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Subvalent Group 14 metal compounds

XV *. Germanium and tin amides $M(NR_2)_2$ as ligands in carbonylchromium(0) chemistry. The crystal structure of the compounds *cis*-$[Cr(CO)_4\{Sn(NR'_2)_2\}_2]$ [M = Ge or Sn, R' = $SiMe_3$ or $NR_2 = \overline{NCMe_2(CH_2)_3C}Me_2$]

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Abstract

The new crystalline complexes $[Cr(CO)_5\{M(NR_2)_2\}]$ [$NR_2 = \overline{NCMe_2(CH_2)_3C}Me_2$ and M = Ge (**1**) or Sn (**2**)] and *cis*-$[Cr(CO)_4\{Sn(NR'_2)_2\}_2]$ (R' = $SiMe_3$) (**3**) are reported. Compounds **1** and **2** were prepared from $[Cr(CO_5)(THF)]$ and $M(NR_2)_2$, while treatment of $[Cr(CO)_{6-n}(NCMe)_n]$ [a *ca.* 12:6:1 mixture of $n = 1$, 2 (*cis*), and 3, respectively] with an excess of $Sn(NR'_2)_2$ yielded a 2:1 mixture of $[Cr(CO)_5\{Sn(NR'_2)_2\}]$ and the less pentane-soluble **3**. Compounds **1**-**3** have been fully characterized. In crystalline **3**, having $l(\langle Cr-Sn \rangle)$ 2.557(1) Å and l[Cr-C(*trans* to Sn)] shorter than l[Cr-C(*cis* to Sn)], there is significant departure from octahedral coordination around Cr [Sn-Cr-Sn' 101.37(3)°]; the N-Sn-N' bond angles [av. 105.0(2)° are essentially identical to that in crystalline $Sn(NR'_2)_2$, although $l(\langle Sn-N \rangle)$ in **3** is slightly shorter than in the free ligand.

1. Introduction

The majority of papers in this series have dealt with monomeric bivalent Group 14 metal complexes MX_2, where M = Ge, Sn or Pb and X^- is a bulky monohapto C-, N-, O-, or S-centred ligand. These V-shaped MX_2 molecules have both a low-lying HOMO (the stereochemically active M-centred lone pair) and LUMO (the p_z orbital); hence they show a wide range of reactivity [1].

There have been four reviews dealing explicitly with transition metal (M') complexes based on MX_2 [1-4]. In our 1990 survey [2] we identified seven types of reaction between MX_2 and a transition metal complex, leading to compounds having one or more of the following bonds: $M'-MX_2$. $M'(\mu-MX_2)M'$, $M'-MX_2X'$, $L_nM'-M$, $M'-X$, $M'(H)(MX_2-H^+)$, or $M'(H)[X_2-H^+\}X']$; additionally, MX_2 may act as a dechlorinating reagent towards $L_nM'-Cl$. Earlier parts of this series devoted to this topic were concerned with: (i) $[M'(CO)_5(MR_2)]$ [M' = Cr or Mo, R = $CH(SiMe_3)_2$], *trans*-$[M'(CO)_4(MR_2)_2]$ (M' = Cr, Mo, or W), and $[Mo(\eta-C_5H_5)(CO)_3(SnR_2X)]$ (X = H or Me) [5]; (ii) M' complexes having $M(NR'_2)_2$ (R' = $SiMe_3$) as ligand [6]; (iii) $[Pb\{MoCp(CO)_3\}_2L]$ [Cp = η-C_5H_5, η-C_5Me_5, or η-$C_5H_3(SiMe_3)_2$-1,3; L is absent or L = THF] [7]; and (iv) $[Fe(\eta-C_5H_5)(CO)_2(MR_2X)]$ (M = Sn or Pb; X = H, F, Cl, Br, I, or OMe) [8].

This paper is concerned with the complexes $[Cr(CO)_5\{M(NR_2)_2\}]$ [M = Ge (**1**) or Sn (**2**) and $NR_2 = \overline{NCMe_2(CH_2)_3C}Me_2$] and *cis*-$[Cr(CO)_4\{Sn(NR'_2)_2\}_2]$ (R' = $SiMe_3$) (**3**). Bis(2,2,6,6-tetramethylpiperidinato)-germanium and -tin were described in part 14 [9]; their crystal structures have been determined (Ge [10] and Sn [9]).

Initially an objective was to attempt to obtain 16-electron carbonylchromium(0) complexes, such as $[Cr(CO)_2L_3]$ or $[Cr(CO)_3L_2]$ [L = $M(NR_2)_2$].

Complexes of Sc, Cr^0, Mo^0, W^0, Rh^I, Ir^I, Pd^0, and Pt^0 have been reported in which $Sn(NR'_2)_2$ (R' =

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* For Part XIV see ref. 9; no reprints available.

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$SiMe_3$) behaves as a ligand; X-ray data are available on five of them; *cis*-$[RhCl(PPh_3)_2\{Sn(NR'_2)_2\}]$, $[M'\{Sn(NR'_2)_2\}_3]$ (M' = Pd or Pt), and $[(M'(CO)\{\mu\text{-}Sn(NR'_2)_2\})_3]$ [2]. The only octahedral bis(stannylene)metal complexes to have previously been obtained invariably has the *trans* configuration: $[M'(CO)_4\{Sn(NR'_2)_2\}_2]$ (M' = Mo or W) [6] and $[M'(CO)_4(MR_2)_2]$ [M' = Cr, Mo, or W; R = $CH(SiMe_3)_2$] [5,11].

2. Experimental details

2.1. Materials and procedures

All manipulations were carried out under argon by use of a high vacuum manifold and conventional Schlenk techniques. Solvents were dried and distilled over sodium/benzophenone (C_6H_6, Et_2O, or THF) or Na/K alloy (C_5H_{12}) prior to use. NMR spectra were recorded on a JEOL PFT 100 (**1** and **2**) or a Bruker AC 250SY (**3**) instrument, and IR spectra on a Perkin–Elmer 1710 FT spectrometer, and mass spectra were obtained with an AEI MS30 instrument. The amides $M[\overline{NCMe_2(CH_2)_3CMe_2}]_2$ (M = Ge or Sn) [9,10] and $Sn[N(SiMe_3)_2]_2$ [12], and $[NEt_4][Cr(CO)_5I]$ [13] were prepared by literature procedures.

2.2. *Preparation of* $[Cr(CO)_5\{Ge[\overline{NCMe_2(CH_2)_3CMe_2}]_2\}]$ *(1)*

Silver tetrafluoroborate (0.30 g, 1.5 mmol) was added to tetraethylammonium pentacarbonyl(iodo)chromate(0) (0.68 g, 1.5 mmol) in tetrahydrofuran (15 cm^3). The mixture was stirred for 3 days at ambient temperature and was then filtered. The orange filtrate was evaporated almost to dryness at 25°C/0.1 Torr. Diethyl ether (30 cm^3) was added to the residue, followed by bis(2,2,6,6-tetramethylpiperidinato)germanium(II) (0.53 g, 1.5 mmol). The mixture was stirred for *ca.* 16 h. Volatiles were removed at 25°C/10^{-1} Torr and pentane (*ca.* 15 cm^3) was added to the residue. Filtration yielded an orange filtrate, which when cooled to −78°C gave orange crystals of the title complex **1** (0.30 g, 38%), m.p. 136–139°C. Anal. Found: C, 49.9; H, 6.32, $C_{23}H_{36}CrGeN_2O_5$ calc.: C, 50.7; H, 6.61%.

2.3. *Preparation of* $[Cr(CO)_5\{Sn[\overline{NCMe_2(CH_2)_3CMe_2}]_2\}]$ *(2)*

Bis(2,2,6,6-tetramethylpiperidinato)tin(II) (1.08 g, 2.7 mmol) was added to a solution of $[Cr(CO)_5(THF)]$ (2.7 mmol) in diethyl ether (30 cm^3), prepared *in situ* in a similar fashion from $[NEt_4][Cr(CO)_5I]$ (1.22 g) and $Ag[BF_4]$ (0.53 g). Volatiles were removed at 25°C/10^{-1} Torr and pentane (10 cm^3) was added to the residue. When the orange filtrate was cooled to −78°C orange crystals of the title complex **2** (0.27 g, 15%) were obtained; decomp. > 70°C. Anal. Found: C, 46.6; H, 5.77; N, 4.63. $C_{23}H_{36}CrN_2O_5Sn$ calc.: C, 46.7; H, 6.09; N, 4.73%.

2.4. *Preparation of cis-*$[Cr(CO)_4\{Sn[N(SiMe_3)_2]_2\}_2]$ *(3)*

Attempted synthesis of $[Cr(CO)_3(NCMe)_3]$ by the procedure described in [14], involving heating of $[Cr(CO)_6]$ with an excess of acetonitrile for 40 h yielded a white, pyrophoric solid, identified from its IR and ^1H NMR spectral and mass spectrometric data as a mixture of $[Cr(CO)_5(NCMe)]$, *cis*-$[Cr(CO)_4(NCMe)_2]$, and $[Cr(CO)_3(NCMe)_3]$ in a ratio of *ca.* 12:6:1 (from integration of the ^1H NMR signals characteristic of each complex) and $[Cr(CO)_6]$. A solution of this mixture (0.50 g, 1.93 mmol) and bis[bis(trimethylsilylamido)]tin(II) (2.54 g, 5.79 mmol) in n-hexane (10 cm^3) was prepared at 25°C. The orange colour of the tin amide persisted for *ca.* 2 h (although darkening began after *ca.* 20 min) but then gradually gave way to a deep red; the solution was set aside for 48 h. Removal of the volatiles at 25°C/10^{-2} Torr yielded a red oil, which upon crystallization from a concentrated diethyl ether solution at −18°C, afforded red crystals which were recrystallized from n-pentane at −18°C to yield the title compound **3**. Anal. Found: C, 31.0; H, 6.56; N, 5.05. $C_{28}H_{72}CrN_4O_4Si_8Sn_2$ calc.: C, 32.2; H, 6.96; N, 6.37%. Solution IR and ^1H NMR spectroscopic data on the red solution prior to removal of the volatiles showed that it was a mixture of $[Cr(CO)_5\{Sn(NR'_2)_2\}]$ and *cis*-$[Cr(CO)_4\{Sn(NR'_2)_2\}_2]$ (**3**) in the ratio of 2:1.

2.5. *X-Ray structure determination for cis-*$[Cr(CO_4\{Sn[N(SiMe_3)_2]_2\}]$ *(3)*

Data were collected, using a crystal sealed in a capillary under argon, on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$ and a maximum scan time of 1 min. A total of 5634 unique reflections was measured for $2 < \theta < 22°$ and $\pm h + k + l$, and 4601 reflections with $|F^2| > 3\sigma(F^2)$ were used in the refinement where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$. There was no crystal decay. A correction (max 1.15, min 0.83) for absorption was applied using DIFABS [15] after isotropic refinement.

The structure was solved by using the heavy atom routines of SHELXS-86 [16] and non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares using programs from the Enraf–Nonius SDP-PLUS package. Hydrogen atoms were held at calculated positions with $U_{iso} = 1.3\ U_{eq}$ for the parent atom. Final parameters were $R = 0.035$, $R' = 0.047$, $S = 1.5$, 424 variables. $\Sigma w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F)_o$ $(\Delta/\sigma)_{max} = 0.03$ and $(\Delta\rho)_{max,min} = +0.72, -0.54$ e $Å^{-3}$. Tables of H atom positions, thermal parameters, and structure factors are available from one of the authors (P.B.H.).

2.6. Crystal data for 3

$C_{28}H_{72}CrN_4O_4Si_8Sn_2$, M 1043.0, monoclinic, space group $P2_1/c$, $a = 25.691(2)$, $b = 11.731(5)$, $c = 17.382(4)$ Å, $\beta = 97.83(1)°$, $U = 5189.3$ Å^3, $Z = 4$, $D_{calc} = 1.34$ g cm^{-3}, $F(000) = 2144$. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 14.5$ cm^{-1}.

3. Results and discussion

3.1. Synthesis and characterization of $Cr(CO)_5$-$\{M[\overline{NCMe_2(CH_2)_3C}Me_2]_2\}]$ [M = Ge (1) and M = Sn (2)]

The orange, crystalline complexes **1** and **2** were made by the reaction depicted in eqn. (1); the chromium(0) precursor was prepared *in situ* from $[NEt_4][Cr(CO)_5I]$ [14].

$$[Cr(CO)_5(THF)] + M(NR_2)_2 \longrightarrow$$

$$[Cr(CO)_5\{M(NR_2)_2\}] + THF \qquad (1)$$

$$NR_2 = NCMe_2(CH_2)_3CMe_2$$

$$M = Ge\ (1)$$

$$M = Sn\ (2)$$

Their formulation is consistent with microanalytical data, solution molecular weights (monomers in C_6H_{12}), IR spectra, and electron impact mass spectrometric data. The latter showed a parent molecular ion P^+ for **2** but not **1**; the highest fragment ion observed for both was $[P - NR_2]^+$, and this was followed sequentially by $[P - NR_2 - (CO)_n]^+$ $(n = 1,\ldots,5)$ and finally $[P - NR_2 - (CO)_5 - Cr]_n^+$.

The IR spectra of **1** and **2** in n-pentane showed three carbonyl stretching bands as expected for an idealized C_{4v} symmetry; on this basis, the bands at 2065m, 1967sh, and 1953s,br cm^{-1} for **1** and 2057m, 1948sb, and 1933s,br for **2** are assigned to A''_1, A'_1, E modes, respectively. These values may be compared with data for the corresponding known complexes $[Cr(CO)_5\{M(NR'_2)_2\}]$ (R' = $SiMe_3$) [6]. The position of the A'_1 mode is of greatest significance since it involves the unique CO *trans* to Sn {and may be compared with the 1980 cm^{-1} band of $[Cr(CO)_6]$}. We conclude that the σ-donor (or inverse π-acceptor) capacity falls in the sequence $Ge(NR_2)_2 > Sn(NR_2)_2 > M(NR'_2)_2 > CO$ [$NR_2 = \overline{NCMe_2(CH_2)_3C}Me_2$, M = Ge or Sn, R' = $SiMe_3$).

3.2. Synthesis and characterization of cis-$[Cr(CO)_4\{Sn[N(SiMe_3)_2]_2\}_2]$ (3)

The precursor chromium complex used in the synthesis was $[Cr(CO)_{6-n}(NCMe)_n]$ obtained by heating $[Cr(CO)_6]$ with an excess of acetonitrile, following the recipe designed to yield $[Cr(CO)_3(NCMe)_3]$ [14]. The latter is notoriously difficult to purify [17] and its adequate characterization does not appear to have been published. From combined IR, MS and especially ^1H NMR data the specimen used here for the synthesis of **3** employing an excess of $Sn[N(SiMe_3)_2]_2$ (eqn. (2)) was a mixture of $n = 1$, $n = 2$, and $n = 3$ in a ratio 12:6:1.

$$[Cr(CO)_{6-n}(NCMe)_n] + \underset{\text{excess}}{Sn(NR'_2)_2} \longrightarrow$$

$$\underset{(3)}{[Cr(CO)_5\{Sn(NR'_2)_2\}} + \underset{(2)}{cis\text{-}[Cr(CO)_4\{Sn(NR'_2)_2\}_2]}$$

Similar spectroscopic examination of the crude product of the reaction according to eqn. (2) showed that it was an approximately 2 : 1 mixture of $[Cr(CO)_5\{Sn(NR'_2)_2\}]$ [6] and *cis*-$[Cr(CO)_4\{Sn(NR'_2)_2\}_2]$ (**3**) together with unreacted $Sn(NR'_2)_2$. Complex **3** was separated from this mixture as red crystals, being the least n-pentane-soluble component of the mixture.

The carbonyl stretching region of the IR spectrum of **3** in hexane showed the following absorption maxima: 2015s, 1939vs, 1910m, and 1895m cm^{-1}, consistent with its *cis* geometry. Although the *trans* isomer has not been reported, Mo and W analogues *trans*-$[M'(CO)_4\{Sn(NR'_2)_2\}_2]$ showed only a single IR carbonyl stretching band at 1938 and 1931 cm^{-1}, respectively. The CO stretching bands are at significantly lower frequency than those for the bis(carbene)chromium analogue *cis*-$[Cr(CO)_4\{\overline{CN(Me)CH_2CH_2N}Me\}_2]$ (**4**): 1983, 1866, 1855, and 1833 cm^{-1} [18], consistent with $Sn(NR'_2)_2$ being a better π acceptor but poorer σ-donor than this bis(amino)carbene.

Multinuclear NMR spectra for **3** in toluene-d_8 at 303 K were determined. The ^1H spectrum showed a single sharp signal in the methyl region at δ 0.15, as did the $^{13}C\{^1H\}$ spectrum at δ 5.91, while the proton-coupled ^{13}C spectrum revealed a binomial quartet, $^1J(^{13}C-^1H)$ 117.5 Hz with additional hyperfine structure, $J = 2.2$ Hz. The signal for the carbonyls *trans* to Sn was at $\delta(^{13}C)$ 222.6, while the mutually *trans*-carbonyls had $\delta(^{13}C)$ 216.6 (the corresponding signals in **4** were at δ 230.0 and δ 222.6, respectively [18]); these features were invariant between −70 and +95°C, confirming the stereochemical integrity of the complex. The ^{29}Si and ^{19}Sn NMR spectra each showed only one signal at δ −2.21 (rel. to $SiMe_4$) and δ − 135.1 (rel. to $SnMe_4$), consistent with the presence of a single isomer. These ^{13}C data show that the π-acceptor capacity (or inverse σ-donor strength) decrease in the sequence $CO > Sn(NR'_2)_2 > \overline{CN(Me)(CH_2)_2N}Me$.

The *cis*-geometry for complex **3** is in many ways surprising. Although a complex of formula $[Cr(CO)_4\{Sn(NR'_2)_2\}_2]$ has not previously been made, the isoleptic Mo and W complexes $[M'(CO)_4\{Sn(NR'_2)_2\}_2]$ (as well as the Ge analogues) had the *trans* configuration,

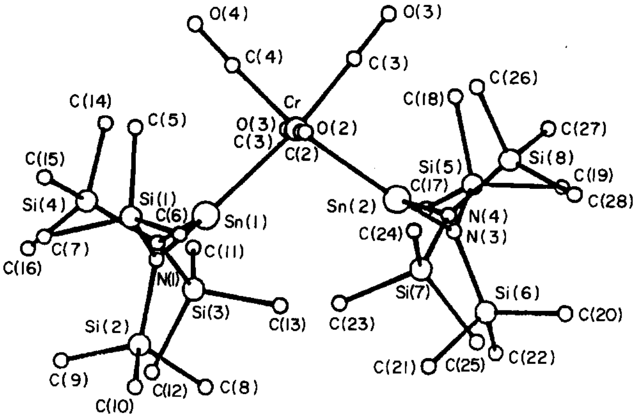

Fig. 1.

as did $[M'(CO)_4\{M(CHR'_2)_2\}_2]$ ($M' = Cr$ and $M = Ge$, or $M' = Cr$ or Mo and $M = Sn$) [5]; but none of these complexes has been authenticated by X-ray. The presumption that the *trans* isomer is preferred appeared to be reasonable on steric grounds. In the case of the related Cr, Mo, or W carbene complexes such as **4**, both *cis* and *trans* isomers are firmly established, the *cis* being converted to *trans* photochemically, whereas the reverse process occurs on heating [18]. Indeed,

TABLE 1. Selected intramolecular distances (Å) with estimated standard deviations in parentheses, for *cis*-$[Cr(CO)_4\{Sn[N(SiMe_3)_2]_2\}_2]$ (3)

Sn(1)–Cr	2.566(1)	Si(7)–N(4)	1.741(5)
Sn(1)–N(2)	2.057(5)	Si(8)–N(4)	1.735(5)
Sn(2)–N(3)	2.039(5)	O(1)–C(1)	1.131(8)
Cr–C(1)	1.891(7)	O(3)–C(3)	1.162(7)
Cr–C(3)	1.843(6)	Sn(1)–N(1)	2.041(4)
Si(1)–N(1)	1.752(5)	Sn(2)–Cr	2.549(1)
Si(2)–N(1)	1.742(5)	Sn(2)–N(4)	2.069(5)
Si(3)–N(2)	1.737(5)	Cr–C(2)	1.872(6)
Si(4)–N(2)	1.748(5)	Cr–C(4)	1.852(7)
Si(5)–N(3)	1.750(6)	O(2)–C(2)	1.43(8)
Si(6)–N(3)	1.753(6)	O(4)–C(4)	1.157(8)

TABLE 2. Selected intramolecular angles (°), with estimated standard deviations in parentheses, for *cis*-$[Cr(CO)_4\{Sn[N(SiMe_3)_2]_2\}_2]$ (3)

Cr–Sn(1)–N(1)	131.9(1)	Cr–Sn(1)–N(2)	122.6(1)
N(1)–Sn(1)–N(2)	104.8(2)	Cr–Sn(2)–N(3)	132.1(1)
Cr–Sn(2)–N(4)	121.4(1)	N(3)–Sn(2)–N(4)	105.2(2)
Sn(1)–Cr–Sn(2)	101.37(3)	Sn(1)–Cr–C(1)	87.0(2)
Sn(1)–Cr–C(2)	91.0(2)	Sn(1) – Cr–C(3)	173.1(2)
Sn(1)–Cr–C(4)	87.6(2)	Sn(2)–Cr–C(1)	91.8(2)
Sn(2)–Cr–C(2)	86.6(2)	Sn(2)–Cr–C(3)	85.5(2)
Sn(2)–Cr–C(4)	171.1(2)	C(1)–Cr–C(2)	177.1(3)
C(1)–Cr–C(3)	92.4(3)	C(1)–Cr–C(4)	89.1(3)
C(2)–Cr–C(3)	89.8(3)	C(2)–Cr–C(4)	92.9(3)
C(3)–Cr–C(4)	85.5(3)	Sn(1)–N(1)–Si(1)	121.4(2)
Sn(1)–N(1)-Si(2)	118.6(3)	Si(1)–N(1)–Si(2)	119.9(3)
Sn(1)–N(2)–Si(3)	121.9(3)	Sn(1)–N(2)–Si(4)	116.0(3)
Si(3)–N(2)–Si(4)	120.0(3)	Sn(2)–N(3)–Si(5)	122.0(3)
Sn(2)–N(3)–Si(6)	118.4(3)	Si(5)–N(3)–Si(6)	119.6(3)
Sn(2)–N(4)-Si(7)	121.6(2)	Sn(2)–N(4)–Si(8)	116.4(2)
Si(7)–N(4)–Si(8)	120.0(3)	Cr–C(1)–O(1)	177.1(6)
Cr–C(2)–O(2)	178.1(5)	Cr–C(3)–O(3)	177.9(6)
Cr–C(4)–O(4)	176.4(5)		

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for *cis*-$[Cr(CO)_4\{Sn[N(SiMe_3)_2]_2\}_2]$ (3)

Atom	x	y	z	U_{eq} [a]
Sn(1)	1686.2(2)	232.2(4)	2131.4(2)	37.2(1)
Sn(2)	3117.6(2)	−197.6(4)	3260.4(2)	38.6(1)
Cr	2157.3(4)	−330.4(8)	3474.8(5)	37.0(1)
Si(1)	1086.8(7)	−2013.5(17)	1261.6(11)	55(1)
Si(2)	1497.3(8)	−200.1(17)	262.9(10)	58(1)
Si(3)	1810.0(9)	2999.7(17)	1796.5(11)	63(1)
Si(4)	743.8(8)	2074.1(19)	2015.6(12)	67(1)
Si(5)	3685.1(8)	1978.9(19)	4266.1(14)	75(1)
Si(6)	4102.2(8)	1278.2(20)	2788.7(14)	76(1)
Si(7)	3460.2(8)	−2342.4(18)	2180.0(11)	59(1)
Si(8)	3865.8(8)	−2315.4(17)	3888.7(11)	58(1)
O(1)	2109(2)	2158(4)	3909(3)	72(3)
O(2)	2208(2)	−2794(4)	2997(3)	70(3)
O(3)	2568(2)	−1031(5)	5107(2)	77(3)
O(4)	1102(2)	−618(5)	4017(3)	86(3)
N(1)	1411(2)	−715(4)	1177(2)	43(2)
N(2)	1398(2)	1846(4)	1883(3)	46(3)
N(3)	3657(2)	1080(4)	3458(3)	53(3)
N(4)	3546(2)	−1638(4)	3070(3)	47(3)
C(1)	2140(2)	1231(6)	3740(3)	47(3)
C(2)	2186(2)	−1855(5)	3166(3)	45(3)
C(3)	2416(2)	−744(6)	4477(3)	50(3)
C(4)	1500(2)	−506(6)	3784(3)	52(3)
C(5)	888(3)	−2207(7)	2247(4)	72(4)
C(6)	1502(3)	−3253(6)	1090(4)	76(4)
C(7)	470(3)	−2086(8)	566(5)	88(5)
C(8)	2123(3)	601(7)	318(4)	79(5)
C(9)	943(4)	748(8)	−145(5)	102(6)
C(10)	1560(4)	−1360(7)	−451(4)	98(5)
C(11)	1713(4)	4171(6)	2490(5)	87(5)
C(12)	1701(4)	3600(6)	791(4)	91(5)
C(13)	2511(3)	2585(7)	2007(5)	81(5)
C(14)	695(3)	2424(9)	3049(5)	113(6)
C(15)	340(3)	774(8)	1792(6)	109(6)
C(16)	430(4)	3239(8)	1395(6)	113(6)
C(17)	3403(4)	3407(7)	4022(6)	106(6)
C(18)	3317(3)	1410(8)	5042(4)	87(5)
C(19)	4383(4)	2136(9)	4746(6)	128(7)
C(20)	4713(3)	414(8)	3039(6)	104(6)
C(21)	3788(3)	888(8)	1804(5)	90(5)
C(22)	4292(4)	2813(8)	2700(6)	128(7)
C(23)	2919(3)	−1677(7)	1505(4)	67(4)
C(24)	3294(4)	−3878(7)	2264(5)	100(6)
C(25)	4073(3)	−2262(9)	1704(4)	103(6)
C(26)	3417(3)	−3295(7)	4321(4)	85(5)
C(27)	4095(3)	−1246(7)	4657(4)	86(5)
C(28)	4450(3)	−3128(8)	3686(5)	98(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

cis-[Cr(CO)$_4$(L)(L')] complexes are generally thermodynamically preferred to the *trans* isomers.

3.3. *The crystal structure of cis[Cr(CO)$_4${Sn[N(SiMe$_3$)$_2$]$_2$}$_2$] (3)*

The molecular structure and atom numbering scheme for complex **3** is shown in Fig. 1. Selected bond lengths and angles, and fractional atomic coordinates are listed in Tables 1–3, respectively.

Although the chromium environment in **3** is best described as distorted octahedral, this is an oversimplification. The extensive steric interaction between the two *cis*-stannylene ligands is evident from the Sn(1)–Cr–Sn(2) angle of 101.37(3)°. The atoms Cr, Sn(1), Sn(2), C(3), C(4), O(3), and O(4) are essentially coplanar and the distortion caused by the opening up of the Sn(1)–Cr–Sn(2) angle is largely compensated by the compression of the *cis* Sn–Cr–C (mean 86.6°) and C(3)–Cr–C(4) [85.5(2)°] angles. The *trans*-axial carbonyls are disposed in an almost linear fashion, C(1)–Cr–C(2) 177.1(3)°.

The two Cr–Sn distances are unequal, 2.566(1) and 2.549(1) Å, but comparable to that in [Cr(CO)$_5${Sn(CHR'$_2$)$_2$}] (**5**), 2.562(2)Å [5a]. The conformation of the Sn(NR'$_2$)$_2$ ligands in **3**, like that of Sn(CHR'$_2$)$_2$ in **5**, is such as to permit effective Cr–Sn π-bonding involving the formally vacant p_z orbital on Sn. The Cr–C(*trans* to Sn) bond lengths, mean 1.847(7) Å, are significantly shorter than Cr–C(*cis* to Sn), 1.881(8) Å, as inversely are the corresponding C–O distances [mean 1.159(9) Å and 1.137(8) Å, respectively]. These data are consistent with CO having a greater *trans* influence than Sn(NR'$_2$)$_2$, and the latter being the poorer π-acceptor.

The Sn(NR'$_2$)$_2$ geometric parameters in **3** are available for comparison with those in the crystalline free ligand [9]. The N–Sn–N' angles are essentially identical, but the mean Sn–N bond length in **3** is slightly shorter than that in Sn(NR'$_2$)$_2$ [2.09(1) Å].

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