

Homoleptic allyl complexes of chromium with trimethylsilylated ligands. Formation and molecular structure of $\{[1-(\text{SiMe}_3)\text{C}_3\text{H}_4]_2\text{Cr}\}_2$, $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{Cr}$, and $[1,1',3-(\text{SiMe}_3)_3\text{C}_3\text{H}_2]_2\text{Cr}$

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Abstract

Reaction of two equivalents of $\text{K}[1-(\text{SiMe}_3)\text{C}_3\text{H}_4]$, $\text{K}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$, or $\text{K}[1,1',3-(\text{SiMe}_3)_3\text{C}_3\text{H}_2]$ with CrCl_2 in THF at -78°C produces the red complexes $\{[1-(\text{SiMe}_3)\text{C}_3\text{H}_4]_2\text{Cr}\}_2$ (**1**), $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{Cr}$ (**2**) and $[1,1',3-(\text{SiMe}_3)_3\text{C}_3\text{H}_2]_2\text{Cr}$ (**3**), respectively. They are thermally stable compounds, remarkably so for the monomeric **2** and **3**, which possess formal 12-electron counts. Single crystal X-ray structures confirm the dimeric nature of $\{[1-(\text{SiMe}_3)\text{C}_3\text{H}_4]_2\text{Cr}\}_2$, which is constructed around a Cr_2 core with $\text{Cr}-\text{Cr}' = 1.9784(7)$ Å. In the monomeric complexes, the allyl ligands are bound in a *trihapto* manner to the metals, with $\text{Cr}-\text{C}$ distances of 2.193(2)–2.257(2) Å in **2** and 2.223(5)–2.319(5) Å in **3**. The allyl ligands adopt staggered conformations, with a 10.4° angle between the C_3 planes in (**2**) and parallel ligands in (**3**). The trimethylsilyl groups in both complexes are in a *syn*, *anti* conformation. The monomeric complexes are high-spin, with four unpaired electrons. The steric shielding provided to the metal by the trimethylsilyl groups is probably responsible for the lack of reactivity of **2** with bulky donors such as PPh_3 , although it forms a monoadduct with the more sterically compact PMe_3 . Density functional theory calculations were performed on $(\text{C}_3\text{H}_5)_2\text{Cr}$, and comparisons made with the structures of the trimethylsilylated derivatives.

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1. Introduction

In 1961, Wilke synthesized the first bis(allyl) metal complex, $(\text{C}_3\text{H}_5)_2\text{Ni}$ [1], and within 5 years his group had prepared many of the currently known homoleptic π -allyl transition metal compounds $(\text{C}_3\text{H}_5)_n\text{M}$ [2]. Since that time, π -allyl compounds have been intensively investigated as catalysts for olefin polymerization [3–7], and as reagents in organic and materials chemistry [8–12].

Many examples exist of mixed ligand allyl complexes, especially those containing cyclopentadienyl rings $\text{Cp}'_x\text{M}(\text{C}_3\text{H}_5)_y\text{L}_z$ [13–22], and homoleptic π -allyl complexes are known that span the d-block transition metals from Groups 4 (e.g. $(\text{C}_3\text{H}_5)_4(\text{Zr},\text{Hf})$ [23]) to 10 (e.g. $(\text{C}_3\text{H}_5)_2(\text{Ni},\text{Pd},\text{Pt})$ [2]). Nevertheless, most of the work with the homoleptic compounds has focused on a small subset of them, including $(\text{C}_3\text{H}_5)_2\text{Ni}$, $(\text{C}_3\text{H}_5)_2\text{Pd}$, and $(\text{C}_3\text{H}_5)_3\text{Cr}$. A major reason for the selection is that metal centers in such allyl complexes are often coordinately unsaturated, and low-energy pathways for decomposition are available. Consequently, most $(\text{C}_3\text{H}_5)_n\text{M}$ compounds of the first row transition metals are thermally unstable, regardless of formal electron count (e.g. even under an inert atmosphere, $(\text{C}_3\text{H}_5)_3\text{V}$ (14e^-) is reported

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to explode at $-30\text{ }^{\circ}\text{C}$, and $(\text{C}_3\text{H}_5)_3\text{Co}$ (18 e^-) decomposes above $-40\text{ }^{\circ}\text{C}$ [2]. The technical difficulties of handling these compounds have inhibited systematic investigations into their properties and potential applications. (It should be noted that second and third-row allyl complexes (e.g. $(\text{C}_3\text{H}_5)_2\text{Pd}$, $(\text{C}_3\text{H}_5)_3\text{Rh}$, $[(\text{C}_3\text{H}_5)_2\text{Mo}]_2$) are typically much more stable than their first-row counterparts [24].)

Bulky cyclopentadienyl rings (e.g. C_5Me_5 , $\text{C}_5\text{Me}_4\text{SiMe}_2(t\text{-Bu})$) have long been used to synthesize compounds of greater variety and stability than are available with Cp alone [25–28]. A similar strategy should be useful with the sterically compact allyl ligand, and some research has indicated the promise in this area. For example, Silver demonstrated that $(\eta^3\text{-}2\text{-Me-C}_3\text{H}_4)_2\text{Fe}(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PMe}_3$, PMe_2Ph , $\text{P}(\text{OMe})_3$) complexes are stable in solution to at least $30\text{ }^{\circ}\text{C}$ [29], whereas the unsubstituted analogues $(\text{C}_3\text{H}_5)_2\text{Fe}(\text{PR}_3)_2$ are not stable above $0\text{ }^{\circ}\text{C}$ [30]. Furthermore, by placing three methyl groups on the allyl ligand, both main group (i.e. allyl tin) [31] and transition metal complexes (Group 4 Cp and C_5Me_5 halide and butadiene species) could be stabilized [32–35]. Various substituted bis(allyl)nickel complexes are known, and some derivatives have been used as catalysts [36–38]. Most of these have sterically small groups (e.g. methyl, ethyl) [39] and stability is not always improved; the heavily substituted bis(1,1,3,3-tetraphenylallyl)nickel, however, has been reported to be stable at $20\text{ }^{\circ}\text{C}$ [40].

Allyl anions with bulky groups as large as trimethylsilyl [41] and *t*-butyl [42] have been known for some time, but other than alkali metal salts, their organometallic derivatives were not prepared until recently. A bis(1,3-bis(trimethylsilyl)allyl)calcium complex has been synthesized and structurally authenticated [43]; its isolation, in contrast to that of the ill-characterized ‘ $(\text{C}_3\text{H}_5)_2\text{Ca}$,’ hints at the potential stabilizing ability of extremely bulky allyl ligands in metal compounds. A samarium complex of the same composition (i.e. $[(\text{C}_3(\text{SiMe}_3)_2\text{H}_3)_2\text{Sm}(\text{thf})_2]$) has been prepared, but not crystallographically characterized [44].

In this paper, we focus on allyl complexes of divalent chromium, for which the parent complex $(\text{C}_3\text{H}_5)_2\text{Cr}$ is known as a thermally stable (m.p. $121\text{--}129\text{ }^{\circ}\text{C}$) dimer [45]. Jolly and co-workers have prepared phosphine adducts of the form $(\eta^3\text{-allyl})_2\text{Cr}(\text{PR}_3)_2$ and $(\eta^3\text{-allyl})_2\text{Cr}(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)$, but none are stable above $-10\text{ }^{\circ}\text{C}$ [46]. We report here Cr(II) complexes containing mono-, bis- and tris(trimethylsilyl) substituted allyl anions, and discuss their structures, reactions and electronic features. Among these compounds are the first monomeric homoleptic bis(π -allyl)chromium(II) species. A portion of this work has appeared elsewhere [47].

2. Experimental

2.1. General considerations

All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques. ^1H -, ^{13}C - and ^{31}P -NMR spectra were collected on a Bruker NMR spectrometer at 300, 75.5 and 121 MHz, respectively. GC–MS data were collected on a Hewlett-Packard 5890 Series II gas chromatograph–mass spectrometer. The infrared data were measured on an ATI Mattson-Genesis FTIR spectrometer as KBr pellets. Melting points were determined in sealed capillaries. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Solution magnetic susceptibility data were obtained in toluene- d_8 on a Bruker spectrometer using the Evans’ NMR method [48–51].

2.2. Materials

Allyltrimethylsilane was purchased from Acros, and degassed prior to use. $\text{AgI}\cdot\text{P}(\text{CH}_3)_3$ was purchased from Aldrich, and used as received. $(\text{C}_3(\text{SiMe}_3)_2)_2\text{H}_4$, $\text{C}_3(\text{SiMe}_3)_3\text{H}_3$ and $\text{Li}[1,3\text{-}(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$ were synthesized according to literature procedures [41]. $\text{K}[1,3\text{-}(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$ was prepared in high yield by transmetalation of $\text{Li}[1,3\text{-}(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$ with potassium *tert*-butoxide in hexane solution. $\text{Li}[1,1',3\text{-}(\text{SiMe}_3)_3\text{C}_3\text{H}_2]$ was prepared from $\text{C}_3(\text{SiMe}_3)_3\text{H}_3$ and *n*-BuLi and transmetalated with potassium *tert*-butoxide. $[(\text{C}_3(\text{SiMe}_3)_2\text{H}_3)_2\text{Cr}]$ was prepared from $\text{K}[1,3\text{-}(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$ and CrCl_2 according to the literature procedure [47]. Solvents for reactions were distilled under nitrogen from Na or K benzophenone ketyl. Chloroform was dried by reflux and distillation over CaH_2 . NMR solvents were vacuum distilled from Na/K (22/78) alloy and stored over 4A molecular sieves.

2.3. Synthesis of bis(1-(trimethylsilyl)allyl)chromium(II) dimer (I)

A three-neck flask fitted with a stopper, gas inlet and dropping funnel was charged with CrCl_2 (0.500 g; 4.00 mmol) in 20 ml THF. $\text{K}[1\text{-}(\text{SiMe}_3)\text{C}_3\text{H}_4]$ (1.245 g; 8.00 mmol) in 20 ml THF was added to the dropping funnel. The apparatus was cooled to $-78\text{ }^{\circ}\text{C}$ using a dry ice/acetone bath. The THF solution of $\text{K}[1\text{-}(\text{SiMe}_3)\text{C}_3\text{H}_4]$ was added dropwise, with stirring, over the course of 15 min. The solution was allowed to warm to room temperature (r.t.) overnight. Removal of solvent under vacuum, followed by extraction of the residue with hexanes, filtration of the extract over a medium porosity glass frit, and removal of hexanes under vacuum, afforded an air- and moisture-sensitive black powder (0.67 g, 58%). Recrystallization from hexanes at $-35\text{ }^{\circ}\text{C}$

yielded red crystals, m.p. 132–134 °C. Anal. Calc. $C_{24}H_{52}Cr_2Si_4$: C, 51.75; H, 9.41. Found: C, 51.27; H, 9.53%. Principle IR bands (KBr), cm^{-1} : 2960 (m), 1598 (w), 1472 (br, w), 1248 (m), 1030 (s), 1015 (s), 853 (s), 550 (br, w). Magnetic susceptibility measurements in solution indicate that the compound is diamagnetic.

2.4. Reaction of $[C_3(SiMe_3)_2H_3]_2Cr$ with $P(CH_3)_3$

In a 125-ml Schlenk flask cooled in an ice bath, a suspension of $[C_3(SiMe_3)_2H_3]_2Cr$ (0.400 g; 0.944 mmol) in hexanes (50 ml) was connected to a closed glass tube containing $AgI \cdot P(CH_3)_3$ (6.00 g; 1.9 mmol). The glass tube was heated with a heat gun; after the phosphine complex melted and PMe_3 was released, a reaction was observed as the initially red–orange chromium solution turned brown–yellow. Removal of solvent yielded a dark red compound, 0.480 g (89%), m.p. 42–46 °C. Anal. Calc. $C_{21}H_{51}CrPSi_4$: C, 50.55; H, 10.30. Found: C, 49.22; H, 10.18%. ^{31}P -NMR (121 MHz, C_6D_6 , 298 K): δ –10.5. Principle IR bands (KBr), cm^{-1} , 2967 (m), 2360 (m), 2330 (m), 1613 (w), 1260 (m), 1082 (m), 1027 (s), 860 (w), 801 (m), 411 (s).

2.5. Synthesis of bis(1,1',3-tris(trimethylsilyl)allyl)chromium(II) (**3**)

A three-neck flask fitted with a stopper, gas inlet and dropping funnel was charged with $CrCl_2$ (0.500 g; 4.00 mmol) in 20 ml THF. $K[1,1',3-(Si(CH_3)_3)_3C_3H_2]$ (2.40 g; 8.00 mmol) in 20 ml THF was added to the dropping funnel. The apparatus was cooled to –78 °C using a dry ice/acetone bath. The THF solution of $K[1,1',3-(Si(CH_3)_3)_3C_3H_2]$ was added dropwise, with stirring, over the course of 15 min. The solution was allowed to warm to r.t. overnight. Removal of solvent under vacuum, followed by extraction of the residue with hexanes, filtration of the extract over a medium porosity glass frit, and removal of hexanes under vacuum, afforded an air- and moisture-sensitive red–orange oil (1.06 g, 47%). The oil crystallized after standing for several days at r.t. to yield 0.50 g (22%) of red crystals. Anal. Calc. $C_{24}H_{58}CrSi_6$: C, 50.82; H, 10.31; Cr, 9.17. Found: C, 50.88; H, 10.33; Cr, 8.52%. Principle IR bands (KBr), cm^{-1} : 2955 (s), 1558 (w), 1410 (br), 1249 (s), 839 (s), 550 (br). Magnetic susceptibility (toluene- d_8): $^{corr}\mu = 4.5$ BM at 300 K, consistent with four unpaired electrons.

2.6. X-ray crystallography

A suitable crystal of **1** and **3** was located, attached to a glass fiber, and mounted on a Siemens SMART system for data collection at 173(2) K. Data collection and structure solution were conducted at the X-ray Crystallography Laboratory at the University of Minnesota.

All calculations were performed with the SHELXTL suite of programs [52]. Final cell constants were calculated from a set of strong reflections measured during the actual data collection. Absorption corrections were performed with the program SADABS [53]. Relevant crystal and data collection parameters for the compounds are given in Table 1.

The space groups were determined from reflection conditions and intensity statistics. Direct-methods solutions were calculated that provided most non-hydrogen atoms from the E-maps. Several full-matrix least-squares/difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the case of the dimeric **1**, two additional chromium positions were found at a rotation of ca. 90°. A disorder is present in which the entire molecule fits in the crystalline lattice at this offset, whereby terminal and bridging allyl groups are dis-

Table 1
Crystal data and summary of X-ray data collection

Compound	$\{[(SiMe_3)_3C_3H_4]_2Cr\}_2$	$[(SiMe_3)_3C_3H_2]_2Cr$
Formula	$C_{24}H_{52}Cr_2Si_4$	$C_{24}H_{58}CrSi_6$
Formula weight	557.02	567.24
Temperature (K)	173(2)	173(2)
Color of crystal	Deep red	Red
Crystal dimensions (mm)	$0.49 \times 0.21 \times 0.15$	$0.40 \times 0.35 \times 0.30$
Space group	$P2_1/n$	$P2_1/n$
Cell dimensions (173(2) K)		
<i>a</i> (Å)	11.043(2)	9.666(2)
<i>b</i> (Å)	27.123(5)	9.535(2)
<i>c</i> (Å)	11.248(2)	19.228(4)
α (°)	90	90
β (°)	111.707(3)	91.800(4)
γ (°)	90	90
<i>V</i> (Å ³)	3130(1)	1771.3(6)
<i>Z</i>	4	2
<i>D</i> _{calc} (Mg m ⁻³)	1.182	1.064
Absorption coefficient (mm ⁻¹)	0.857	0.537
Radiation type	Mo–K α (0.71073 Å)	Mo–K α (0.71073 Å)
Limits of data collection	$1.50^\circ \leq \theta \leq 25.07^\circ$	$2.12^\circ \leq \theta \leq 25.28^\circ$
Index ranges	$-13 \leq h \leq 13$, $-29 \leq k \leq 32$, $-13 \leq l \leq 10$	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-15 \leq l \leq 22$
Total reflections collected	17 533	10 620
Unique reflections	5524 (<i>R</i> _{int} = 0.0392)	3108 (<i>R</i> _{int} = 0.0346)
Transmission factors	0.8388–1.0000	0.8526–1.0000
Data/restraints/parameters	5524/130/434	3108/0/165
<i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> = 0.0374, <i>R</i> _w = 0.0890	<i>R</i> = 0.0501, <i>R</i> _w = 0.1490
Goodness of fit on <i>F</i> ²	0.997	1.148
<i>R</i> indices (all data)	<i>R</i> = 0.0522, <i>R</i> _w = 0.0959	<i>R</i> = 0.0563, <i>R</i> _w = 0.1515
Max/min peak in final difference map (e ⁻ Å ⁻³)	0.521/–0.188	0.690/–0.379

ordered over similar positions. The disordered occupancy converged to 72:28. Restraints were imposed to coax the minor component of the disorder to be equivalent to the major component.

The initial refinement of **3** stalled at $R_1 = 0.07$. A non-merohedral twin was detected, and the data were corrected for the effects of twinning with ROTWIN. The twin components were determined to be in a 0.430:0.099 ratio, and the refinement improved by 2%.

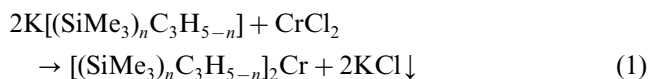
2.7. Computational details

Geometry optimization calculations were performed using the GAUSSIAN 98W suite of programs [54]. The B3PW91 functional, which incorporates Becke's three-parameter exchange functional [55] with the 1991 gradient-corrected correlation functional of Perdew and Wang [56], was used; this hybrid functional has previously been shown to provide realistic geometries for organometallic species [57,58]. The Gaussian basis set 6-31+G(d) was used for geometry optimization, and 6-311+G(2d,2p) for final energy calculations. Zero-point corrections were applied to the energies of the final geometries.

3. Results

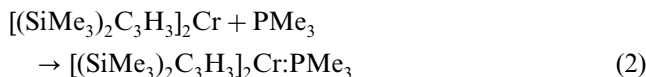
3.1. Syntheses of $\{[C_3(SiMe_3)H_4]_2Cr\}_2$ (**1**), $[C_3(SiMe_3)_2H_3]_2Cr$ (**2**), and $[C_3(SiMe_3)_3H_2]_2Cr$ (**3**)

The syntheses of the silyl-substituted bis(π -allyl)chromium complexes involve metathesis reactions carried out under an inert atmosphere at $-78^\circ C$ (Eq. (1); $n = 1-3$):



The bis(π -allyl)chromium compounds are recovered in modest yield as air- and moisture-sensitive red solids, soluble in ethers and both aromatic and aliphatic hydrocarbons. They are stable indefinitely under an inert atmosphere at room temperature; the heavily substituted complex **3** can survive brief (minutes) exposure to the air without substantial decomposition. The diamagnetism of **1** is an understandable consequence of its dimeric structure (see below), which is similar to that of the unsubstituted parent compound. Compounds **2** and **3** are monomeric species in the solid state (see below and Ref. [47]), and both exhibit a magnetic moment consistent with four unpaired electrons at room temperature. The monomers are formally 12-electron species, and their thermal stability is remarkable in light of their severe electron deficiency.

Complex **2** does not react with PPh_3 at atmospheric pressure and ambient temperatures; the compound is recovered unchanged from the reaction mixtures. The smaller PMe_3 will form a stable 1:1 adduct, however (Eq. (2)):



The formally 14-electron complex is a deep red oily solid, which slowly releases the PMe_3 ligand over a period of weeks. Its ^{31}P -NMR spectrum contains a peak at $\delta -10.5$, which is shifted upfield from that of free PMe_3 ($\delta -62$) [59], but not as much as that of the 18-electron complex $(C_5H_5)(\eta^3-C_3H_3)Cr(PMe_3)$ ($\delta +49.4$) [60]. Perhaps because of its greater steric encumbrance, **3** does not form an adduct with PMe_3 under the same conditions as does **2**. Compound **1** also does not react with PMe_3 ; in this respect it resembles the unsubstituted complex $[(C_3H_5)_2Cr]_2$ (see below).

3.2. Solid state structure of $\{[1-(SiMe_3)C_3H_4]_2Cr\}_2$ (**1**)

Compound **1** crystallizes from hexanes as a dimer with a Cr–Cr core. Each chromium atom is bonded to a terminal η^3 -(trimethylsilyl)allyl ligand. Two trimethylsilylallyl ligands bridge the metal centers, with the C_3 planes approximately parallel to the Cr_2 axis. The trimethylsilyl substituents are in a *syn* arrangement on all the ligands; if the $SiMe_3$ groups were not present, the compound would be isostructural with the parent dimer, $[(C_3H_5)_2Cr]_2$ [45], and with the heavier homologue, $[(C_3H_5)_2Mo]_2$ [61]. A summary of bond distances and angles for **1** is given in Table 2; an ORTEP view of the complex is displayed as Fig. 1.

Table 2
Selected bond distances (Å) and angles ($^\circ$) for **1**

Atoms	Distance	Atoms	Angle
Cr(1)–Cr(2)	1.9784(7)	C(8)–C(9)	1.429(7)
Cr(1)–C(19)	2.123(6)	C(13)–C(14)	1.383(9)
Cr(1)–C(9)	2.149(6)	C(14)–C(15)	1.394(8)
Cr(1)–C(1)	2.192(11)	C(19)–C(20)	1.406(9)
Cr(1)–C(2)	2.241(6)	C(20)–C(21)	1.433(9)
Cr(1)–C(3)	2.303(5)	C(1)–C(2)–C(3)	123.8(11)
Cr(2)–C(7)	2.129(7)	C(2)–C(3)–Si(1)	122.1(7)
Cr(2)–C(21)	2.164(9)	C(9)–C(8)–C(7)	126.9(6)
Cr(2)–C(13)	2.226(6)	C(8)–C(9)–Si(2)	121.2(4)
Cr(2)–C(14)	2.228(4)	C(13)–C(14)–C(15)	125.8(5)
Cr(2)–C(15)	2.287(7)	C(14)–C(15)–Si(3)	123.2(6)
Cr(2)–C(20)	2.378(5)	C(19)–C(20)–C(21)	125.4(7)
Cr(2)–C(8)	2.382(4)	C(20)–C(21)–Si(4)	122.6(7)
C(1)–C(2)	1.371(9)		
C(2)–C(3)	1.383(8)		
C(7)–C(8)	1.430(8)		

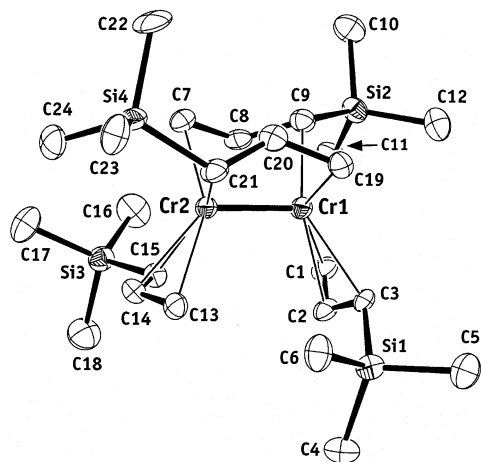


Fig. 1. ORTEP diagram of the non-hydrogen atoms of $\{[1-(\text{SiMe}_3)\text{C}_3\text{H}_4]_2\text{Cr}\}_2$ (**1**), giving the numbering scheme used in the text. Thermal ellipsoids are displayed at the 50% level.

The Cr–Cr distance of 1.9784(7) Å in **1** is close to the 1.97 Å length in $[(\text{C}_3\text{H}_5)_2\text{Cr}]_2$, and is consistent with the presence of a Cr–Cr quadruple bond [62,63]. Of the two terminal allyl ligands, that on Cr(2) (C13–C14–C15) is the more symmetrically bonded, with the end carbons at distances of 2.228(4) and 2.287(7) Å ($\Delta = 0.06$ Å). The latter bears the trimethylsilyl substituent, which is only 0.01 Å from the C_3 plane. In contrast, the end carbons of the terminal allyl on Cr(1) vary in distance from 2.192(11) Å (Cr1–C1) to 2.303(5) (Cr1–C3) ($\Delta = 0.11$ Å). The trimethylsilyl group, bonded to C3, lies 0.12 Å (3.8°) out of the C_3 plane, away from the metal. It is notable that in each case the TMS-substituted end of the allyl ligand displays the longer Cr–C distance, a finding that is in contrast to a recent theoretical analysis of substituted allyl ligands in $[(\text{allyl})\text{Pd}(\text{PH}_3)_2]^+$ cations [64,65]. In such species, the silicon-bearing ends of the ligands exhibit the shortest metal–carbon distances.

The bridging allyl ligands display nearly symmetrical bonding to the two chromium atoms; the Cr1–C9 and Cr2–C7 distances vary by only 0.02 Å, and the Cr1–C19 and Cr2–C21 distances differ by 0.04 Å. In both cases, the (slightly) shorter Cr–C bonds belong to the TMS-substituted ends of the ligands. Unlike the case with the terminal allyl ligands, the trimethylsilyl groups do not lie in the allyl planes; Si(2) and Si(4) are displaced by 0.89 and 0.65 Å from their C_3 planes, forming angles of 28.7 and 20.0°, respectively. These distortions serve to minimize steric congestion, but whether they reflect other electronic effects (e.g. silyl hyperconjugation) is not clear.

3.3. Solid state structure of $[(\text{SiMe}_3)_3\text{C}_3\text{H}_2]_2\text{Cr}$ (**3**)

Compound **3** crystallizes from hexanes as a monomer with crystallographically imposed inversion symmetry. A summary of bond distances and angles for **3** is given

in Table 3; an ORTEP view of the complex is displayed as Fig. 2.

The allyl ligands in **3** are arranged about the metal in a staggered configuration; this is the same arrangement found in **2** [47]. Owing to the inversion center, the two C_3 allyl planes are parallel. The ligands are bound in a *trihapto* manner to the chromium center, but the bis(trimethylsilyl)-substituted end of the allyl ligand is displaced to one side, with Cr–C1 and Cr–C3 bond lengths of 2.319(5) and 2.238(4) Å, respectively. The 0.081 Å variation possibly reflects the greater steric bulk of the C1 end of the allyl ligand, as the variation averages 0.047 Å in the symmetrically substituted **2**.

The trimethylsilyl groups are in a *syn, syn-anti* configuration, and display a combination of both in-plane and out-of-plane positions relative to their C_3 planes. The two *syn*-TMS groups lie with 0.3 Å of the allyl plane, whereas the silicon atom of the *anti*-TMS group is 1.08 Å out of the plane, and forms an angle of 34.9° with it. As a consequence of the bending of the TMS groups, the environment around C(3) is distinctly pyramidal; the sum of the C–C–Si and Si–C–Si angles is 349°. Interligand contact distances are understandably closer than in the less heavily substituted **2**; the C(6)···C(9) distance, for example, is 3.77 Å, within van der Waals contact for two methyl groups. Nevertheless, there are no distortions that can be obviously traced to the operation of agostic interactions with hydrogen atoms of the trimethylsilyl groups.

3.4. Computational modeling of $(\text{C}_3\text{H}_5)_2\text{Cr}$

The staggered and eclipsed structures of $(\text{C}_3\text{H}_5)_2\text{Cr}$ (Fig. 3) were calculated at the B3PW91/6-311+G(2d,2p)//B3PW91/6-31+G(d) level. The energy difference between the two forms (including ZPE corrections) is only 0.33 kcal mol⁻¹ in favor of the staggered form. The slight preference for the former is not energetically

Table 3
Selected bond distances (Å) and angles (°) for **3**

Atoms	Distance	Atoms	Angle
Cr–C2	2.223(5)	C3–Cr–C1'	112.17(16)
Cr–C3	2.238(4)	C1'–Cr–C1	180.0(2)
Cr–C1	2.319(5)	C2–C1–Si1	118.3(4)
C1–C2	1.400(6)	C1–C2–C3	127.6(4)
C2–C3	1.435(6)	C2–C3–Si2	114.4(3)
C2'–Cr–C2	180.0	C2–C3–Si3	115.9(3)
C2–Cr–C3'	142.48(16)	Si2–C3–Si3	119.0(2)
C3'–Cr–C3	180.0	Si2–C3–Cr1	125.7(2)
C2–Cr–C1'	144.16(16)	Si3–C3–Cr1	102.01(19)
		Displacement of Si(1)	29.9° (= 0.91 Å)
		Displacement of Si(2)	28.4° (= 0.89 Å)
		Displacement of Si(3)	28.4° (= 0.89 Å)

Symmetry transformations used to generate equivalent atoms: $-x+1, -y+1, -z+1$.

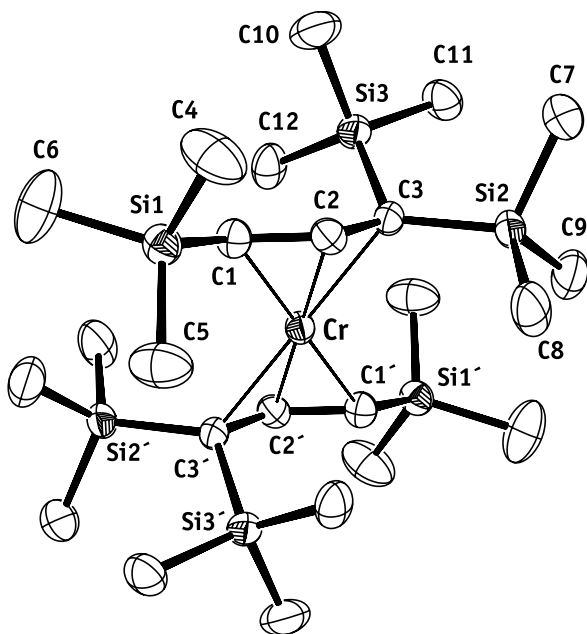


Fig. 2. ORTEP diagram of the non-hydrogen atoms of [1,1',3-(SiMe₃)₃C₃H₅]₂Cr (**3**), giving the numbering scheme used in the text. Thermal ellipsoids are displayed at the 50% level.

significant at this level of theory. The calculated bond distances for the staggered form are within 0.02 Å of those observed in **2**; i.e. the Cr–(C1,C3) and Cr–C2 distances of 2.228 and 2.213 Å can be compared to the experimental averages of 2.233 and 2.194 Å, respectively. The two allyl planes are computed to be exactly parallel; the observed angle in **2** is 10.4°, a difference likely due to crystal packing, as the ligands are parallel in **3**. In general, the trimethylsilyl groups, although important in stabilizing the chromium complex, appear to exert relatively little influence on the metal–carbon geometry.

The frontier molecular orbitals and their energies for (C₃H₅)₂Cr are depicted in Fig. 4. It is worth noting that the ordering is qualitatively similar to that calculated by Decleva et al. for (C₃H₅)₂Ni using a CI method [66]. In both schemes, the HOMO is constructed from the π–π

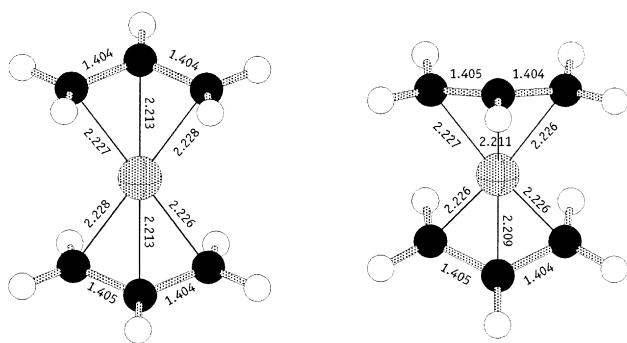


Fig. 3. Calculated structure of (C₃H₅)₂Cr molecule, staggered (left) and eclipsed (right).

overlap of the allyl ligand set of *a_u* symmetry, and is non-bonding with respect to the metal d orbitals. Four non-bonding 3d orbitals constitute the HOMO-*n* (*n* = 1–4) orbitals; HOMO-5 is generated from the allyl π orbital combination of *b_g* symmetry with the d_{xz} orbital. The relatively close spacing of the four frontier orbitals (≤0.3 eV) is responsible for the high-spin state of (C₃H₅)₂Cr. The large HOMO–LUMO gap of 5.25 eV is consistent with a thermodynamically stable compound; this is borne out with the trimethylsilylated compounds **2** and **3**.

4. Discussion

Even though bis(allyl)chromium(II) has been known for over 35 years [67], the compounds described here are the first homoleptic chromium derivatives to contain allyls other than the parent C₃H₅ ligand. The bulk of the trimethylsilylated ligands shows a progressive effect on the structure and reactivity of the resulting complexes. The presence of a single trimethylsilyl group produces the dimeric {[1-(SiMe₃)C₃H₄]₂Cr}₂ (**1**), whose multiply bonded structure is like the parent [(C₃H₅)₂Cr]₂ [45], but the bis- and *tris*-trimethylsilylated ligands generate monomeric high-spin (four unpaired electrons) bis(π-allyl)chromium(II) complexes [(SiMe₃)_{*n*}C₃H_{5-*n*}]₂Cr that are thermally stable at room temperature, even with their extremely low 12-electron counts.

Although (η³-C₃H₅)₃Cr reacts with P-donor ligands to give 1:1 adducts [68], the parent [(C₃H₅)₂Cr]₂ does not undergo simple addition reactions with donor ligands to yield stable complexes [46]. The phosphine adducts of (C₃H₅)₂Cr that Jolly and co-workers have described (i.e. (η³-allyl)₂Cr(PR₃)₂ and (η³-allyl)₂Cr(R₂PC₂H₄PR₂)) have been prepared by substitution reactions on phosphine adducts of chromium(II) chloride [46]. Thus the direct reaction of PMe₃ with **2** to yield a phosphine adduct represents a new mode of reactivity for a homoleptic allyl complex of chromium(II). The fact that the phosphine is slowly lost over a period of several weeks suggests that steric bulk of the allyl ligands may be limiting the strength of the phosphine metal interaction. This conjecture is supported by the lack of reactivity of the more sterically encumbered **3** with PMe₃.

Although perhaps not completely surprising, it is interesting to note that the computed structure of (C₃H₅)₂Cr presents a molecular orbital picture that is qualitatively similar to that previously calculated for (C₃H₅)₂Ni [66]. This suggests that the (trimethylsilyl)-substituted allyl complexes could serve as models for monomeric (C₃H₅)₂Cr, which is unstable with respect to dimerization.

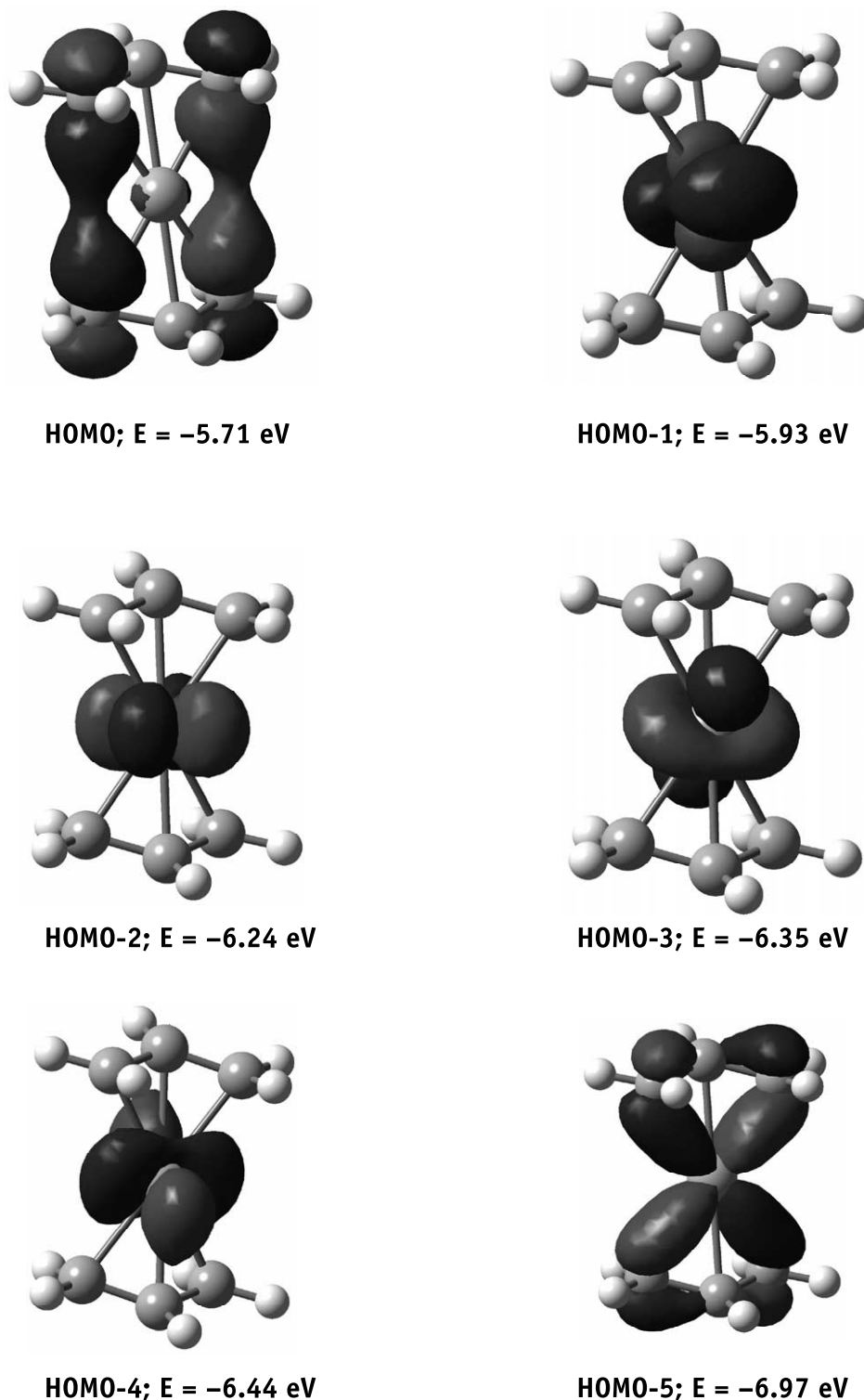


Fig. 4. Frontier molecular orbitals of $(C_3H_5)_2Cr$ (HOMO to HOMO-5).

5. Conclusions

The use of bulky trimethylsilylated allyl ligands has permitted the isolation and structural characterization of homoleptic complexes of $(\pi\text{-allyl})_2Cr(II)$ that, depending on the amount of steric bulk, can be isolated in

either dimeric or monomeric forms. X-ray crystallography has been used to confirm the η^3 -binding of the allyl ligands in the monomers. The thermal stability of the monomers (and of the phosphine adduct formed with **2**) indicates that the general strategy of employing sterically enhanced ligands, long a successful approach in

cyclopentadienyl chemistry, can be extended to allyl chemistry as well.

The generally good agreement between the experimentally determined and calculated structures of the monomeric complexes is encouraging, and suggests that the trimethylsilyl groups may be relatively structurally innocent. The rich variety of substituents that are available in sterically bulky allyls (e.g. alkyls, aryls, asymmetrically substituted ligands, etc.) points to a potentially large area of transition metal organometallic chemistry that will now be experimentally accessible, and will benefit from intensive investigation.

6. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 207170 for compound **1** and 207171 for compound **3**. Data for **2** were previously deposited as no. 167364. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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