

## Coordination Chemistry

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# Beyond Takai's Olefination Reagent: Persistent Dehalogenation Emerges in a Chromium(III)- $\mu_3$ -Methyldiyne Complex

Simon Trzmiel, Jan Langmann, Daniel Werner, Cäcilia Maichle-Mössmer, Wolfgang Scherer,\* and Reiner Anwander\*

**Abstract:** Reaction of  $\text{CHI}_3$  with six equivalents of  $\text{CrCl}_2$  in THF at low temperatures affords  $[\text{Cr}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$  as the first isolable high-yield  $\text{Cr}^{\text{III}}$   $\mu_3$ -methyldiyne complex. Substitution of the terminal chlorido ligands via salt metathesis with alkali-metal cyclopentadienides generates isostructural half-sandwich chromium(III)- $\mu_3$ -methyldynes  $[\text{Cp}^R_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})]$  ( $\text{Cp}^R = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5, \text{C}_5\text{H}_4\text{SiMe}_3$ ). Side and decomposition products of the  $\text{Cl}/\text{Cp}^R$  exchange reactions were identified and structurally characterized for  $[\text{Cr}_4(\mu_2\text{-Cl})_4(\mu_2\text{-I})_2(\mu_4\text{-O})(\text{thf})_4]$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{CrCl}(\mu_2\text{-Cl})_2\text{Li}(\text{thf})_2]$ . The  $\text{Cl}/\text{Cp}^R$  exchange drastically changed the ambient-temperature effective magnetic moment  $\mu_{\text{eff}}$  from 9.30/9.11  $\mu_B$  (solution/solid) to 3.63/4.32  $\mu_B$  ( $\text{Cp}^R = \text{C}_5\text{Me}_5$ ). Reactions of  $[\text{Cr}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$  with aldehydes and ketones produce intricate mixtures of species through oxy/methyldiyne exchange, which were partially identified as radical recombination products through GC/MS analysis and  $^1\text{H}$  NMR spectroscopy.

## Introduction

Carbyne or alkylidyne moieties display archetypal ligands in organo(transition)metal chemistry.<sup>[1]</sup> In particular, alkylidyne complexes of the high-oxidation-state heavier group 6 metals molybdenum and tungsten emerged as eminent alkyne metathesis catalysts.<sup>[2]</sup> Such discrete complexes feature multiply bonded terminal moieties of the type  $\text{M}\equiv\text{CR}$  ( $\text{M} = \text{Mo}, \text{W}$ ) and have been studied comprehensively.<sup>[3,4]</sup> On the other hand, derivatives of the first-row homologue chromium are very rare. While molecules  $[\text{X}_3\text{Cr}\equiv\text{CH}]$  ( $\text{X} = \text{F}, \text{Cl}$ ) have been

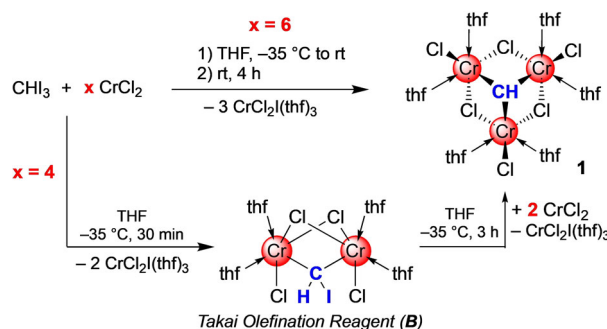
observed in an argon matrix (8 K),<sup>[5]</sup> heteroatom-substituted carbyne derivatives such as  $[(\text{C}_5\text{Me}_5)\text{Cr}(\equiv\text{CNiPr}_2)(\text{CNrBu})_3]\text{PF}_6$ <sup>[6]</sup> and the trimetallic cluster  $[\text{Cp}_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})]$  (**A**)<sup>[7]</sup> display crystalline compounds.<sup>[7]</sup> Purple trivalent **A** has remained the only structurally characterized methyldiyne complex of chromium.<sup>[7,8]</sup> On the other hand, the  $\text{M}_3(\mu_3\text{-CH})$  entity exhibits a common structural motif detected throughout *d*-transition metal chemistry (Ti, Fe, Co, Ru, Re and Os).<sup>[9]</sup> Prominent examples of the  $\mu_3$ -alkylidyne compound class are tricobalt nonacarbonyl clusters, which were investigated comprehensively by Seyferth et al.<sup>[10]</sup> Methyldiyne complexes structurally related to **A** comprise  $[(\text{Cp}^*\text{Ti}(\mu_2\text{-O}))_3(\mu_3\text{-CH})]$ <sup>[11]</sup> and  $[\text{Cp}^*_3\text{Mo}_3(\mu_2\text{-O})_2(\mu_2\text{-CH}_2)(\mu_3\text{-CH})]$ <sup>[12]</sup> the reactivity of which has been investigated as well.

Complex **A** has been obtained by thermal treatment (60 °C) of  $[\text{CpCr}(\text{CH}_3)(\mu_2\text{-Cl})_2]$  via multiple abstraction of hydrogen from a methyl ligand,<sup>[13]</sup> while its reactivity was not commented on.<sup>[7]</sup> Dehalogenation of organic halides features another viable pathway to alkylidyne/methyldiyne complexes.<sup>[14]</sup> Both pathways can proceed via intermediate alkylidene/methyldiene species. For chromium, well-defined alkylidene species are just as rare as alkylidyne complexes.<sup>[15,16]</sup> The most prominent chromium alkylidene complex is Takai's olefination/cyclopropanation reagent  $[\text{Cr}_2\text{Cl}_2(\mu_2\text{-Cl})_2(\mu_2\text{-CHI})(\text{thf})_4]$  (**B**, shown in Scheme 1).<sup>[16]</sup> The active reagent is routinely generated in situ applying the dehalogenation protocol, with  $\text{CrCl}_2$  and  $\text{CHX}_3$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) as the main components in varying ratios.<sup>[17]</sup> Recently, we succeeded in determining the solid-state structure of the Takai haloalkylidene complex **B**,<sup>[18]</sup> only confirming the connectivity originally proposed by Takai. By taking a closer look at the formation of the Takai olefination reagent, we have now uncovered the chromium(III) methyldiyne species  $[\text{Cr}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$  (**1**), which is the first isolable chromium(III) methyldiyne complex.

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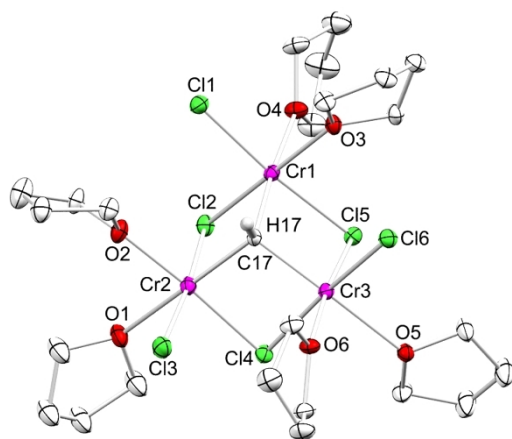
**Scheme 1.** Synthesis of methyldiyne complex **1**, directly (upper path) or via the Takai olefination reagent **B** (lower path).

$\text{Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$  (**1**) as the ultimate product of the  $\text{CrCl}_2/\text{CHI}_3$  reaction. Interestingly, complex **1** engages in selective halogenido exchange reactions, preserving the  $\text{M}_3(\mu_3\text{-CH})$  entity. Preliminary conversions of aldehydes or ketones revealed reaction pathways involving radical intermediates.

## Results and Discussion

### Formation of Methylidyne Complex $[\text{Cr}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$ (**1**) in the Reaction of Chromium(II) Chloride with Iodoform

The Takai olefination reagent is routinely generated in situ via a 3:1 mixture of  $\text{CrCl}_2$  and  $\text{CHX}_3$  (Scheme 1). The original report also mentioned the use of a 4:1 ratio in case of bromoform which did not significantly affect the yield and *E/Z* ratio of the alkenyl halide product.<sup>[17]</sup> Therefore we pondered about whether use of excessive  $\text{CrCl}_2$  would affect, if at all, the formation of Takai reagent **B**. Surprisingly, the reaction of  $\text{CrCl}_2$  with  $\text{CHI}_3$  in a 6:1 molar ratio at  $-35^\circ\text{C}$  in THF afforded the red methylidyne complex  $[\text{Cr}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$  (**1**) in up to 70% yield (Scheme 1, Figure 1) along with the precipitation of three equivalents of  $\text{CrCl}_2\text{I}(\text{thf})_3$ .



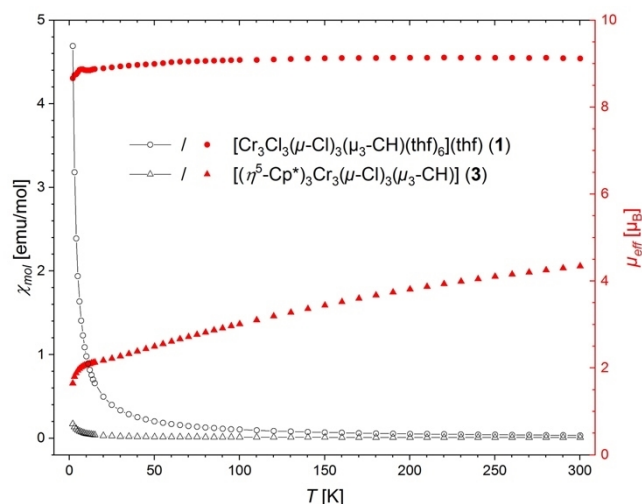
**Figure 1.** Crystal structure of **1**, ellipsoids shown at 50% probability, THF lattice solvent and hydrogen atoms are omitted for clarity. Selected interatomic distances/angles are listed in the Supporting Information (ESI, Figure S17).<sup>[32]</sup>

Compound **1** is also accessible via **B** and addition of another two equivalents of  $\text{CrCl}_2$  (Scheme 1). Crystallization from the THF solution at  $-35^\circ\text{C}$  yielded compound **1** as a microcrystalline solid. Repeated crystallization increased the overall yield, but to the expense of co-crystallizing  $\text{CrCl}_2\text{I}(\text{thf})_3$ . Crystallization from less concentrated solutions gave red plates suitable for X-ray diffraction (XRD) analysis. The crystal structure of **1** shows the known tetrahedral  $\text{M}_3(\mu_3\text{-CH})$  structural motif, with three chromium atoms forming a nearly equilateral triangle (Figure 1). Three  $\mu_2$ -bridging chlorido ligands complement the cluster core, resembling a truncated cube. One terminal chlorido and two THF

molecules each complete the slightly distorted octahedral coordination of the  $\text{Cr}^{\text{III}}$  atoms.<sup>[19]</sup>

The  $\text{Cr}-(\mu_3\text{-CH})$  distances in **1** of 2.018(3)/2.019(3)/2.022(3) Å appear slightly longer than those in Theopold's compound  $[\text{Cp}_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})]$  (**A**; 1.935(10) and 1.949(14) Å), as are the bridging  $\text{Cr}-\text{Cl}$  distances (2.3328(7) to 2.4186(7) Å versus 2.348(4) to 2.360(4) Å).<sup>[7]</sup> The average  $\text{Cr}-\text{Cr}$  distance of 3.167 Å is also considerably longer than in **A** (2.82 Å), which has been referred to as an unusually short contact (range for  $\text{Cr}-\text{Cr}$  single bonds: 2.65–2.97 Å).<sup>[7]</sup> Correspondingly, both the  $\text{Cr}-\text{Cl}-\text{Cr}$  and  $\text{Cr}-\text{C}-\text{Cr}$  angles are more flat in **1** (81.88(2)–82.96(2)°; 102.72(12)–103.66(12)°) than in **A** (73.0(1) and 73.9(1)°; 92.4(6) and 93.8(5)°).

The  $^1\text{H}$  NMR spectroscopic investigation of **1** in  $[\text{D}_8]\text{THF}$  did not reveal any signal for the  $\mu_3\text{-CH}$  proton in the range of  $-500$  to  $500$  ppm, presumably caused by paramagnetic broadening.<sup>[20]</sup> Also, any distinct  $\mu_3\text{-CH}$  vibration band was not detectable by IR-spectroscopy (ESI, Figure S26). The effective magnetic moment of **1** in dissolved and solid form was determined by the Evans method<sup>[21]</sup> and SQUID magnetic measurements, respectively. Both methods consistently point to ferro- or ferrimagnetic coupling between the individual  $\text{Cr}^{\text{III}}$  centers already at ambient temperature. The derived values of  $\mu_{\text{eff}}$  (Evans method:  $9.30 \mu_{\text{B}}$ ; SQUID:  $9.11 \mu_{\text{B}}$ ) are significantly larger than those expected for three uncoupled  $\text{Cr}^{\text{III}}$  centers ( $6.71 \mu_{\text{B}}$ ). Notably, the effective moment of solid **1** is nearly temperature independent down to 2 K (Figure 2, Figure S30). A fit of the field-dependent molar magnetization  $M_{\text{mol}}(H)$  at 2 K with a Brillouin function (the Landé *g*-factor was assumed to be 2.0) yields a spin quantum number of  $S = 4.45(4)$  which is in line with a  $S = 9/2$



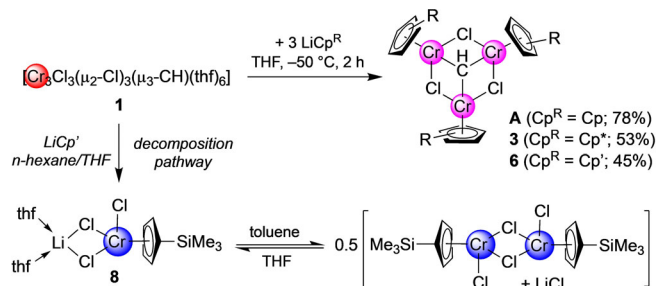
**Figure 2.** Temperature-dependent molar magnetic susceptibility  $\chi_{\text{mol}}(T)$  (black open symbols; left ordinate) and effective magnetic moment  $\mu_{\text{eff}}(T)$  (red filled symbols; right ordinate) as obtained by SQUID magnetic measurements on crystalline powders of **1** and **3** in applied fields  $H = 3$  kOe and 10 kOe, respectively. The  $\chi_{\text{mol}}(T)$  data were corrected for diamagnetic contributions (**1**:  $-4.243 \times 10^{-4} \text{ emu mol}^{-1}$ ; **3**:  $-3.071 \times 10^{-4} \text{ emu mol}^{-1}$ ; calculated from Pascal's constants),<sup>[23]</sup> and a spin-only *g* factor of 2.0 was assumed in the calculation of  $\mu_{\text{eff}}(T)$ . Note, that **1** contains an additional THF solvent molecule per formula unit in the crystal packing.

ground state (Figure S32). A similar large  $\mu_{\text{eff}}$  value of 9.61 was found for the related chromium chlorocarbene complex  $[\text{Cr}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CCl})(\text{thf})_6]$  assuming an  $S = 9/2$  ground state.<sup>[8]</sup> We note, that also the tetranuclear  $\text{Cr}^{\text{III}}/\text{Cr}^{\text{II}}$  complex  $[\text{Cp}^{\text{R}}_4\text{Cr}_4(\mu_2\text{-H})_5(\mu_3\text{-H})_2]$  ( $\text{Cp}^{\text{R}} = \eta^5\text{-tetramethyl-ethyl-cyclopentadienyl}$ ) displays a temperature-independent high  $\mu_{\text{eff}}$  of  $8.1 \mu_{\text{B}}$  with  $S = 3.4(2)$  which is due to intramolecular ferromagnetic couplings and in line with a  $S = 7/2$  ground state.<sup>[22]</sup>

Compound **1** was found to be infinitely stable in the solid state, while high purity samples showed minor decomposition in THF at  $-35^\circ\text{C}$  over several weeks. Thermal decomposition of **1** in THF occurred rapidly above  $40^\circ\text{C}$  (as indicated by a gradual color change from red to yellow). Similarly, progressive decomposition of **1** was observed in non-coordinating solvents like toluene as indicated by the formation of a precipitate as well as decoloration. Utilization of high-purity reactants is crucial for the successful synthesis of **1**, as water-containing solvents or oxygen-containing impurities of iodoform or  $\text{CrCl}_2$  (99.99% trace metal basis, anhydrous  $\text{CrCl}_2$ ) led to partially inseparable decomposition/side products, as evidenced for the serendipitous identification of  $[\text{Cr}_4(\mu_2\text{-Cl})_4(\mu_2\text{-I})_2(\mu_4\text{-O})(\text{thf})_4]$  (**2a**) and mixed-valent  $[\text{Cr}_4\text{Cl}(\mu_2\text{-Cl})_4(\mu_2\text{-I})_2(\mu_4\text{-O})(\text{thp})_4]$  (**2b**, thp = tetrahydropyran) by XRD analysis. As complexes **2** were obtained in minute amounts and the crystals were of poor quality, the crystal structures represent only connectivities (Figures 3/S18/S19). The molecular structure of **2a** is isostructural to  $[\text{Cr}_4(\mu_2\text{-Cl})_6(\mu_4\text{-O})(\text{thf})_4]$  reported by Cotton et al. with two iodo ligands instead of chlorides.<sup>[24]</sup> The core of complexes **2** features a  $[\text{M}_4\text{O}]^{6+}$  entity with the central oxygen tetrahedrally coordinated by the metal atoms. Each 5-coordinate chromium(II) engages further in two chlorido and one iodo bridge, and the coordination of a THF molecule. The single 6-coordinate chromium(III) in **2b** is additionally coordinated by a terminal chlorido ligand. Compounds **2** probably formed at an early stage of the reaction, most likely due to solvent water impurities. However, neither **2a** nor **2b** could be reproduced by the admittance of deliberate amounts of water to the reaction mixture.

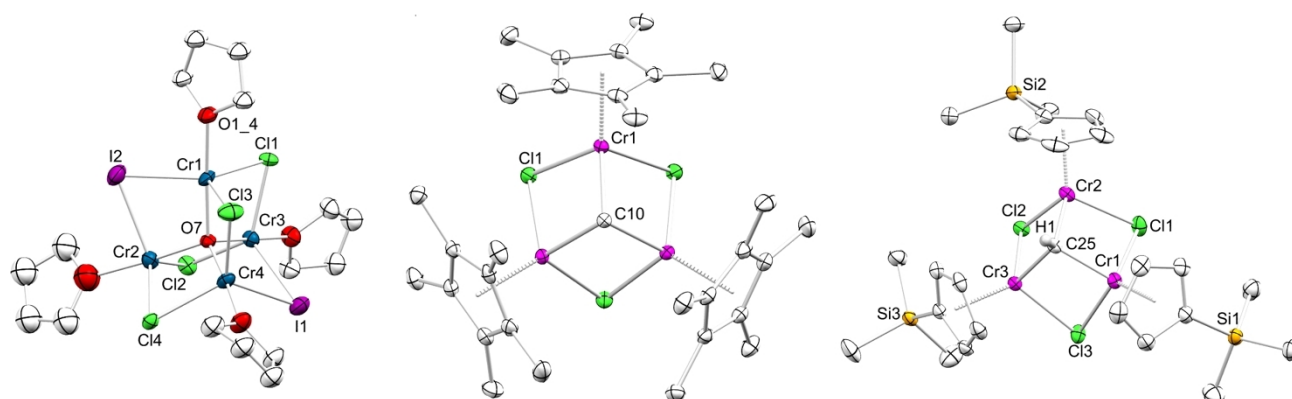
### Formation of Half-Sandwich Methylidyne Complexes $[\text{Cp}^{\text{R}}_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_4]$ via Selective $\text{Cl}/\text{Cp}^{\text{R}}$ Exchange

With compound **1** accessible in decent yields, we targeted the selective exchangeability of the terminal chlorido ligands. As the cyclopentadienyl ligand proved a stabilizing ligand for the  $\text{M}_3(\mu_3\text{-CH})$  entity in general, and specifically for compound **A**, we probed the reactivity of **1** toward  $\text{NaCp}$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ) and the substituted cyclopentadienides  $\text{LiCp}^*$  and  $\text{LiCp}'$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ,  $\text{Cp}' = [\text{C}_5\text{H}_4(\text{SiMe}_3)]$ ) (Scheme 2).



**Scheme 2.** Synthesis of trimetallic half-sandwich methylidyne complexes; representation of the suggested equilibrium of ate complex **8** in solution.

Reaction of **1** with three equivalents of  $\text{NaCp}$  in THF at  $-50^\circ\text{C}$  yielded a clear dark purple solution. Crystallization from *n*-pentane gave purple needles of  $[\text{Cp}_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})]$  (**A**) in good yield (78%). Lower yields at elevated temperatures and absence of metathesis salt most likely result from the instability of **1** dissolved in THF and its partial decomposition during the reaction, through unknown reduction pathways. Moreover, chromocene  $[\text{Cp}_2\text{Cr}]$  could be identified as a major impurity by  $^1\text{H}$  NMR spectroscopy ( $[\text{D}_8]\text{THF}$ ,  $\delta = 319.4$  ppm) being separable by sublimation at  $40^\circ\text{C}$ . Other  $\text{Cr}^{\text{II}}$  and  $\text{Cr}^{\text{III}}$  species present in reaction mixtures, even at  $-50^\circ\text{C}$ , were not assignable by NMR spectroscopy (distinct signals in the range 10 to 50 ppm), but could be removed by crystallization. The  $^1\text{H}$  NMR spectrum



**Figure 3.** Connectivity of  $[\text{Cr}_4(\mu_2\text{-Cl})_4(\mu_2\text{-I})_2(\mu_4\text{-O})(\text{thf})_4]$  (**2a**, left), ellipsoids shown at 30% probability, lattice solvent and hydrogen atoms are omitted for clarity. Crystal structures of  $[(\eta^5\text{-Cp}^*)_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})]$  (**3**, middle) and  $[(\eta^5\text{-Cp}')_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})]$  (**6**, right), ellipsoids shown at 50% probability, lattice solvent and hydrogen atoms (except for the methylidyne hydrogen atom in **6**) are omitted for clarity. Selected interatomic distances/angles are listed in the Supporting Information (Figures S18/S20/S23).<sup>[32]</sup>

of **A** measured in  $[D_8]THF$  at ambient temperature shows a broad singlet at  $\delta = 30.27$  ppm (in  $CDCl_3$  at  $\delta = 31.05$  ppm), in agreement with the literature.<sup>[7]</sup>

The 3-equivalent reaction of **1** with  $LiCp^*$  in THF at  $-50^\circ C$  led to an instant color change from dark red to dark green. Crystallization from concentrated toluene/*n*-hexane mixtures gave dark green crystals of  $[(\eta^5-Cp^*)_3Cr_3(\mu_2-Cl)_3(\mu_3-CH)]$  (**3**) featuring a structural motif similar to **1** (Figure 1) and **A**. Compound **3** crystallizes in the trigonal space group  $R\bar{3}$  and displays a local symmetry of  $C_3$  with Cr—Cr distances of 2.9103(5) Å, slightly longer than in **A**. The Cr—Cl distances of 2.3416(5) to 2.3615(5) Å as well as the Cr—C—Cr angles involving the central  $\mu_3-CH$  moiety ( $92.71(11)^\circ$ ) match those in **A**. The  $^1H$  NMR spectrum of crystalline **3** in  $[D_8]THF$  at ambient temperature shows a slightly broadened singlet at  $\delta = -5.8$  ppm assignable to  $C_5(CH_3)_5$ . The ambient-temperature magnetic moment drastically changed upon  $Cl/Cp^R$  exchange as evidenced by the Evans method in solution ( $\mu_{eff} = 3.63 \mu_B$ ) and in the solid state by SQUID measurements ( $\mu_{eff} = 4.32 \mu_B$ ). These values are in accordance with the results obtained for dissolved **A** (Evans method:  $\mu_{eff} = 3.55 \mu_B$ )<sup>[7]</sup> and substantially below the effective magnetic moment expected in case of three uncoupled  $Cr^{III}$  centers ( $\mu_{eff} = 6.71 \mu_B$ ). A possible explanation may be the establishment of antiferromagnetic interactions causing the observed gradual decrease of  $\mu_{eff}$  for solid **3** upon cooling (Figure 2, Figures S31/S33).<sup>[7]</sup> A similar temperature-dependent decrease of the effective magnetic moment upon cooling has been observed earlier in the related complex **A** and considered as an evidence for antiferromagnetic couplings between the chromium ions.<sup>[7]</sup> A further analogy to **A** is that reaction mixtures of **3** show a multitude of paramagnetically shifted proton signals, due to partial reduction and decomposition of complex **1**. Identified side products comprise  $Cp^*_2Cr$  ( $\delta = -6.2$  ppm,  $[D_8]THF$ )<sup>[25]</sup> and  $[Cp^*CrCl_2]_2$  ( $\delta = -71.5$  ppm,  $CDCl_3$ ).<sup>[26]</sup> Overall, the synthesis of such half-sandwich complexes is extremely sensitive toward change of reaction conditions and choice of precursor. While switching the solvent from THF to toluene led to the isolation of trivalent  $[Cp^*CrCl_2(thf)]$  (**4**), probing the direct synthesis of **3** from  $[Cp^*Cr(\mu_2-Cl)]_2/CHI_3$  gave only partial halogenido exchange in  $[(Cp^*Cr)_2(\mu_2-Cl)(\mu_2-I)]$  (**5**) (synthesis details and crystal structures, see Supporting Information).

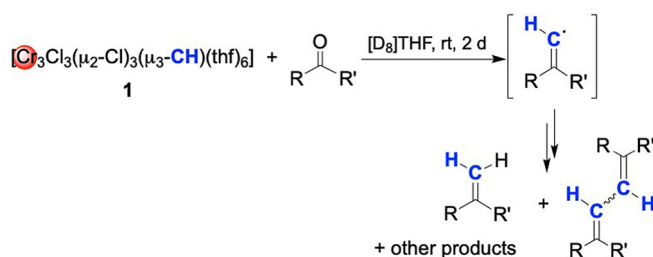
Salt metathesis of **1** with three equivalents of  $LiCp^*$  in THF at  $-50^\circ C$  gave a dark red/violet solution. After several extraction steps, crystallization from *n*-hexane yielded dark purple needles of  $[(\eta^5-Cp^*)_3Cr_3(\mu_2-Cl)_3(\mu_3-CH)]$  (**6**). The crystal structure of **6** is isostructural to **A** and **3** (Figure 3), with similar Cr—Cl distances of 2.3243(4) Å to 2.3519(4) Å. Not unexpectedly, the Cr—Cr distances of 2.8192(3) Å to 2.8363(3) Å match those in **A**. The  $^1H$  NMR spectrum of **6** recorded in  $[D_8]THF$  at ambient temperature shows two broadened signals at  $\delta = 35.35$  and 30.39 ppm for the aromatic protons of the  $Cp^*$  ligands, and one sharp singlet at  $\delta = 0.49$  ppm for the  $SiCH_3$  protons ( $\mu_{eff} = 2.70 \mu_B$ ). Again, the  $^1H$  NMR spectrum of the reaction mixture of **6** shows numerous other signals. To prove similar reaction/decomposition behavior as found for **A** and **3**, chromocene  $Cp'_2Cr$  (**7**) was synthesized independently from  $CrCl_2$  and  $LiCp^*$ . Crystallization of **7** from *n*-hexane produced orange crystals suitable for an X-ray diffraction study (Figure S24). The  $^1H$  NMR spectrum of **7** measured in  $[D_8]THF$  at ambient temperature displays signals at  $\delta = 322.33$  ppm, 249.42 ppm, and  $-3.32$  ppm (Figure S5). Half-sandwich ate complex  $[(\eta^5-Cp')CrCl(\mu_2-Cl)_2Li(thf)_2]$  (**8**) could be crystallized as another side product from reactions in THF. The crystal structure of deep blue **8** proved the existence of an intramolecular ate complex (Figure S25). Compound **8** provides further evidence for the equilibrium theory proposed by Rojas et al. (Scheme 2) and explains the virtually non-existent (non-separable) amount of metathesis salt in the reaction mixtures of **1** and compounds  $MCp^R$ .<sup>[27]</sup> Nearly identical solubilities of the side products clearly counteract the isolation of these compounds. In general, the proneness of **1** to reduction (and the formation of  $Cp^R_2Cr^{II}$ ) can be minimized by performing the reactions at low temperatures in less polar solvents. In THF, the reactions proceeded with minor impurities only at  $-50^\circ C$ , while in *n*-hexane and *n*-pentane acceptable results were obtained at  $-35^\circ C$ . Toluene is unsuitable as a solvent, since decomposition of **1** was significant within minutes, even at low temperatures.

Reactivity of Methylidyne Complex **1** toward Aldehydes and Ketones

The Takai and Takai-Utimoto olefination reagents engage in (*E*)-selective olefinations of aldehydes, with high functional group tolerance.<sup>[28,29]</sup> Later, reagent extensions involved the formation of (heteroatom-)substituted cyclopropane products.<sup>[30]</sup> It was of interest how the methylidyne complex **1** would affect such olefination reactions. Direct NMR-scale reactivity studies turned out difficult to interpret because of paramagnetic shifting and broadening. However, filtration of the reaction mixtures over aluminum oxide facilitated the observation of organic products via  $^1H$  NMR spectroscopy. The conversions of benzaldehyde and pivaldehyde with **1** in  $[D_8]THF$  were complete after 1 h at ambient temperature.<sup>[31]</sup> During this period, the mixtures changed color from deep red to turbid green brown, leading to a multitude of products as detected by GC/MS analysis (see Figures S34 to S43). Most of these compounds are suggested to be formed by radical recombination, involving transient olefinic radical, as a result from methylidyne/oxy exchange (Scheme 3). 1D and 2D NMR spectroscopies could not resolve the observed overlapping signals of the product mixtures (Figures S6 to S12). For example, the benzaldehyde reaction revealed the forma-

### Reactivity of Methylidyne Complex **1** toward Aldehydes and Ketones

tallization of **7** from *n*-hexane produced orange crystals suitable for an X-ray diffraction study (Figure S24). The  $^1H$  NMR spectrum of **7** measured in  $[D_8]THF$  at ambient temperature displays signals at  $\delta = 322.33$  ppm, 249.42 ppm, and  $-3.32$  ppm (Figure S5). Half-sandwich ate complex  $[(\eta^5-Cp')CrCl(\mu_2-Cl)_2Li(thf)_2]$  (**8**) could be crystallized as another side product from reactions in THF. The crystal structure of deep blue **8** proved the existence of an intramolecular ate complex (Figure S25). Compound **8** provides further evidence for the equilibrium theory proposed by Rojas et al. (Scheme 2) and explains the virtually non-existent (non-separable) amount of metathesis salt in the reaction mixtures of **1** and compounds  $MCp^R$ .<sup>[27]</sup> Nearly identical solubilities of the side products clearly counteract the isolation of these compounds. In general, the proneness of **1** to reduction (and the formation of  $Cp^R_2Cr^{II}$ ) can be minimized by performing the reactions at low temperatures in less polar solvents. In THF, the reactions proceeded with minor impurities only at  $-50^\circ C$ , while in *n*-hexane and *n*-pentane acceptable results were obtained at  $-35^\circ C$ . Toluene is unsuitable as a solvent, since decomposition of **1** was significant within minutes, even at low temperatures.



**Scheme 3.** Reactions of **1** with aldehydes and ketones.





tion of styrene as the only component identifiable by  $^1\text{H}$  NMR spectroscopy. Striking was the observation of trace amounts of (2-iodoethenyl)-benzene by GC/MS analysis. As the synthesis of **1** produces a substantial amount of the iodinated side product  $\text{CrCl}_2\text{I}(\text{thf})_3$  (approximate solubility of  $1\text{ mg mL}^{-1}$  in THF at  $17^\circ\text{C}$ ), product contamination with iodine seems inevitable. ICP (Inductively Coupled Plasma) analysis of recrystallized samples of compound **1** indicated a persistent iodine content of roughly 3.3 %.

Other causes for the iodine contamination could be the presence of decomposition product **2** or non-reacted Takai reagent  $[\text{Cr}_2\text{Cl}_2(\mu_2\text{-Cl})_2(\mu_2\text{-CHI})(\text{thf})_4]$  (**B**), which are both easily soluble in THF and hence difficult to separate via crystallization.

Compound **1** did not show any reactivity toward alkynes  $\text{HC}\equiv\text{CSiMe}_3$ ,  $\text{HC}\equiv\text{CPh}$  and  $\text{PhC}\equiv\text{CPh}$ , neither alkyne metathesis nor insertion/addition-type reactions. The latter investigations were carried out in  $[\text{D}_8]\text{THF}$  and monitored by  $^1\text{H}$  NMR spectroscopy over several hours, also by heating to the decomposition temperature of **1**. Finally, the reactivity of  $[(\eta^5\text{-Cp}^*)_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})]$  (**3**) toward benzaldehyde or benzophenone was examined under similar conditions, but the  $^1\text{H}$  NMR spectra were inconclusive and only indicated decomposition of the methylidyne complex. Further research is needed to elucidate the reactivity of the organometallic compounds.

## Conclusion

The chromium(III)  $\mu_3$ -methylidyne complex  $[\text{Cr}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$  features the ultimate C-X cleavage product in the dehalogenation sequence of haloforms  $\text{CHX}_3$  (here:  $\text{CrCl}_2/\text{CHI}_3$  mixture). The decent yields of the methylidyne complex enabled a series of reactivity studies. The terminal chlorido ligands can be selectively displaced via salt metathesis with alkali-metal cyclopentadienides to afford rare examples of half-sandwich chromium(III) methylidyne,  $[(\eta^5\text{-Cp}^*)_3\text{Cr}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})]$ . Despite the paramagnetic nature of  $\text{Cr}^{\text{III}}$ , these compounds exhibit only slightly broadened signals in the  $^1\text{H}$  NMR spectra, facilitating the observation of in situ derivatizations. Treatment of  $[\text{Cr}_3\text{Cl}_3(\mu_2\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$  with ketones and aldehydes led to olefination, entailing the formation of various products probably formed by radical recombination. The methylidyne complexes under study do not promote alkyne metathesis reactions or insertions/additions with acetylenes, but display exceptional magnetic behavior. Finally, our study underlines the importance of complying with correct  $\text{CrCl}_2$ /haloform ratios for efficient olefination reactions.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** chromium · cyclopentadienyl · magnetism · methylidyne · olefination

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- [32] Deposition Numbers 2084204, 2084205, 2084206, 2084207, 2084208, 2084209, 2084210, 2084211 and 2084212 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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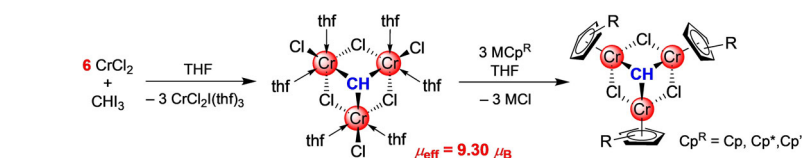
## Research Articles



## Coordination Chemistry

S. Trzmiel, J. Langmann, D. Werner,  
C. Maichle-Mössmer, W. Scherer,\*  
R. Anwander\* ————— ■■■■-■■■■

Beyond Takai's Olefination Reagent:  
Persistent Dehalogenation Emerges in  
a Chromium(III)- $\mu_3$ -Methylidyne Complex



The methylidyne complex  $[\text{Cr}^{\text{III}}_3\text{Cl}_3(\mu\text{-Cl})_3(\mu_3\text{-CH})(\text{thf})_6]$  displays the ultimate product of the  $\text{CrCl}_2/\text{CHI}_3$  redox reaction, significantly affecting carbonylic group

transformation; the trimetallic compound also exhibits unusual magnetic behavior and provides ready access to half-sandwich clusters.

