Chromium carbides and cyclopropenylidenes†

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Carbon tetrabromide can be reduced with CrBr₂ in THF to form a dinuclear carbido complex, [CrBr₂(thf)₂][CrBr₂(thf)₂]<sub>μ</sub>-Cl, along with formation of [CrBr₃(thf)₃]. An X-ray diffraction (XRD) study of the pyridine adduct displayed a dinuclear structure bridged by a carbido ligand between 5- and 6-coordinate chromium centers. The carbido complex reacted with two equivalents of aldehydes to form α,β-unsaturated ketones. Treatment of the carbido complex with alkenes resulted in a formal double-cyclopropanation of alkenes by the carbido moiety to afford spiropentanes. Isotope labeling studies using a <sup>13</sup>C-enriched carbido complex, [CrBr₂(thf)₂][CrBr₂(thf)₂]<sub>μ</sub>-Cl, identified that the quaternary carbon in the spiropentane framework was delivered by carbide transfer from the carbido complex. Terminal and internal alkynes also reacted with the carbido complex to form cyclopropenylidene complexes. A solid-state structure of the diethylocyclopropenylidene complex, prepared from 3-hexyne, showed a mononuclear cyclopropenylidene chromium<sub>μ</sub>-Cl structure.

Recently, Hill and co-workers have reported a bent dimetallacarbyne, which has a rather dimetallacarbyne character, called dirhoda-heterocyclic carbene. The dimetallacarbyne species<sup>19,40</sup> can bind various Lewis acids to form trinuclear µ₃-carbides, which have been investigated by Takemoto and Matsuzaka.<sup>41,42</sup>

Carbido complexes have been generally prepared by deprotonation of methylidyne, metallaion of halocarbynes, or multiple C-X bond cleavages of various carbide sources, such as CO<sub>2</sub>,<sup>39,44,46</sup> Cl<sub>4</sub>,<sup>45</sup> CHCl<sub>3</sub>,<sup>35</sup> and CS<sub>2</sub>.<sup>36,37</sup> Although functionalization of lithiocarbynes [OC][<sup>13</sup>C]<sub>f</sub>M<sub>f</sub>Li(thf)<sub>2</sub> (M = Mo, W; Tp<sup>*</sup> = tris(3,5-dimethyl-1-pyrazolyl)borate), prepared by lithiation of bromocarbynes [OC][<sup>13</sup>C]<sub>f</sub>M<sub>f</sub>B<sub>r</sub>4 has been widely explored by Hill and co-workers,<sup>43,47–58</sup> reactivity studies on carbide transfer of carbido ligands as a C1 source have not been developed. Herein, we report reduction of CBr<sub>4</sub> with CrBr<sub>2</sub> and

Introduction

Carbide is a special ligand in organometallic<sup>1–3</sup> materials,<sup>4–6</sup> and bioinorganic chemistry,<sup>7–9</sup> i.e. the core structure in nitrogens.<sup>7</sup> Despite numerous studies on stable interstitial carbido clusters<sup>3,10–11</sup> and carbido materials<sup>4–6</sup> as well as gas-phase generation of metal carbides,<sup>12–14</sup> examples of more exposed and reactive molecular metal carbides, such as mononuclear, dinuclear, or trinuclear complexes, are still rare.<sup>9</sup> As shown in Fig. 1, several types of molecular metal carbide species have been reported. Terminally bound carbide species can be categorized into two types based on their electronic structures. The neutral carbido complexes [L₂MCl<sub>μ</sub>-C] (M = Ru<sup>17,19</sup>, Os<sup>9</sup>, Cl₄<sup>26,40,42</sup> L = PPh₃, PC₅₃, NHC), originally synthesized by Heppert in 2002,<sup>17</sup> can form dative bonding Lewis pairs with various transition metals.<sup>21–27</sup> The anionic terminal carbide [Ar<sub>2</sub>BN,Mo<sub>μ</sub>-C] (Ar = m-Xylyl) has been prepared by Cummins and co-workers via deprotonation of a terminal methylidyne complex.<sup>28</sup> Akin to the neutral terminal carbides,<sup>17–21</sup> the anionic carbides also bind various metals to form dinuclear structures, but those dinuclear carbido complexes have a metallocarbyne character.<sup>27–31</sup> In addition to those two types of dinuclear carbido complex, dimetallacumulene structures of dinuclear µ-carbides have been reported generally with late-transition metals.<sup>32–38</sup>

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Fig. 1. Examples of metal carbido complexes: neutral terminal carbide, anionic terminal carbide. dative bonding µ-carbide, metallocarbyne, dimetallacumulene, dimetallocarbene, trinuclear µ₃-carbide, and interstitial carbide.

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structural characterization of a chromium carbide as well as a reactivity study for carbide transfer.

Results and discussion

Halocarbyne and carbide transfer to aldehydes by the CX₄–CrX₂ reagent (X = Cl, Br)

Falck and Mioskowski have reported a chlorocarbyne transfer reaction to aldehydes by treatment with a mixture of CCl₄ and CrCl₂ in a 1:6 ratio. Recently, we have achieved characterization of a trinuclear chromium chlorocarbyne complex, [CrCl(thf)₃][μ₃-Cl][μ-Cl]₃, obtained from the CCl₄–CrCl₂ reagent, and the chlorocarbyne complex indeed underwent chlorocarbyne transfer to aldehydes to afford chloroallylic alcohols 1-Cl (Scheme 1a). In addition to formation of 1-Cl, Corey–Fuchs-type homologation products 2, terminal alkenes, were also formed via Cl-abstraction as a formal carbide transfer from the chlorocarbyne complex. A bromocarbyne transfer reaction has also been reported for the bromide analogues CBr₄ and CrBr₂, which was prepared in situ by reduction of CrBr₃ with LiAlH₄. We have revisited the classical protocol of preparation of CrBr₂ by treatment of chromium(0) with hydrobromic acid. Although the Cr²⁺ ion is still fairly reducing (Cr²⁺/Cr³⁺ = −0.424 V vs. SHE), a blue solid of the chromium(II) bromide hydrate [CrBr₂(H₂O)₆] was readily precipitated out from an aqueous mixture of chromium(0) powder and hydrobromic acid at 0 °C. Having a pure solid of anhydrous CrBr₂ in hand, we demonstrated the bromocarbyne transfer to aldehydes by use of the isolated CrBr₂. To our surprise, in addition to formation of the bromoallylic alcohol 1a-Br and terminal alkylne 2a, an α,β-unsaturated ketone 3a was also formed (Scheme 1b). Interestingly, pre-mixing CrBr₂ and CrBr₂ in THF prior to treatment with aldehydes resulted in the formation of the α,β-unsaturated ketone 3a as a major product. Unfortunately, formation of unidentifiable products by further reactions of 3a with THF promoted by some low-valent chromium species lowered the yields of 3a. Combinations of different halogens CCl₄–CrBr₃ and CBr₄–CrCl₂ were also attempted, but a mixture of all four products 1a-Cl, 1a-Br, 2a, and 3a was formed in both cases due to halogen-scrambling.

Reduction of CBr₄ with CrBr₂

Given the idea of formation of the α,β-unsaturated ketone 3a, we inquired if the more reactive tetrahalomethane CBr₄ could be further reduced by chromium(u) to form a chromium carbide species rather than a bromocarbyne species. Akin to the reduction of CCl₄ with CrCl₂ recently reported by our group, treatment of CBr₄ with 6 equivalents of CrBr₂ in THF at 0 °C produced [CrBr₃(thf)₃] as a brown solid along with a green supernatant. After removal of [CrBr₃(thf)₃], a green solid was obtained from the green supernatant and identified as paramagnetic 4-thf in 90% yield (Scheme 2). The green product 4-thf is stable in the solid state at room temperature, but slightly unstable in solution even at low temperature (−78 °C) to form [CrBr₃(thf)₃] and some unidentified chromium species. An XRD study of 4-thf revealed a dinuclear structure, namely [CrBr₂(-thf)₃][CrBr₂(thf)₃][μ-C], where a carbido ligand is bridging between 5- and 6-coordinate chromium centers (Fig. S35†). Upon crystallization of 4-thf to obtain a better crystal for the XRD study, complex 4-thf gradually decomposed in solution to form a precipitate of [CrBr₆(thf)₃]. The conclusive structural characterization was performed with a pyridine adduct, 4-py, which was obtained quantitatively by addition of pyridine to 4-thf in THF. The molecular structure of 4-py (Fig. 2a) still maintains a dinuclear chromium moiety bridged by a carbido ligand in a linear fashion (Cr₁–C₁–Cr₂ = 174.5(6)°). The 5-coordinate chromium center is best described as distorted square pyramidal (τₕ = 0.29) with the carbido ligand on the apical position along with a short Cr₁–C₁ bond (1.634(10) Å), while the other chromium center represents a distorted octahedral geometry with a long Cr₂–Cr₂ bond (2.035(10) Å). Akin to the reported mononuclear neutral carbidies and dinuclear dative bonding carbidies, two X-type ligands (halides) and two L-type ligands (THF, pyridine, PR₃ or NHC) are transoid to each other on the basal positions in the 5-coordinate environment, but the τₕ values of 4-thf (τₕ = 0.41) and 4-py (τₕ = 0.29) are larger than those of the mononuclear neutral carbidies (τₕ = 0.07−0.16)⁵⁷−⁶⁰ and dinuclear dative bonding carbidies (τₕ = 0.01−0.23)⁴¹−⁴⁵ of ruthenium and osmium. Given the S = 2 nature of 4-thf in THF by Evans’ method (μₜ = 4.84 μₑ)⁴⁹ as well as in the solid state (μₑ = 5.03)⁵⁵, the Wiberg bond indices of

Scheme 1 Reactions of aldehydes with the CX₄–CrX₂ reagent (a) X = Cl, (b) X = Br.

Scheme 2 Synthesis of 4-thf by reduction of CBr₄ with CrBr₂ and ligand-exchange with pyridine to form 4-py.
Cr1–C1 and Cr2–C1 bonds were calculated as 2.02 and 1.08, respectively, for 4-thf and 2.07 and 1.12 for 4-py. Bonding analyses of the neutral terminal carbides \([\text{[Me}_3\text{P})_2\text{Cl}_2\text{M} \equiv \text{C}]\) \([\text{M} = \text{Fe}, \text{Ru})\] have been previously reported by Krapp, Pandey, and Frenking.\(^\text{44}\) Although the Wiberg bond indices were ca. 2 for the M–C bond in the neutral terminal carbides, an M≡C triple bond character has been shown with two π- and one σ-type bonding orbitals. Molecular orbitals of 4-thf as well as 4-py also depicted two π-bonding interactions of the carbido ligand more delocalized around the 5-coordinate chromium center and a three-center two-electron \([\text{Cr–C–Cr}]\) σ-interaction (Fig. 2c). Therefore, the canonical structure of the carbido complex 4 could be better described as a dative bonding μ-carbide\(^\text{31–35}\) than the metallocarbyne character.\(^\text{27–31}\)

A plausible pathway of formation of the carbido complex 4-thf from CBr4 and CrBr2 is shown in Scheme 3. Akin to other Cr–C bond formations by reduction of haloalkanes with chromium\(^\text{the metallocarbyne character.}\) Frenking.\(^\text{44}\) Although the Wiberg bond indices were ca. 2 for the M–C bond in the neutral terminal carbides, an M≡C triple bond character has been shown with two π- and one σ-type bonding orbitals. Molecular orbitals of 4-thf as well as 4-py also depicted two π-bonding interactions of the carbido ligand more delocalized around the 5-coordinate chromium center and a three-center two-electron \([\text{Cr–C–Cr}]\) σ-interaction (Fig. 2c). Therefore, the canonical structure of the carbido complex 4 could be better described as a dative bonding μ-carbide\(^\text{31–35}\) than the metallocarbyne character.\(^\text{27–31}\)

Isotope labeling studies

To spectroscopically confirm the carbido ligand delivered from CBr4, the isotopologue \([\text{[CrBr}_2(\text{thf})_3]^{3}\text{[CrBr}_2(\text{thf})_3]}^{\text{[μ–13C]}\text{]}\text{]}\) \((4\text{-13C})\) was prepared from \(^{13}\text{C}\text{Br}_4\). An IR spectrum of \(4\text{-13C}\) revealed an absorption of the \([\text{Cr–C–Cr}]\) 3-centered vibration at 762 cm\(^{-1}\), which was red-shifted from 788 cm\(^{-1}\) observed in the unlabeled carbide 4-thf (Fig. 2b). Measurement of a \(^{13}\text{C}\) NMR spectrum for \(4\text{-13C}\) was also attempted, but \(^{13}\text{C}\) NMR signals other than solvents could not be located probably due to the paramagnetic feature of the chromium carbide. Akin to the \textit{in situ} preparation of the CBr4–CrBr2 reagent, the isolated carbido complex 4-thf readily reacted with 2 equivalents of aldehydes (Scheme 4) to form the \(\alpha\β\sum\text{unsaturated ketones 3a (22%)}\) and 3b (20%).\(^\text{55}\)

Accordingly, a \(^{13}\text{C}\)-labeled \(\alpha\β\sum\text{unsaturated ketone 3a–13C}\) was also prepared by use of \(4\text{-13C}\). The NMR spectrum of 3a–13C displayed an enriched \(^{13}\text{C}\) NMR signal selectively on the \(\alpha\)-position at 130.85 ppm, which was coupled with \(\alpha\β\sum\text{H at 6.10 ppm (}J_{\text{CH}} = 157 \text{ Hz). The deuterium labeling study was also demonstrated using a deuterated aldehyde, 3-phenylpropanal-\textit{d}. The \(^1\text{H}\) NMR spectrum of 3a–d displayed deuterium signals on both \(\alpha\)– and \(\beta\)-positions at 6.15 ppm and 6.88 ppm, respectively, implying that some H-shift event took place from the aldehyde to the \(\alpha\)-carbon of the \(\alpha\β\sum\text{unsaturated ketone, which was delivered from the carbido ligand. As illustrated in Scheme 5, two plausible pathways to give the \(\alpha\β\sum\text{unsaturated ketones 3 could be considered from two canonical structures of 4-thf.} \text{Path A shows [2 + 2]-cycloaddition of the first aldehyde to the Cr≡C}}\)

![Scheme 3](image3.png)

Scheme 3 Reduction of C–Br bonds with CrBr2 and formation of 4-thf \((\text{Cr} = \text{CrBr}_2(\text{thf})_3)\).

![Scheme 4](image4.png)

Scheme 4 Reactions of 4-thf with aldehydes.

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bond, while Path B represents insertion of the aldehyde into the Cr–C or dative bond. Analyses of the quenched reaction mixture of aldehydes with 4-thf as well as the pre-mixed CBr₄–CrBr₂ revealed the formation of ketone 5a. The ketone 5a could be formed by hydrolysis of one of the intermediates represented in Path B, implying that the insertion pathway B is the more likely pathway.

**Double-cyclopropanation by complex 4-thf to alkenes**

To gain further insight into the electronic structure of the dinuclear carbide 4, we hypothesized that a reactivity study of 4-thf with unsaturated substrates, such as alkenes or alkynes, would give some idea about which canonical structure of 4-thf is more dominant. A terminal alkene, 4-phenyl-1-butene, gradually reacted with 4-thf, resulting in precipitation of a mixture of [CrBr₂(thf)₂]ₙ and [CrBr₃(thf)₃] (Scheme 6). After work-up, analyses by NMR and GC-MS spectroscopy revealed formation of spiroptentane 6a (24% isolated yield) as a mixture of diastereomers (distal : proximal : medial = 28 : 17 : 55), and the spiroptentane 6a was also prepared in 22% yield (distal : proximal : medial = 32 : 20 : 48) by the CBr₄–CrBr₂ reagent prepared in situ (Fig S15†). Addition of ethylene (1 atm) to a THF solution of 4-thf resulted in the formation of the parent spiroptentane (6b). To conclusively confirm the formation of spiroptentanes 6a and 6b by carbide transfer from 4-thf, the ¹³C-enriched carbide 4-¹³C was treated with 4-phenyl-1-butene and ethylene, respectively. As a result, the quaternary carbons in the spiroptentane skeleton were indeed ¹³C-enriched in the ¹³C NMR spectra (Fig. 3) of 6a-¹³C (19.51 ppm, 21.19 ppm, and 21.22 ppm) and 6b-¹³C (9.30 ppm).

Spiroptentane is still a challenging framework to assemble by organic synthetic methods such as reduction of tetrakis(1-haloalkyl)methanes due to multiple side-reactions and isomerization. Formal “double-cyclopropanation” by a carbido moiety to alkenes has been reported in the gas phase by use of carbon vapor, which was generated by arc discharge, but isomerization of the resulting spiroptentanes also proceeded under such harsh conditions. Although the yields of the obtained spiroptentanes 6a and 6b are still low, the carbido complex 4-thf underwent “double-cyclopropanation” to alkenes similar to the carbon vapor but without isomerization.

**Synthesis of cyclopropenylidene complexes**

Reaction of 4-thf with alkynes smoothly proceeded to form a precipitate of [CrBr₃(thf)₂]ₙ. After removal of [CrBr₃(thf)₂]ₙ,
paramagnetic green products 7a and 7b were obtained from a DME solution (Scheme 7). A single crystal suitable for an XRD study was obtained by crystallization of the 3-hexyne analogue 7c (μeff = 3.69 μμ) from a DME solution layered with hexane. As shown in Fig. 4, a solid-state structure of 7c displayed a cyclopropenylidene ligand on a chromium(II) bromide [CrBr3(thf)] along with a typical Cr(μ)-carbene dative bond (2.039(3) Å).7d–7f Akin to the reported chromium cyclopropenylidene complexes,7g–7i as well as the free cyclopropenylidenes,7j,7k the cyclopropenylidene complex 7c also has a slightly shorter C–C bond (C2–C3: 1.351(4) Å) on the backbone than the other C–C bonds (C1–C2: 1.383(4) Å, C1–C3: 1.395(4) Å) in the cyclopropenylidene unit, implying delocalization of π-electrons over the 3-membered ring. IR spectra revealed a characteristic absorption of the cyclopropenylidene unit at 1796 cm⁻¹, which was red-shifted to 1783 cm⁻¹ by the 13C-enriched cyclopropenylidene 7c-13C. In contrast to the similar IR absorption observed in 7b/7b-13C at 1809/1796 cm⁻¹, the IR spectra of the mono-substituted cyclopropenylidene complexes 7a/7a-13C delivered from the terminal alkyne showed two absorptions of the cyclopropenylidene ligand at 1351/1325 cm⁻¹ and 1740/1720 cm⁻¹ (Fig. S27†).

Despite the tetrabromide complex 4-thf reacting with alkynes, a mixture of tribromide 7 and dibromide [CrBr2(thf)]n was obtained. Thus, the third bromide in 7 could be provided by disproportionation of the resulting chromium(II) cyclopropenylidene A or another equivalent of carbide 4. Although the source of bromide in the formation of 7 is still unclear, use of two equivalents of carbide 4 to alkynes dramatically improved the yields of cyclopropenylidene complexes 7a (1 equiv.: 29% yield; 2 equiv.: 44% yield), 7b (1 equiv.: 26% yield; 2 equiv.: 95% yield), and 7c (1 equiv.: 6% yield; 2 equiv.: 35% yield). Note that addition of [CrBr2(thf)]n into the reaction was also attempted, but the yields of the cyclopropenylidene complexes were not improved.

Formation of a cyclopropenylidene unit by reaction of the ruthenium carbido complex [(Ph3P)2Cl2Ru≡C] with alkyne has been reported by Johnson and co-workers.44 The ruthenium carbide reacted only with an electron-deficient alkyne, dimethylacetylene dicarboxylate (DMAD), to form a cyclopropenylidene complex. In contrast to the ruthenium carbide [(Ph3P)2Cl2Ru≡C], our chromium carbide 4-thf reacted with electron-rich alkynes to form cyclopropenylidene complexes 7a, 7b, and 7c, while no reaction of 4-thf with DMAD in THF was observed along with a gradual decomposition of unreacted 4-thf in solution. Addition of alkenes as well as DMAD to cyclopropenylidene complexes 7a, 7b, and 7c has also been attempted, but identifiable products could not be obtained.

Conclusions

This work has shown that the CBr₄-CrBr₂ reagent possesses bromocarbene and carbide transfer abilities to aldehydes. In the CBr₄-CrBr₂ reagent, the first example of a chromium carbido complex was isolated and structurally characterized. DFT calculations and NBO analyses of the carbido complex proposed a dative bonding μ-carbide character. Reactivity studies on carbide transfer of the carbido ligand with aldehydes and alkynes as well as isotope labeling studies have been demonstrated. It is noteworthy that a formal double-cyclopropanation of the carbido complex to alkenes might support the dative bond character of the carbido moiety. In addition, rare examples of cyclopropenylidene complexes have been prepared by treatment of the carbido complex with terminal and internal alkynes. Further investigation of carbide transfer is in progress.

Data availability

All experimental data, NMR spectra, FT-IR spectra, UV-Vis spectra, GC-MS data, crystallographic data, and computational analyses are provided in the ESI†.

Author contributions

K. Irifune prepared compounds and carried out reactions. T. Kurogi performed spectroscopy, crystallography, and computational studies and analyzed the data. T. Kurogi and K. Takai supervised this study and wrote the manuscript. All authors discussed the results and contributed to the preparation of the final manuscript.

Conflicts of interest

There are no conflicts to declare.

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Preliminary studies of the first steps of Paths A and B, [2 + 2]-cycloaddition of C═O to Cr≡C and insertion of aldehyde into Cr–C, respectively, with the help of DFT calculations showed that the intermediate formed by the first insertion reaction in Path B (+12.2 kcal mol$^{-1}$) was much more stable than the [2 + 2]-cycloaddition product in Path A (+33.6 kcal mol$^{-1}$) compared with $\Delta G$(sol) values from 4-thf and PhCHO of 0 kcal mol$^{-1}$. However, disproportionation of chromium species can also be considered during the reaction with aldehydes as observed in the reaction of 4-thf with alkynes, and it hampered mechanistic studies of these two reaction pathways.