N2—Cu—N1	80.97 (12)	C7—N3—N6	129.9 (3)
N1—Cu—F2	92.13 (13)	C7—N4—N2	106.1 (3)
N2—Cu—F2	87.29 (11)	C12—N5—C8	116.8 (4)
C1—N1—C5	117.7 (3)	N1—C5—C6	110.9 (3)
C5—N1—Cu	115.0 (2)	N2—C6—N3	109.1 (3)
C6—N2—N4	109.2 (3)	N2—C6—C5	119.3 (3)
C6—N2—Cu	113.8 (2)	N4—C7—N3	109.8 (3)
C6—N3—C7	105.8 (3)	N4—C7—C8	124.9 (3)
C6—N3—N6	124.0 (3)	N3—C7—C8	125.3 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—HN1···N5	0.82	2.24	2.859 (5)	132
N6—HN2···F3^{i}	0.84	2.45	3.096 (6)	135
N6—HN2···F4^{i}	0.84	2.71	3.376 (6)	138

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

The title structure was solved by the heavy-atom method. Amine H atoms were located from a difference synthesis. All other H atoms were included in calculated positions (C—H 0.93 Å) and displacement parameters were fixed at $1.2U_{\rm iso}$ of the bound atom.

Data collection: *SHELXTL-Plus* (Sheldrick, 1990*b*). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1995). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1212). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Chelate-Stabilized Tungsten–Imido–Monoalkyl Complex, $[WCl(PhN)(CH_2CMe_3)\{o\text{-}C_6H_4(NSiMe_3)_2\}]$

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Abstract

The title compound, [*N*,*N*′-bis(trimethylsilyl)-*o*-phenylenediamido-*N*,*N*′](chloro)(neopentyl)(phenylimido-*N*)-tungsten(VI), $[WCl(C_5H_{11})(C_6H_5N)(C_{12}H_{22}N_2Si_2)]$, has been synthesized and its crystal structure determined. The geometry around the W atom, imposed by the bidentate *o*-phenylenediamido ligand and the bulky neopentyl ligand, is that of a distorted trigonal bipyramid. A relatively short W—N(imido) bond length of 1.741 (4) Å is interpreted as arising from the interaction of the lone pair of electrons on the imido N atom and the tungsten metal center.

Comment

Recently, the chemistry of high oxidation state metal–alkyl complexes has been studied extensively because of their role in olefin polymerization and metathesis reactions (Ivin, 1982; Jordan, 1991). The title compound, $[\{o\text{-}C_6H_4(NSiMe_3)_2\}(PhN)W(CH_2CMe_3)Cl]$, (I), is of great interest because it possesses only one alkyl group and one chloride ligand. The compound is thus an intermediate between dihalide complexes (catalyst precursors for Ziegler–Natta polymerization reactions) and dialkyl complexes (catalyst precursors for metathesis reactions). In spite of the great interest in these compounds, only a

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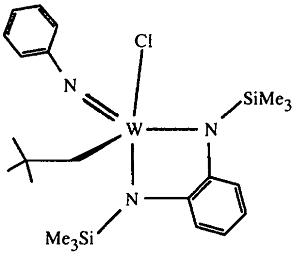
few have been structurally characterized (Fischer, Kress, Osborn, Ricard & Wesolek, 1987; Sundermeyer, Weber & Pritzkow, 1993).



(I)

A displacement ellipsoid drawing of (I) with the atom-labeling scheme is shown in Fig. 1. The coordination geometry around the W atom is between trigonal bipyramidal (with the N1 and Cl atoms occupying the axial sites) and square pyramidal (with the imido N3 ligand occupying the apical position). The geometry is best described as a distorted trigonal bipyramid, where the N1—W—Cl bond angle is 160.2 (1)°. The mean deviation from the equatorial plane defined by atoms W, N2, N3 and C19 is only 0.02 Å (trigonal bipyramid), while the mean deviation from the basal plane defined by atoms N1, N2, Cl and C19 is 0.3 Å (square pyramid). This geometry can be described as intermediate between the square pyramidal observed in $[\{o\text{-}C_6H_4(NSiMe_3)_2\}(PhN)WCl_2]$ (VanderLende, Abboud & Boncella, 1994) and the trigonal bipyramidal observed in $[\{o\text{-}C_6H_4(NSiMe_3)_2\}(PhN)W(CH_2CMe_3)_2]$ (Boncella, Wang, VanderLende, Huff & Abboud, 1997). In the latter compound, a square-pyramidal geometry could not be attained due to the bulky neopentyl groups as compared with two chloro groups in the former compound.

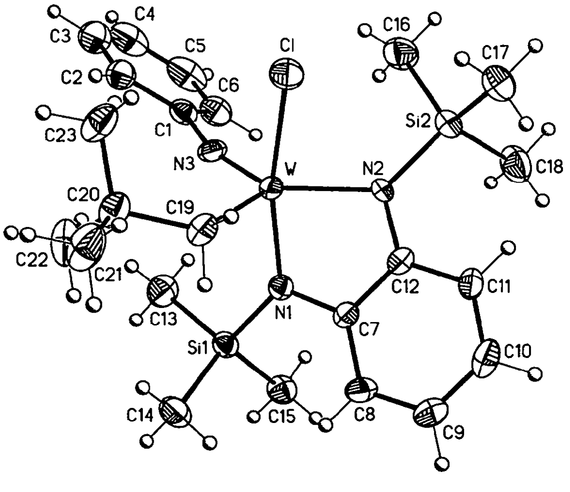


Fig. 1. The molecular structure of (I), with 50% probability ellipsoids, showing the atom-numbering scheme.

The W—N3 bond length of 1.741 (4) Å indicates that there is significant interaction between the N3 lone pair of electrons and the tungsten center. The phenyl ring on the imido group leans away from the neopentyl group resulting in a W—N3—C1 bond angle of 165.1 (4)°. These bond lengths and angles are within normal ranges for tungsten–imido complexes (Nugent & Mayer, 1988; Feldman, Davis, Thomas & Schrock, 1990) in which the W—N bond can be considered to be triply bound, with the lone pair of the N atom donating to an empty $d\pi$ orbital of the d^0 W atom.

Experimental

Using Schlenck techniques, $[\{o\text{-}C_6H_4(NSiMe_3)_2\}(PhN)WCl_2]$ was allowed to react with one equivalent of Me_3CCH_2MgCl in Et_2O at 195 K for 15 min. The reaction was stirred at room temperature for another 45 min before the solvent was removed under reduced pressure. Recrystallization by slowly cooling a pentane solution of $[\{o\text{-}C_6H_4(NSiMe_3)_2\}(PhN)W(CH_2CMe_3)Cl]$ to 253 K afforded red–orange crystals after 8 h. The high air sensitivity of (I) necessitated isolation of the crystals in a dry box. Crystals were placed in Paratone oil (Paratone 8277; Exxon Chemical Company) before being removed from the dry box.

Crystal data

$[WCl(C_5H_{11})(C_6H_5N)(C_{12}H_{22}N_2Si_2)]$
$M_r = 632.04$
Triclinic
$P\bar{1}$
$a = 9.3531\ (1)$ Å
$b = 11.2640\ (2)$ Å
$c = 14.1166\ (2)$ Å
$\alpha = 96.705\ (1)°$
$\beta = 93.814\ (1)°$
$\gamma = 111.296\ (1)°$
$V = 1366.63\ (3)$ Å^3
$Z = 2$
$D_x = 1.536$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1.5\text{–}27.5°$
$\mu = 4.43$ mm^{-1}
$T = 173\ (2)$ K
Needle
0.23 × 0.10 × 0.09 mm
Red

Data collection

Smart Platform diffractometer
ω scans
Absorption correction: by integration (Sheldrick, 1995)
$T_{\min} = 0.465$, $T_{\max} = 0.716$
8884 measured reflections
6107 independent reflections

5743 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\max} = 27.49°$
$h = -12 \rightarrow 11$
$k = -14 \rightarrow 15$
$l = -11 \rightarrow 19$
Standard reflections: see below
intensity decay: <1%

Refinement

Refinement on F^2
$R[F > 2\sigma(F)] = 0.034$
$wR(F^2) = 0.091$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 1.00$ e Å^{-3}
$\Delta\rho_{\min} = -1.46$ e Å^{-3}

$S = 1.08$
6069 reflections
272 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 3.7698P]$
where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXTL95*
Extinction coefficient: 0.0021 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

W—N1	1.973 (4)	W—C19	2.182 (5)
W—N2	2.013 (4)	W—Cl	2.422 (1)
W—N3	1.741 (4)	N3—C1	1.388 (6)
N1—W—N2	82.62 (15)	N3—W—N2	126.6 (2)
N3—W—C19	108.8 (2)	N1—W—Cl	160.2 (1)
N1—W—C19	88.0 (2)	N2—W—Cl	86.4 (1)
N2—W—C19	124.5 (2)	C19—W—Cl	84.7 (1)
N3—W—Cl	95.9 (1)	C1—N3—W	165.1 (4)
N3—W—N1	103.9 (2)		

H atoms were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.96 and 0.97 Å were used for methyl and secondary C atoms, respectively. A distance of 0.93 Å was used for sp^2-C atoms. H-atom displacement parameters were $1.2U_{\rm eq}$ ($1.5U_{\rm eq}$ for methyl atoms) of the parent C atom. A hemisphere of frames, 0.3° in ω, were collected. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability. The average e.s.d. for a C—C bond was 0.007 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART* and *SAINT* (Siemens, 1995). Data reduction: *SHELXTL95* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXTL95*. Program(s) used to refine structure: *SHELXTL95*. Molecular graphics: *SHELXTL95*. Software used to prepare material for publication: *SHELXTL95*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1269). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Mercury(II) Trifluoroacetate–Bipyridyl System

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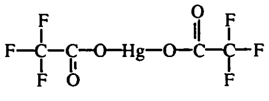
Abstract

Three complexes of mercury(II) trifluoroacetate and 2,2′-bipyridyl, of different stoichiometry, have been investigated and their structures compared with the previously published structure of bis[(2,2′-bipyridyl-*N,N*′)bis(trifluoroacetato-*O*)mercury(II)], $[Hg(C_2F_3O_2)_2(C_{10}H_8N_2)]_2$ (BHG). The complete series, AHG {(2,2′-bipyridyl-*N,N*′)(trifluoroacetato-*O*)mercury(II) hemi[tetrakis(trifluoroacetato-*O*)mercury(II)], $[Hg(C_2F_3O_2)(C_{10}H_8N_2)][Hg(C_2F_3O_2)_4]_{0.5}$}, BHG, GHG {bis(2,2′-bipyridyl-*N,N*′)(trifluoroacetato-*O*)mercury(II) (2,2′-bipyridyl-*N,N*′)tris(trifluoroacetato-*O*)mercury(II), $[Hg(C_2F_3O_2)(C_{10}H_8N_2)_2][Hg(C_2F_3O_2)_3(C_{10}H_8N_2)]$}, and DHG {bis(2,2′-bipyridyl-*N,N*′)mercury(II) bis(trifluoroacetate), $[Hg(C_{10}H_8N_2)_2](C_2F_3O_2)_2$}, shows the progressive replacement of trifluoroacetate by bidentate 2,2′-bipyridyl. Within the series, mercury may be coordinated to zero, one or two bidentate bipyridyl groups. In the extreme case, *i.e.* DHG, the complex ion $[Hg(bipyridyl)_2]^{2+}$ is formed with exclusion of trifluoroacetate from the mercury coordination.

Comment

On account of the ease with which the trifluoroacetyl group may be replaced, mercury(II) trifluoroacetate (HGTFA) has proved to be a valuable reagent in the study of the stereochemical configuration around mercury particularly by N-donor and certain O-donor ligands.



$F{-}CF_2{-}C({=}O){-}O{-}Hg{-}O{-}C({=}O){-}CF_2{-}F$

HGTFA

The structures of the products of the complexation of HGTFA with monodentate N-donors, *e.g.* bis(pyridine) (Halfpenny, Small & Thorpe, 1978), tris(pyridine) (Halfpenny & Small, 1978, 1995), a bidentate N-donor, 4-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene (Breuer & Small, 1995), a bi- and tridentate N-donor, 2,4,6-tri(2-