(2)	0.0416(4)	0.045(2)	0.065(3)	0.193(5)	0.011(2)	0.014(2)	0.004(3)
C(15)	4e	0.4207(4)	0.3090(2)	0.1296(3)	0.068(2)	0.069(2)	0.110(3)	-0.000(2)	0.019(2)	-0.029(2)
C(16)	4e	0.8030(4)	0.0210(2)	0.3605(3)	0.076(2)	0.112(3)	0.065(2)	0.000(2)	-0.019(2)	-0.028(2)
C(17)	4e	0.8623(3)	-0.0675(2)	0.1504(3)	0.042(2)	0.061(2)	0.063(2)	0.009(1)	-0.001(1)	0.006(2)
C(18)	4e	0.6549(4)	-0.1227(2)	0.3181(3)	0.075(2)	0.090(3)	0.066(2)	0.013(2)	0.006(2)	0.031(2)

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