Beyond Takai’s Olefination Reagent: Persistent Dehalogenation Emerges in a Chromium(III)-μ₃-Methylidyne Complex

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

Abstract: Reaction of CH$_I_3$ with six equivalents of CrCl$_3$ in THF at low temperatures affords [Cr$_3$Cl$_3$(μ$_3$-Cl)$_3$(μ$_3$-CH)(thf)$_3$] as the first isolable high-yield Cr$_{III}$ μ$_3$-methylidyne complex.

Substitution of the terminal chlorido ligands via salt metathesis with alkali-metal cyclopentadienides generates isostructural half-sandwich chromium(III)-μ$_3$-methylidylenes [Cr$_6$Cl$_3$(μ$_3$-Cl)$_3$(μ$_3$-CH)] (Cr$_6$ = C$_3$H$_6$, C$_6$Me$_6$, C$_5$H$_5$SiMe$_3$). Side and decomposition products of the Cr$_3$Cl$_3$ exchange reactions were identified and structurally characterized for [Cr$_6$(μ$_3$-Cl)$_3$(μ$_3$-CH)](thf)$_3$ and [η$_2$-C$_3$H$_5$SiMe$_3$]CrCl(μ$_3$-Cl)$_3$Li-(thf)$_3$. The Cr$_3$Cl$_3$ exchange drastically changed the ambient-temperature effective magnetic moment $\mu_E$ from 9.30/9.11 $\mu_B$ (solution/solid) to 3.63/4.32 $\mu_B$ (Cr$_6$ = C$_6$Me$_6$). Reactions of [Cr$_3$Cl$_3$(μ$_3$-Cl)$_3$(μ$_3$-CH)](thf)$_3$ with aldehydes and ketones produce intricate mixtures of species by oxidative methylidyne exchange, which were partially identified as radical recombination products through GC/MS analysis and $^1$H NMR spectroscopy.

Introduction

Carbyne or alkylidyne moieties display archetypal ligands in organo(transition)metal chemistry. In particular, alkylidyne complexes of the high-oxidation-state heavier group 6 metals molybdenum and tungsten emerged as eminent alkyne metathesis catalysts. Such discrete complexes feature multiply bonded terminal moieties of the type M=CR (M = Mo, W) and have been studied comprehensively. On the other hand, derivatives of the first-row homologue chromium are very rare. While molecules $[X_2$Cr=CH] (X = F, Cl) have been observed in an argon matrix (8 K), heteroatom-substituted carbyne derivatives such as $[[C_2$Me$_5$]Cr≡CN$Pr_2(CN$Bu)$_3$]- [PF$_6$], and the trimetallic cluster $[C_3$Cr$_2$(μ$_3$-Cl)$_3$(μ$_3$-CH)] (A) display crystalline compounds. Purple trivalent A has remained the only structurally characterized methylidyne complex of chromium. On the other hand, the M(μ$_3$-CH) entity exhibits a common structural motif detected throughout d-transition metal chemistry (Ti, Fe, Co, Ru, Re and Os). Prominent examples of the μ$_3$-alkylidyne compound class are tricobalt nonacarbonyl clusters, which were investigated comprehensively by Seyferth et al. Methylidyne complexes structurally related to A comprise $[[C_3$Ti$_2$(μ$_3$-O)$_3$(μ$_3$-CH)] and $[C_3$Mo$_3$(μ$_3$-O)$_3$(μ$_3$-CH)](μ$_3$-CH)$_2$ the reactivity of which has been investigated as well.

Complex A has been obtained by thermal treatment (60°C) of $[C_3$Cr$_2$(CH)$_2$(μ$_3$-Cl)$_3$], via multiple abstraction of hydrogen from a methyl ligand, while its reactivity was not commented on. Dehalogenation of organic halides features another viable pathway to alkylidyne/methylidyne complexes. Both pathways can proceed via intermediate alkylidene/methylidyne species. For chromium, well-defined alkylidene species are just as rare as alkylidyne complexes. The most prominent chromium alkylidyne complex is Takai’s olefination/cyclopropanation reagent $[C_3$Cl$_3$(μ$_3$-Cl)$_3$(μ$_3$-CH)](B, shown in Scheme 1). The active reagent is routinely generated in situ applying the dehalogenation protocol, with Cr$_3$Cl$_3$ and CH$_3$X (X = Cl, Br, I) as the main components in varying ratios. Recently, we succeeded in determining the solid-state structure of the Takai halolkyldiene complex B 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) methylidyne species $[C_3$Cl$_3$(μ$_3$-CH)].
Cl)₃(μ₂-CH)(thf)₃] as the ultimate product of the CrCl₃/CH₃I reaction. Interestingly, complex 1 engages in selective halogenido exchange reactions, preserving the M₆(μ₂-CH) entity. Preliminary conversions of aldehydes or ketones revealed reaction pathways involving radical intermediates.

Results and Discussion

Formation of Methylidyne Complex [CrCl₃(μ₂-CH)]₃(μ₂-CH)(thf)₃] (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 CrCl₃ and CHX₃ (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 alkyl halide product. Therefore we pondered whether use of excessive CrCl₃ would affect, if at all, the formation of Takai reagent B. Surprisingly, the reaction of CrCl₃ with CHI₃ in a 6:1 molar ratio at −35°C in THF afforded the red methylidyne complex [CrCl₃(μ₂-CH)]₃(μ₂-CH)(thf)₃] (1) in up to 70% yield (Scheme 1, Figure 1) along with the precipitation of three equivalents of CrCl₃·(thf)₄.

![Figure 1. Crystal structure of 1, ellipsoids shown at 50% probability, THF lattice solvent and hydrogen atoms are omitted for clarity.](Image)

Selected interatomic distances/angles are listed in the Supporting Information (ESI, Figure S17).

Compound 1 is also accessible via B and addition of another two equivalents of CrCl₃ (Scheme 1). Crystallization from the THF solution at −35°C yielded compound 1 as a microcrystalline solid. Repeated crystallization increased the overall yield, but to the expense of co-crystallizing CrCl₃·(thf)₄. Crystallization from less concentrated solutions gave red plates suitable for X-ray diffraction (XRD) analysis. The crystal structure of 1 shows the known tetrahedral M₆(μ₂-CH) structural motif, with three chromium atoms forming a nearly equilateral triangle (Figure 1). Three μ₂-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 CrIII centers.

The Cr–(μ₂-CH) distances in 1 of 2.018(3)/2.019(3)/2.022(3) Å appear slightly longer than those in Theopold’s compound [Cp₃Cr(μ₂-CH)]₄ (A: 1.935(10) and 1.949(14) Å), as are the bridging Cr–Cl distances (2.3328(7) to 2.4186(7) Å versus 2.348(4) to 2.360(4) Å). The Cr–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 W/C138 contact (range for Cr–Cr single bonds: 2.65–2.97 Å). Correspondingly, both the Cr–Cl-Cr and Cr-C-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 1H NMR spectroscopic investigation of 1 in [D₈]THF did not reveal any signal for the μ₂-CH proton in the range of −500 to 500 ppm, presumably caused by paramagnetic broadening. Also, any distinct μ₂-CH vibration band was not detectable by IR-spectroscopy (ESI, Figure S36). The effective magnetic moment of 1 in dissolved and solid form was determined by the Evans method and SQUID magnetic measurements, respectively. Both methods consistently point to ferro- or ferrimagnetic coupling between the individual CrIII centers already at ambient temperature. The derived values of μeff (Evans method: 9.30 μB; SQUID: 9.11 μB) are significantly larger than those expected for three uncoupled CrIII centers (6.71 μB). 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 Mm(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 state.

![Figure 2. Temperature-dependent molar magnetic susceptibility χm(T)](black open symbols; left ordinate) and effective magnetic moment μeff(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 χm(T) data were corrected for diamagnetic contributions (T; 4.243×10⁻⁴ emu mol⁻¹; 3; 3.071×10⁻⁴ emu mol⁻¹; calculated from Pascal’s constants) and a spin-only g factor of 2.0 was assumed in the calculation of μeff(T). Note, that 1 contains an additional THF solvent molecule per formula unit in the crystal packing.

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ground state (Figure S32). A similar large \( \mu_{\text{eff}} \) value of 9.61 was found for the related chromium chlorocarbene complex \([\text{CrCl}(\mu_2\text{-Cl})_3(\mu_2\text{-CCl})(\text{thf})_3]\) assuming an S = 9/2 ground state.\(^{[3]}\) We note, that also the tetranuclear \( \text{Cr}^{III}/\text{Cr}^{VI} \) complex \([\text{Cr}^6(\mu_4\text{-H})_6(\mu_4\text{-H})]\) \((\text{Cr}^8 = \eta^1\text{-tetramethyl-ethyl-cyclopentadienyl})\) displays a temperature-independent high \( \mu_{\text{eff}} \) of 8.1 \( \mu_B \) with \( S = 3.4(2) \) which is due to intramolecular ferromagnetic couplings and in line with a \( S = 7/2 \) ground state.\(^{[22]}\)

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 decolorization. Utilization of high-purity reactants is crucial for the successful synthesis of 1, as water-containing solvents or oxygen-containing impurities of iodiform or \( \text{CrCl}_3 \) (99.99 % trace metal basis, anhydrous \( \text{CrCl}_3 \)) led to partially inseparable decomposition/side products, as evidenced for the serendipitous identification of \([\text{Cr}_2(\mu_2\text{-Cl})_2(\mu_2\text{-I})_4(\mu_4\text{-O})(\text{thf})_3] \) (2a) and mixed-valent \([\text{Cr}_2\text{Cl}(\mu_2\text{-Cl})_2(\mu_2\text{-I})_4(\mu_4\text{-O})(\text{thf})_3] \) (2b, \( \text{thp} = \text{tetrahydropyran} \)) 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 isostuctural to \([\text{Cr}_2(\mu_2\text{-Cl})_2(\mu_4\text{-O})(\text{thf})_3] \) reported by Cotton et al. with two iodido ligands instead of chloridos.\(^{[24]}\) The core of complexes 2 features a \([\text{M}_2\text{O}_6]^{4+}\) entity with the central oxygen tetrahedrally coordinated by the metal atoms. Each 5-coordinate chromium(II) engages further in two chlorido and one iodido 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 Methyldyne Complexes \([\text{Cp}^\delta,\text{Cr}(\mu_2\text{-Cl})_7(\mu_2\text{-CH})(\text{thf})_3] \) via Selective \( \text{Cl}/\text{Cp}^\delta \) 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 \( \text{M}_3(\mu_2\text{-CH}) \) 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 \( \text{LiCp}^\delta \) and \( \text{LiCp}^\gamma \) (\( \text{Cp}^\delta = \text{C}_5\text{Me}_5 \), \( \text{Cp}^\gamma = [\text{C}_5\text{H}_4\text{(SiMe}_3)_2] \) (Scheme 2).

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 \([\text{Cp}_5\text{Cr}(\mu_2\text{-Cl})_2(\mu_2\text{-CH})] \) (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 \([\text{Cp}_5\text{Cr}] \) could be identified as a major impurity by \( ^1\text{H} \) 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 \([\text{Cr}_2(\mu_2\text{-Cl})_2(\mu_2\text{-I})_2(\mu_4\text{-O})(\text{thf})_3] \) (2a, left), ellipsoids shown at 30% probability, lattice solvent and hydrogen atoms are omitted for clarity. Crystal structures of \([\eta^1\text{-Cp}^\delta,\text{Cr}_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH})] \) (B, middle) and \([\eta^1\text{-Cp}^\gamma,\text{Cr}_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH})] \) (6, right), ellipsoids shown at 50% probability, lattice solvent and hydrogen atoms (except for the methyldyne hydrogen atom in 6) are omitted for clarity. Selected interatomic distances/angles are listed in the Supporting Information (Figures S18/S20/S23).\(^{[27]}\)
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.[7]

The 3-equivalent reaction of 1 with LiCp$^*$ in THF at −50°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$^*$)$_2$Cr($\mu_3$-Cl)$_2$($\mu_3$-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–Cr distances of 2.3416(5) to 2.3651(5) Å as well as the Cr-Cr-C angles involving the central $\mu_3$-CH moiety (92.71(11)$^\circ$) match those in A. The $^1$H 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$_7$(CH)$_3$. The ambient-temperature magnetic moment drastically changed upon Cl/Cp exchange as evidenced by the Evans method in solution ($\mu_{\text{eff}}$ = 3.63 $\mu_B$) and in the solid state by SQUID measurements ($\mu_{\text{eff}}$ = 4.32 $\mu_B$). These values are in accordance with the results obtained for dissolved A (Evans method: $\mu_{\text{eff}}$ = 3.55 $\mu_B$)[7] and substantially below the effective magnetic moment expected in case of three uncoupled Cr$^{III}$ centers ($\mu_{\text{eff}}$ = 6.71 $\mu_B$). A possible explanation may be the establishment of antiferromagnetic interactions causing the observed gradual decrease of $\mu_{\text{eff}}$ for solid 3 upon cooling (Figure 2, Figures S31/S33).[7] 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.[7] Another 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$^*$,Cr (δ = −6.2 ppm, [D$_8$]THF)[23] and [Cp$^*$,CrCl$_2$] (δ = −71.5 ppm, CDCl$_3$).[24] 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(thf)] (4), proving the direct synthesis of 3 from [Cp$^*$,Cr($\mu_3$-Cl)$_2$]·CH$_2$I, only partial halogenido exchange in ([Cp$^*$,Cr($\mu_3$-Cl)$_2$($\mu_3$-I)] (5) (synthesis details and crystal structures, see Supporting Information).

Salt metathesis of 1 with three equivalents of LiCp$^*$ in THF at −50°C gave a dark red/violet solution. After several extraction steps, crystallization from n-hexane yielded dark purple needles of [($\eta^5$-Cp$^*$)$_2$Cr($\mu_3$-Cl)$_2$($\mu_3$-CH)] (6). The crystal structure of 6 is isoostructural to A and 3 (Figure 3), with similar Cr–Cr distances of 2.3243(4) Å to 2.3519(4) Å. Not unexpectedly, the Cr–Cl distances of 2.8192(3) Å to 2.8363(3) Å match those in A. The $^1$H 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 ($\mu_{\text{eff}}$ = 2.70 $\mu_B$). Again, the $^1$H 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$^*$,Cr (7) was synthesized independently from CrCl$_3$ and LiCp$^*$. Crystallization of 7 from n-hexane produced orange crystals suitable for an X-ray diffraction study (Figure S24). The $^1$H 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($\mu_3$-Cl)Li(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 M Cp$^*$,Cr.[27] 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$^*$,Cr)[28] 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°C, while in n-hexane and n-pentane acceptable results were obtained at −35°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 olefination of aldehydes, with high functional group tolerance.[28,29] Later, reagent extensions involved the formation of (heteroatom-)substituted cyclopropane products.[30] 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 $^1$H NMR spectroscopy. The conversions of benzaldehyde and pivaldehyde with 1 in [D$_8$]THF were complete after 1 h at ambient temperature.[13] 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-

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**Scheme 3.** Reactions of 1 with aldehydes and ketones.
tion of styrene as the only component identifiable by $^1$H NMR spectroscopy. Striking was the observation of trace amounts of (2-iodoethenyl)-benzene by GC/MS analysis. As the synthesis of $\text{1}$ produces a substantial amount of the iodinated side product $\text{CrCl}_3(\text{thf})_3$, the product contamination with iodine seems inevitable. ICP (Inductively Coupled Plasma) analysis of recrystallized samples of compound $\text{1}$ indicated a persistent iodine content of roughly 3.3%.

Other causes for the iodine contamination could be the presence of decomposition product $\text{2}$ or non-reacted Takai reagent [Cr$_2$Cl$_3$(μ-Cl)$_2$(μ-CH)(thf)$_4$] (B), which are both easily soluble in THF and hence difficult to separate via crystallization.

Compound $\text{1}$ did not show any reactivity toward alkynes $\text{HC≡C}$SiMe$_3$, $\text{HC≡C}$Ph and PhC≡CPh, neither alkynyl metalation nor insertion/addition-type reactions. The latter investigations were carried out in [D$_8$]THF and monitored by $^1$H NMR spectroscopy over several hours, also by heating to the decomposition temperature of $\text{1}$. Finally, the reactivity of [(η$^5$-Cp*$^*$)$_2$Cr$(\mu$-Cl)$_2$(μ-CH)] (3) toward benzaldehyde or benzophenone was examined under similar conditions, but the $^1$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) μ$_2$-methylidyne complex [Cr$_2$Cl$_3$(μ-Cl)$_2$(μ-CH)(thf)$_4$] features the ultimate C-X cleavage product in the dehalogenation sequence of haloforms CHX$_3$(here: CrCl$_2$/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, [η$^5$-Cp*$^*$Cr$(\mu$-Cl)$_2$(μ-CH)]. Despite the paramagnetic nature of Cr$^{III}$, these compounds exhibit only slightly broadened signals in the $^1$H NMR spectra, facilitating the observation of in situ derivatizations. Treatment of [Cr$_2$Cl$_3$(μ-Cl)$_2$(μ-CH)(thf)$_4$] 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 alkynyl metathesis reactions or insertions/additions with acetylenes, but display exceptional magnetic behavior. Finally, our study underlines the importance of complying with correct 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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31) Compound I proved comparatively less reactive toward ketones resulting in predominant recovery of the unreacted educts after 2 to 3 days (e.g., 88% for benzophenone, see Figure S7; quantifications for reactions with 9-fluorenone and cyclohexa-one were infeasible). For the reactions with benzophenone and 9-fluorenone, the allylidene exchange products 1,1-diphenyl-ethylene (Figure S45) and 9-methylene-9H-fluorene (Figure S50) were found as the only products identifiable by ‘H NMR spectroscopy (Figures S7 to S10). GC/MS analysis revealed trace amounts of numerous other compounds in the product solutions, among them iodinated olefination products as well as radical recombination products.

32) Deposition Numbers 2084204, 2084205, 2084206, 2084207, 2084208, 2084209, 2084210, 2084211, 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. Manuscript received: May 17, 2021

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