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Synthesis of chromium(III) bis(benzamidinate) complexes via single electron oxidation

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Abstract

Single-electron oxidation of the known Cr(II) bis(amidinate) Cr[$(Me_3SiN)_2CPh]_2$ (**1**) provides synthetic access to neutral Cr(III) complexes. The complexes Cr[$(Me_3SiN)_2CPh]_2X$ were prepared by reaction of **1** with AgO_2CPh (X = O_2CPh, **2**), of **1** with iodine in THF (X = I/THF, **3**), or of **1** with iodine in pentane, followed by addition of 2-adamantanone (X = I/2-adamantanone, **4**). Treatment of **2** or **3** with C_3H_5MgCl resulted in the thermally stable allyl complex (X = η^3-C_3H_5, **5**). A preliminary kinetics study of the reaction of **1** with excess allyl benzoate and allyl acetate was performed. The molecular structures of **2**, **3** and **5** were confirmed by single crystal X-ray diffraction.

Keywords: Chromium complexes; X-ray structure; Amidinate ligands; Allyl; Oxidation

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1. Introduction

Transition metal allyl complexes are key intermediates in catalytic applications for organic synthesis [1]. In 1977, Nozaki, Hiyama and co-workers reported the stoichiometric use of $CrCl_2$ for coupling allylic halides and aldehydes to produce alcohols [2]. The single-electron oxidative addition process that generates reactive Cr(III) allyl complexes from Cr(II) chloride and allyl chloride is illustrated in Scheme 1 [3]. Chlorine atom abstraction by $CrCl_2$ forms $CrCl_3$ and an allyl radical, which then reacts with a second equivalent of $CrCl_2$ to give a Cr(III) allyl species [4]. The ease with which allyl halides form Cr(III) organometallic complexes when treated with $CrCl_2$ obviates the need for the metal additives required for less reactive organic halide substrates, like the catalytic cobalt [5] or nickel [6] salts added to $CrCl_2$ for reactions involving alkyl halides or alkenyl and aryl halides, respectively. Not only are additives not required for $CrCl_2$ activation of allylic halides, if present Ni(II) salts promote unwanted Wurtz coupling reactions [7].

The Cr(III) allyl complexes produced by single-electron oxidative addition exhibit reactivity features that render them useful for synthetic organic chemists [7]. They preferentially react with aldehydes and generally show good functional group tolerance. Anti configured allyl alcohol products are obtained whether the initial substituted allyl halide has an *E* or *Z* configuration [7]. This diastereoselectivity is suggested to be due to the directing effects of steric interactions between the aldehyde and the substituent on the η^1-allyl ligand in the chair configured transition state

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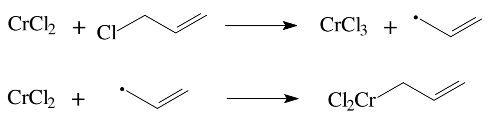
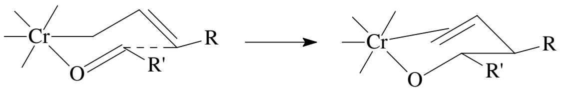


Scheme 1. Single-electron oxidative addition of allyl chloride to $CrCl_2$ to form reactive Cr(III) allyl species.



Scheme 2. Steric interactions in the transition state of carbon-carbon bond formation responsible for the anti diastereoselectivity of Cr-mediated coupling of aldehyde and allyl ligands.

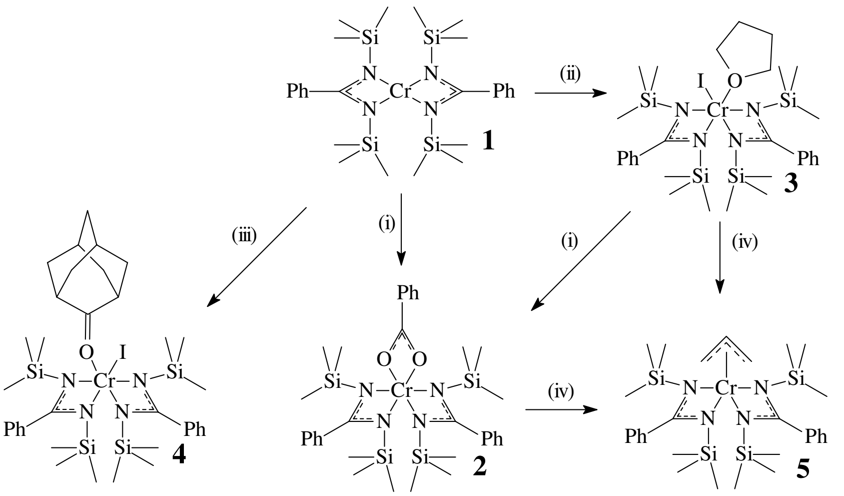
of the C–C bond-forming step (Scheme 2) [1a,7,8]. In 1996, Fürstner and co-workers rendered the reaction catalytic in chromium, using Me_3SiCl to break the inert Cr(III)–oxygen bond, and Mn as the stoichiometric reductant to regenerate the active Cr(II) species [9]. In the decade since Fürstner's report of the catalytic reaction, several groups have reported chiral ligand systems to render the coupling of allyl halides and aldehydes catalytic and enantioselective [8,10–16].

As part of our investigation of well-defined paramagnetic organometallic chromium compounds of relevance to catalytic carbon-carbon bond formation [17], we were interested in synthesizing thermally-stable Cr(III) allyl complexes with tunable ancillary ligands. As previously reported, reaction of $CpCr[(Me_3SiN)_2CPh]Cl$ with allyl Grignard resulted in reduction to the corresponding Cr(II) complex [18]. In this paper, we use single electron oxidation reactions of a Cr(II) complex first prepared by Edelmann and co-workers, $Cr[(Me_3SiN)_2CPh]_2$ (**1**) [19], in order to synthesize Cr(III) bis(benzamidinate) compounds, including the thermally stable η^3-allyl derivative.

2. Results and discussion

Much of the research on Cr amidinate complexes has focused on $Cr_2(amidinate)_4$ complexes [20] containing Cr–Cr quadruple bonds [21]. However, there exists a range of structural possibilities for $Cr(LX)_2$ (LX = bidentate, monoanionic ligand) complexes, from dimers with the common paddlewheel geometry [20] to square planar bis-ligand monomers [22], to flattened tetrahedral $Cr(LX)_2$ compounds [19a,23]. The relative stabilities of these species, as well as their tendency to distort from the ideal structures, are linked to the steric demands of the ligands, which are not solely dictated by the size of the donor atom substituents. The critical role of intraligand steric repulsion between the amidinate N groups and the substituent on the central C atom has been demonstrated by several research groups [22d,24]. The importance of interligand steric interactions in controlling the stereochemistry in an extensive variety of bis-chelate metal(II) complexes was investigated in detail in the 1960s and 1970s [22ab, 25], and these considerations remain remarkably useful in evaluating the distortions from the electronically preferred square planar geometry observed in some Cr(II) bis-chelate complexes [23].

To synthesize the target $M[(Me_3SiN)_2CPh]_2(\eta^3\text{-}C_3H_5)$ compound for M = Cr, we initially investigated the synthetic route successfully applied for the corresponding M = Ti [26] and M = V [27] complexes. The reaction of $CrCl_3(THF)_3$ with 2 equivalents of $(tmeda)Li[(Me_3SiN)_2CPh]$ gives the Cr(III) bis(amidinate) "ate" complex, $[PhC(NSiMe_3)_2]_2Cr(\mu\text{-}Cl)_2Li(tmeda)$, where tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine. The structure of $[PhC(NSiMe_3)_2]_2Cr(\mu\text{-}Cl)_2Li(tmeda)$ [28] is similar to the Ti(III) complex with identical ligands prepared by Gambarotta and co-workers [26]. The low yield and slow deposition of LiCl from the Cr(III) "ate" complex encouraged the



Scheme 3. Synthesis of Cr(III) bis(amidinate) complexes from **1**. Experimental conditions: (i) AgO_2CPh, THF; (ii) I_2, THF; (iii) (a) I_2, pentane, (b) 2-adamantanone; (iv) C_3H_5MgCl, THF.

development of alternative synthetic routes to the desired allyl complex [29].

Single-electron oxidation has been shown to be a useful synthetic strategy to prepare well-defined, mixed ligand complexes [17,30]. In order to obtain neutral Cr(III) bis(amidinate) complexes, the oxidation of the known Cr(II) complex **1** was investigated (Scheme 3). Treatment of **1** with AgO_2CPh generated Ag metal and the Cr(III) benzoate complex, $Cr[(Me_3SiN)_2CPh]_2(O_2CPh)$ (**2**) (Fig. 1). The viability of **2** had been presaged by the isolation and structural characterization of a related complex, $Cr[(Me_3SiN)_2CPh]_2[(HN)_2CPh]$ [31], an unexpected minor byproduct in the preliminary reactivity studies performed on $CpCr[(Me_3SiN)_2CPh]Cl$ [18]. The bidentate coordination of the benzoate ligand is consistent with the marked affinity of Cr(III) for the 6-coordinate, pseudo-octahedral geometry.

Oxidation of **1** with I_2 in THF gives the 6-coordinate solvated complex $Cr[(Me_3SiN)_2CPh]_2(I)(THF)$ (**3**) in moderate yields. The synthesis of $Mn[(Me_3SiN)_2CPh]_2I$ has previously been reported using a similar synthetic strategy: salt metathesis by reaction of $MnI_2(THF)_2$ with $Mg[(Me_3SiN)_2CPh]_2(THF)_2$, followed by oxidation with iodine [32]. Crystals of **3** suitable for X-ray diffraction were obtained by recrysallization from a mixture of pentane and THF (Fig. 2). Reaction of the Cr(III) iodide **3** with AgO_2CPh provided an alternative synthetic route to the Cr(III) benzoate **2** via formation of the insoluble AgI salt. Treatment of **1** with I_2 in pentane followed by addition of 2-adamantanone (OAd, $C_{10}H_{14}O$) provides access to the ketone adduct of the Cr(III) iodide, $Cr[(Me_3SiN)_2CPh]_2(I)(OAd)$ (**4**). Efforts to obtain X-ray quality crystals of **4** were unsuccessful. However, the corresponding Cr(III) chloride complex of 2-adamantanone, obtained by a similar oxidation of **1** in pentane with $PbCl_2$ followed by addition of the ketone, was amenable to characterization by single crystal X-ray diffraction (see Supplementary data).

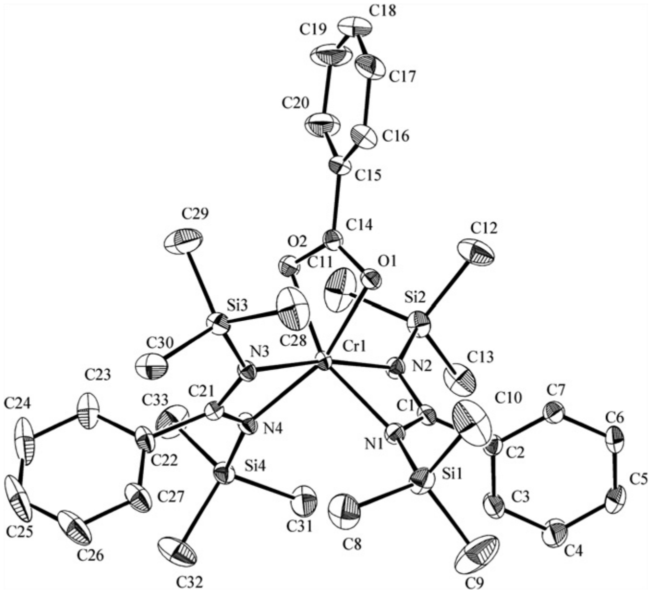


Fig. 1. ORTEP diagram of $Cr[(Me_3SiN)_2CPh]_2(O_2CPh)$ (**2**; 50% ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cr(1)–N(1) = 2.0364(13), Cr(1)–N(2) = 2.0620(13), Cr(1)–N(3) = 2.0395(14), Cr(1)–N(4) = 2.0450(14), Cr(1)–O(1) = 2.0584(12), Cr(1)–O(2) = 2.0553(11), N(1)–Cr(1)–N(2) = 66.28(5), N(3)–Cr(1)–N(4) = 66.42(6), O(1)–Cr(1)–O(2) = 64.22(5), Cr(1)–N(1)–Si(1) = 139.69(8), Cr(1)–N(2)–Si(2) = 135.23(7), Cr(1)–N(3)–Si(3) = 137.91(8), Cr(1)–N(4)–Si(4) = 136.59(8), N(1)–C(1)–N(2) = 114.90(14), N(3)–C(21)–N(4) = 114.67(15).

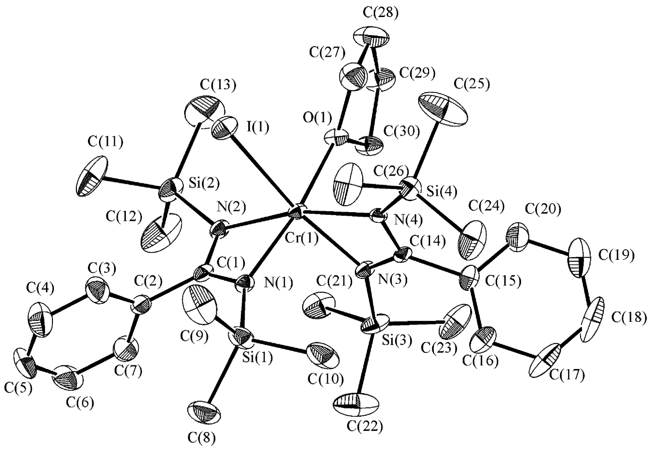


Fig. 2. ORTEP diagram of $Cr[(Me_3SiN)_2CPh]_2(I)(THF)$ (**3**; 50% ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cr(1)–I(1) = 2.7664(5), Cr(1)–N(1) = 2.023(3), Cr(1)–N(2) = 2.081(3), Cr(1)–N(3) = 2.050(3), Cr(1)–N(4) = 2.083(3), Cr(1)–O(1) = 2.103(2), N(1)–Cr(1)–N(2) = 66.21(11), N(3)–Cr(1)–N(4) = 65.93(10), I(1)–Cr(1)–O(1) = 90.45(6), I(1)–Cr(1)–N(1) = 90.57(7), I(1)–Cr(1)–N(2) = 87.83(7), I(1)–Cr(1)–N(3) = 168.02(8), I(1)–Cr(1)–N(4) = 102.10(7), Cr(1)–N(1)–Si(1) = 139.95(16), Cr(1)–N(2)–Si(2) = 139.04(16), Cr(1)–N(3)–Si(3) = 139.43(16), Cr(1)–N(4)–Si(4) = 141.87(15), N(1)–C(1)–N(2) = 115.4(3), N(3)–C(21)–N(4) = 121.9(3).

As shown in Scheme 2, the distinct selectivity profile of the $CrCl_2$-mediated coupling of allyl halides and aldehydes is attributed to the nature of the transition state for the key carbon-carbon bond-forming reaction step [1a,7,8]. This mechanism requires the aldehyde to coordinate cis to the η^1-allyl ligand. It is significant to note that in all of the 6-coordinate Cr bis(amidinate) complexes we have structurally characterized, the two amidinates are related by an approximate C_2 axis and the remaining two coordination sites posses a cis orientation. While this geometry is presumably required for the chelating benzoate **2**, and is likely reinforced by the bridging $Cr(\mu\text{-}Cl)_2Li$ structural unit in $[(Me_3SiN)_2CPh]_2Cr(\mu\text{-}Cl)_2Li(tmeda)$ [26,28], its recurrence in the halide/solvent and halide/ketone structures is encouraging [29b]. This situation is in contrast to some of the chiral ligand systems currently used with Cr in catalytic, asymmetric reactions, where the trans configurations of neutral and anionic ligands has led to mechanistic proposals involving the bimolecular reaction of two Cr complexes in the C–C bond formation step [10,33].

Reaction of the Cr(III) iodide **3** with C_3H_5MgCl in THF led to the formation of the allyl complex, $Cr[(Me_3SiN)_2CPh]_2(\eta^3\text{-}C_3H_5)$ (**5**). Related alkylation reactions have been reported in the patent literature, where the treatment of $Cr[(Me_3SiN)_2CPh]_2Cl$ with stoichiometric

$LiCH_2SiMe_3$ produced an active catalyst for olefin oligomerization [29a]. The relatively low recrystalized yield of **5** (25–40%) is presumably due to the high pentane solubility of the complex: while the Cr(III) allyl complex could also be synthesized by reaction of Cr(III) benzoate with the allyl Grignard, or sequential addition of I_2 then C_3H_5MgCl to Cr(II) complex **1**, the isolated recrystallized yield of **5** from pentane fell in the same range for each synthetic route. Addition of 1,4-dioxane appeared to assist in the separation of byproduct Mg salts, but did not lead to higher yields of the allyl product. The X-ray structure of **5** (Fig. 3) exhibited the allyl ligand disordered over two positions. The same disorder was reported for the V(III) analog of **5** [27], whose authors suggested that the unusual distortions reported previously for the allyl ligand of the Ti(III) complex might also be due to this type of disorder [26].

Despite the widespread interest in the synthesis of Cr(III) alkyl complexes due to their involvement in Cr-based olefin polymerization catalysts [34], examples of Cr(III) allyl complexes amenable to systematic study at room temperature are rare. Compared to other $[CrR_3(THF)_n]$ species, the homoleptic allyl complex is second in thermal stability only to the venerable tris(aryl) compounds [35], and is more robust than the corresponding benzyl, alkyl or vinyl complexes [36]. However, the proposed bimolecular thermal decomposition of $Cr(C_3H_5)_3$ to give $(C_3H_5)Cr(\mu\text{-}C_3H_5)_2Cr(C_3H_5)$ and 1,5-hexadiene is a recurring reactivity motif in Cr(III) allyl chemistry [36]. These reactions have been pursued in detail by Jolly and co-workers for $CpCr(\eta^3\text{-}C_3H_5)_2$ and various substituted derivatives [37]. In 2005, Stryker and co-workers reported the single-electron oxidation of the 18e Cr(II) $CpCr(\eta^3\text{-}C_3H_5)(CO)_2$ to the corresponding 17e $Cr(III)[CpCr(\eta^3\text{-}C_3H_5)(CO)_2][PF_6]$ complex, which is indefinitely stable as a solid at room temperature [38]. The thermal stability of Gabbaï's $Cp^*Cr(C_6F_5)(\eta^3\text{-}CH_2Ph)$ benzyl complex [39] suggests that with a suitable monodentate anionic ligand, 15e $CpCr(X)(\eta^3\text{-allyl})$ spin quartet complexes may be accessible, in contrast with the reduction to Cr(II) observed for the putative $CpCr[(Me_3SiN)_2CPh](C_3H_5)$ intermediate [18]. The thermal stability of **5** in the solid state and in solution is presumably due to the steric protection of the η^3-allyl provided by the bulky *N*,*N*′-bis(trimethylsilyl)-benzamidinate ligands, leading to an increased barrier to bimolecular decomposition pathways.

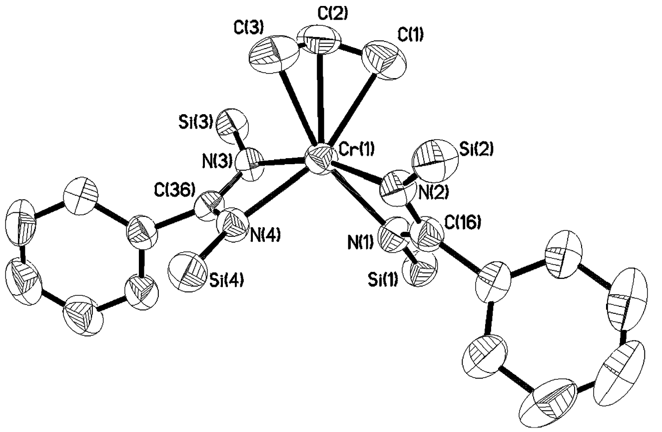


Fig. 3. ORTEP diagram of $Cr[(Me_3SiN)_2CPh]_2(\eta^3\text{-}C_3H_5)$ (**5**; 50% ellipsoids). Hydrogen atoms and amidinate methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cr(1)–N(1) = 2.0733(19), Cr(1)–N(2) = 2.105(2), Cr(1)–N(3) = 2.0835(19), Cr(1)–N(4) = 2.0726(19), Cr(1)–C(1) = 2.272(3), Cr(1)–C(2) = 2.256(4), Cr(1)–C(3) = 2.229(3), N(1)–Cr(1)–N(2) = 65.09(8), N(3)–Cr(1)–N(4) = 65.36(8), C(1)–Cr(1)–C(3) = 65.21(15), C(1)–C(2)–C(3) = 129.4(6), Cr(1)–N(1)–Si(1) = 137.09(12), Cr(1)–N(2)–Si(2) = 142.15(12), Cr(1)–N(3)–Si(3) = 140.98(11), Cr(1)–N(4)–Si(4) = 137.91(12), N(1)–C(16)–N(2) = 115.9(2), N(3)–C(36)–N(4) = 115.5(2).

Previously, UV–visible spectroscopy had been employed to monitor the progress of the oxidative addition reaction of iodomethane with $CpCr[(ArNCMe)_2CH]$ (Ar = 2,6-diisopropylphenyl, $2,6\text{-}(CHMe_2)_2C_6H_3$) under pseudo-first-order conditions [40]. Initial reactions of Cr(II) bis(amidinate) **1** and excess $H_2C{=}CHCH_2Cl$ proceeded too rapidly for the same procedure to be followed: the color change that accompanied the reaction was essentially complete before the sealable UV–vis cell could be loaded and removed from the glovebox. Given the manifest stability of the Cr(III) benzoate complex **2**, it seemed probable that the reaction of **1** with allyl benzoate to give **2** and **5** should be thermodynamically favorable. Dilute pentane solutions of **1** were prepared (typically 20 mg of **1** in 100 mL of pentane, $[\mathbf{1}] = 3.5 \times 10^{-4}$ M), excess $H_2C{=}CHCH_2O_2CPh$ was added, and the growth of the absorbance band at 439 nm was monitored by UV–vis spectroscopy. Plots of k_{obs} vs $[C_3H_5OBz]$ were linear under the pseudo-first-order conditions employed, consistent with the generally-accepted mechanism for single-electron oxidative addition of organic substrates by Cr(II) illustrated in Scheme 1. The second order rate constant obtained by this preliminary kinetics study was calculated to be $(4.4 \pm 0.4) \times 10^{-2}\ M^{-1}s^{-1}$. The reaction of **1** and allyl acetate was investigated by the same procedure, with a resulting second order rate constant of $(2.8 \pm 0.2) \times 10^{-2}\ M^{-1}s^{-1}$. The slightly higher reactivity of the benzoate may be attributed to a decrease in the C–O bond dissociation energy in $H_2C{=}CHCH_2\text{–}O_2CR$ for R = Ph compared to R = Me [3].

3. Conclusions

The known Cr(II) bis(amidinate) complex $Cr[(Me_3SiN)_2CPh]_2$ [19] was demonstrated to be a useful synthetic precursor to new Cr(III) complexes, including a thermally stable η^3-allyl complex. A preliminary kinetics study on the rate of reaction of $Cr[(Me_3SiN)_2CPh]_2$ with allylic carboxylates was performed. As previously noted in other systems, addition of electron donating ligands with N donor atoms increases the rate at which Cr(II) reacts with organic substrates in one-electron oxidative addition reactions [4,40]. In this case, complex **1** reacts in pentane with allylic esters, a class of reactants outside of the scope typically employed in organic synthetic applications of $CrCl_2$, where allyl bromides and chlorides are normally used [7,10–15], although use of allyl tosylates and mesylates have also been reported [7].

4. Experimental

4.1. General considerations

All compounds were synthesized and stored under N_2 using standard Schlenk and glovebox techniques. Samples for X-ray diffraction, melting point determination, elemental analysis, and infrared spectroscopy were prepared in a glovebox. Melting point determinations were performed in flame-sealed tubes and are uncorrected. Infrared spectra were obtained from KBr pellets on a Perkin–Elmer 1600 Series FTIR. All UV–visible measurements were conducted in pentane solution in a specially constructed cell for air-sensitive samples: a Kontes Hi-Vac® Valve with PTFE plug was attached by a professional glassblower to a Hellma 10 mm path length quartz absorption cell with a quartz-to-glass graded seal. The kinetics measurements were collected using a Varian Cary 50 Bio UV–visible spectrophotometer, and the data were fit to a first order growth equation using the instrument software. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, ON, Canada. Spectroscopic and physical data for complexes **2**–**5** are collected in Table 1.

Anhydrous THF and pentane were dried by passage through a column of activated alumina [41]. Anhydrous reagents (2.0 M C_3H_5MgCl in THF, $LiN(SiMe_3)_2$, PhCN, tmeda *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, AgO_2CPh) were purchased from Aldrich and used as received. Iodine (Aldrich) was sublimed prior to use. 2-Adamantanone (Aldrich) was used as received. Allyl acetate (Aldrich) and allyl benzoate (TCI America) were degassed by three freeze-pump-thaw cycles, and then dried over molecular sieves prior to use. $Cr[(Me_3SiN)_2CPh]_2$ (**1**) was synthesized in a modification of the literature procedure [19a,22d], from $CrCl_2(tmeda)$ [42] and $(tmeda)Li[(Me_3SiN)_2CPh]$ [26].

4.2. Synthesis of $[(Me_3SiN)_2CPh]_2Cr(\mu\text{-}Cl)_2Li(tmeda)$

To a solution of $(tmeda)Li[(Me_3SiN)_2CPh]$ (390.4 mg, 1.01 mmol) in 30 mL of THF, $CrCl_3(THF)_3$ (189.1 mg, 0.505 mmol) was added as a solid. The reaction mixture immediately turned a teal blue color. After stirring overnight, the reaction mixture was greenish-blue to incident light and green to transmitted light. The solvent was removed *in vacuo*. The reaction mixture was extracted with pentane, filtered through Celite, and concentrated *in vacuo*. To the solution was added 200 μL of tmeda. The solution was filtered through Celite again, and cooled to −30 °C overnight to give dark crystals of $[(Me_3SiN)_2CPh]_2Cr(\mu\text{-}Cl)_2Li(tmeda)$ (101.1 mg, 26% yield). Elemental analysis: calculated (found) C: 49.72% (49.47%); H: 8.08% (8.42%); N: 10.87% (11.24%).

4.3. Synthesis of $Cr[(Me_3SiN)_2CPh]_2(O_2CPh)$ (2)

To a solution of **1** (573.8 mg, 0.990 mmol) in 40 mL THF, AgO_2CPh (230.0 mg, 1.004 mmol) was added as a solid. The reaction mixture immediately darkened, and a precipitate was visible. After stirring overnight, the solvent was removed *in vacuo*. The reaction mixture was extracted with pentane and filtered through Celite to remove the grey metallic precipitate from the red-brown solution. The solvent was again removed in vacuo, redissolved in a minimum of pentane, filtered through Celite, and cooled to −30 °C overnight to give black metallic crystals of **2** (447.3 mg, 65% yield).

4.4. Synthesis of $Cr[(Me_3SiN)_2CPh]_2(I)(THF)$ (3)

To a solution of **1** (584.7 mg, 1.01 mmol) in 35 mL THF, I_2 (128.1 mg, 0.505 mmol) was added as a solid. After stirring overnight, the solvent was removed *in vacuo*. The residue was extracted with a mixture of pentane and THF (5:1). The solution was concentrated *in vacuo*, filtered, and cooled to −30 °C for several days to give green crystals of **3** (494.1 mg, 63% yield).

4.5. Synthesis of $Cr[(Me_3SiN)_2CPh]_2(I)$(2-adamantanone) (4)

To a solution of **1** (152.9 mg, 0.264 mmol) in 15 mL pentane, I_2 (35.6 mg, 0.140 mmol) was added as a solid. The purple solution turned yellow-brown to incident light, red to transmitted light. After the solution was stirred for 45 min, 2-adamantanone (39.3 mg, 0.262 mmol) was added to the reaction mixture as a solution in 5 mL of pentane. As the pentane solution of 2-adamantanone was added, the

Table 1
Spectroscopic and physical data for $Cr[(Me_3SiN)_2CPh]_2X$

Compound # (X)	M.p. (°C)	UV–visible	Elemental analysis: calculated (found)		
		λ (ε $M^{-1}cm^{-1}$)	C (%)	H (%)	N (%)
2 (O_2CPh)	181–182	437 nm (166)	56.61 (56.92)	7.34 (7.66)	8.00 (8.17)
3 (I/THF)	168–170	460 nm (237)	46.31 (46.14)	7.00 (6.89)	7.20 (7.39)
4 (I/OAd)	179–181	401 nm (640)	50.51 (50.87)	7.06 (7.37)	6.54 (6.88)
5 (C_3H_5)	164–165	432 nm (786)	56.17 (55.93)	8.29 (8.61)	9.03 (9.28)

solution turned green. The solution was concentrated *in vacuo*, filtered, and cooled to −30 °C for several days to give dark crystals of **4** in two crops (119.7 mg, 54% yield).

4.6. Synthesis of $Cr[(Me_3SiN)_2\ CPh]_2(\eta^3\text{-}C_3H_5)$ (**5**)

To a solution of **5** (377.9 mg, 0.486 mmol) in 35 mL THF, C_3H_5MgCl (0.28 mL of 2.0 M solution in THF, 0.56 mmol) was added by syringe. The solution immediately turned to a red-brown color. After stirring for 90 min, the solvent was removed *in vacuo*. The residue was extracted with 30 mL of pentane, filtered through Celite, and the solvent was again removed *in vacuo*. The residue was extracted with a minimum amount of pentane, filtered through Celite, and cooled −30 °C for several days to give dark crystals of **5** in two crops (111.8 mg, 37% yield).

4.7. X-ray crystallographic data

Crystal data for $C_{33}H_{51}CrN_4O_2Si_4$ (**2**): $M = 700.17$, Monoclinic, space group $P2(1)/c$, $a = 11.6635(5)$ Å, $b = 17.6196(7)$ Å, $c = 19.5093(9)$ Å, $\beta = 98.526(2)°$, $\alpha,\gamma = 90°$, $U = 3965.0(3)$ Å^3, $Z = 4$, $D_c = 1.173$ g cm^{-3}, μ (Mo Kα) = 0.71069 Å, $T = 173(2)$ K, Rigaku/ADSC CCD, total reflections 35996, unique reflections $I > 0.00\sigma(I)$ 8441, observed reflections 8441 ($R_{int} = 0.044$). The structure was solved by direct methods [43] and expanded using Fourier techniques. Full-matrix least-squares refinement was conducted using SHELXL-97 [44]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Crystal data for $C_{30}H_{54}CrIN_4OSi_4$ (**3**): $M = 778.03$, Orthorhombic, space group $Pbca$, $a = 20.6181(8)$ Å, $b = 17.6960(6)$ Å, $c = 21.3316(9)$ Å, α, β, $\gamma = 90°$, $U = 7783.0(5)$ Å^3, $Z = 8$, $D_c = 1.328$ g cm^{-3}, μ (Mo Kα) = 0.71069 Å, $T = 173(2)$ K, Rigaku/ADSC CCD, total reflections 63931, unique reflections $I > 0.00\sigma(I)$ 7289, observed reflections 7289 ($R_{int} = 0.102$). The structure was solved by direct methods [43] and expanded using Fourier techniques. Full-matrix least-squares refinement was conducted using SHELXL-97 [44]. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined.

Crystal data for $C_{29}H_{51}CrN_4Si_4$ (**5**): $M = 620.10$, Triclinic, space group $P\bar{1}$, $a = 10.942(2)$ Å, $b = 11.921(2)$ Å, $c = 15.426(3)$ Å, $\alpha = 68.131(4)°$, $\beta = 78.321(3)°$, $\gamma = 87.146(6)°$, $U = 1827.8(6)$ Å^3, $Z = 2$, $D_c = 1.127$ g cm^{-3}, μ (Mo Kα) = 0.71073 Å, $T = 291(2)$ K, Siemens 1K SMART/CCD, total reflections 35996, unique reflections $I > 2\sigma(I)$ 6361, observed reflections 9773 ($R_{int} = 0.0208$). Direct methods and Fourier techniques were used to solve the structure; refinement was conducted by full-matrix least-squares methods on F^2 using SHELXTL-PC V5.03. All non-hydrogen atoms were refined anisotropically. The allyl ligand was disordered over two positions. All hydrogen atoms were included at geometrically idealized positions that were updated with each refinement cycle.

4.8. Kinetics measurements

In a glovebox, a sample of **1** (20.4 mg, 0.0352 mmol) was dissolved in pentane and diluted to the mark in a 100 mL volumetric flask (concentration 3.52×10^{-4} M). An excess of allyl benzoate (128.9 mg, 0.795 mmol, 22.6 mmol per mmol of **1**) was added to the volumetric flask, and the solution was thoroughly mixed. An aliquot was loaded into the UV–visible absorption cell for air-sensitive samples (described above), the cell was sealed and removed from the glovebox, and the sample was then transferred to the spectrophotometer. The absorption at 439 nm was recorded every 5 min for 300 min. The resulting kinetics trace of absorbance vs time was fit to a first-order growth curve to give the rate constant $k_{obs} = 0.0179$ min^{-1}. Three other experimental runs were performed similarly, with 20.6 mg, 20.4 mg, and 20.1 mg of **1**, 100.0 mL, 50.0 mL, and 100.0 mL of pentane, and 95 mg, 100 mg, and 191 mg of allyl benzoate, respectively. The k_{obs} obtained for runs 2, 3, and 4 with allyl benzoate were 0.0132 min^{-1}, 0.0342 min^{-1}, and 0.0286 min^{-1}, respectively. From the slope of the straight line plot of k_{obs} vs $C_3H_5O_2CPh$ concentration for the four experiments ($R^2 = 0.9782$), the second order rate constant k for the reaction with allyl benzoate was determined to be 0.044 ± 0.004 M^{-1} s^{-1}.

A series of four experiments using allyl acetate instead of allyl benzoate were also performed using the procedure described above. In each case, a volume of 100.0 mL of pentane was used, and the absorption at 439 nm was monitored every 5 min for 300 min. In the four runs, the masses of **1** used were 20.0 mg, 21.0 mg, 20.1 mg, and 20.4 mg and the volumes of allyl acetate added by 250 μL syringe were 60 μL, 45 μL, 72 μL, and 102 μL, respectively. The observed k_{obs} values obtained for the four runs were 0.0089 min^{-1}, 0.0048 min^{-1}, 0.0104 min^{-1}, and 0.0155 min^{-1}, respectively. From the slope of the straight line plot of k_{obs} versus $C_3H_5O_2CMe$ concentration for the four experiments ($R^2 = 0.9788$), the second order rate constant k for the reaction with allyl acetate was determined to be 0.028 ± 0.002 M^{-1} s^{-1}.

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Appendix A. Supplementary material

CCDC 634934, 634935, 634936, 634937 and 635124 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.053.

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