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A Diruthenium μ-Carbido Complex That Shows Singlet-Carbene-like Reactivity

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Supporting Information

ABSTRACT: Low-temperature deprotonation of the cationic μ-methylidyne complex $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-CH})][BF_4]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with $KN(SiMe_3)_2$ affords a thermally unstable μ-carbido complex $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-C})]$ (**2**), as evidenced by trapping experiments with elemental S or Se and ^{13}C NMR spectroscopic observation. The reactivity of **2** toward CO_2, $Ph_2S^+CH_2^-$, EtOH, and an intramolecular C−H bond indicates that the μ-carbido carbon in **2** has an ambiphilic (nucleophilic and electrophilic) nature consistent with the formulation of **2** as the first example of a transition-metal-substituted singlet carbene. DFT study suggests that the Ru substituents in **2** are stronger σ-donor and weaker π-donor to the carbene center than amino substituents in N-heterocyclic carbenes.

Carbenes are neutral two-coordinate carbon species of the general type CX_2, whose chemistry has received much attention for many years.[1] Recently, significant progress has been made in the chemistry of N-heterocyclic carbenes (NHCs),[2] especially in their application as ligands in metal complexes and as catalysts or reagents for small molecule activation. The fascinating properties of NHCs owe much to the strongly π-donating and moderately σ-withdrawing nature of the amino substituents,[2] which makes these molecules stable nucleophilic singlet carbenes (Figure 1a). In this respect, much

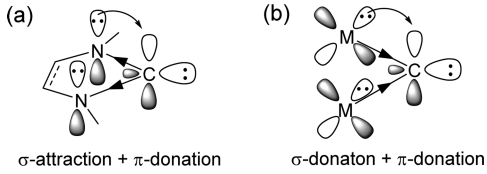

Figure 1. Donor properties of substituents in (a) NHCs and (b) transition-metal-substituted singlet carbenes.

effort has been devoted to the synthesis and study of stable carbenes bearing a wider variety of heteroatomic substituents,[3] including π-donating alkoxo,[4] phosphino,[5] and thiolato,[6] groups but also π-accepting silyl[5,7] and boryl[8] groups. However, the synthetic design of heteroatom substituents has so far remained inside the border of p-block in the periodic table. To our knowledge, no transition metal elements have been used as substituent atoms directly bonded to a carbene center, although NHCs bearing metal-functionalized organic substituents[9] as well as transition-metal-substituted heavier carbene analogues (i.e., germylenes, stannylenes, and plumbylenes) have been reported.[10]

When a transition metal fragment is used as a substituent on a carbene center, it will serve as a π-donor substituent if it has enough d electrons for π-back bonding (Figure 1b). Unlike electronegative p-block group substituents, which are usually σ-attractors, metal fragments are generally more electropositive than carbon and are expected to be σ-donor substituents. These characteristics of metal fragments may open up a new strategy for electronic tuning of carbene's reactivity, especially making highly nucleophilic carbenes.[11] In addition, metal substituents may allow cooperative reactivity between metal and carbene centers as well as redox-based reactivity tuning.

We earlier reported a cationic diruthenium μ-methylidyne complex $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-CH})][BF_4]$ (**1**), in which the electron-deficient μ-methylidyne ligand is effectively stabilized by π-back-donation from the Cp*Ru fragments.[12] We envisioned that deprotonation of **1** would produce a neutral μ-carbido complex $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-C})]$ (**2**), for which a singlet-carbene-like structure could be expected. We previously isolated a Ru_2Pt μ_3-carbido complex $[(Cp^*Ru)_2(\mu\text{-NHPh})(\mu\text{-H})(\mu_3\text{-C})\{PtMe(PMe_3)_2\}][OTf]$,[13] in which the diruthenium μ-carbido fragment $\{(Cp^*Ru)_2(\mu\text{-NHPh})(\mu\text{-H})(\mu\text{-C})\}$ is coordinated to the Pt(II) fragment $\{PtMe(PMe_3)_2\}^+$ like a π-donor-stabilized singlet carbene ligand. Herein we report evidence for the generation of **2** and the singlet-carbene-like reactivity of this species.

Initial attempts for the deprotonation of **1** were done by treating **1** with amide bases $MN(SiMe_3)_2$ (M = Li, Na, K) or $LiNPr^i_2$ at −80 °C in THF and warming the reaction mixture to room temperature, which, however, gave a complicated mixture in all cases as monitored by ^1H NMR spectroscopy.

Next, we examined low-temperature trapping of the target complex **2** with elemental sulfur, which has been used to demonstrate transient generation of singlet carbenes.[2a,3d,14] We found that the addition of 1 equiv of $KN(SiMe_3)_2$ (0.5 M in toluene) to a stirred slurry of **1** in THF at −90 °C followed by treatment with solid S_8 gave the μ-thiocarbonyl complex $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-CS})]$ (**3a**) (Scheme 1), which was isolated in 61% yield and crystallographically characterized (Figure 2).[15] Similar treatment of **1** with $KN(SiMe_3)_2$ and elemental selenium gave the μ-selenocarbonyl complex **3b**, which was also crystallographically characterized (Figure 2).[15] To our knowledge, **3b** is the first example of a complex containing $\mu\text{-}\eta^1\text{:}\eta^1$-CSe ligand.[16]

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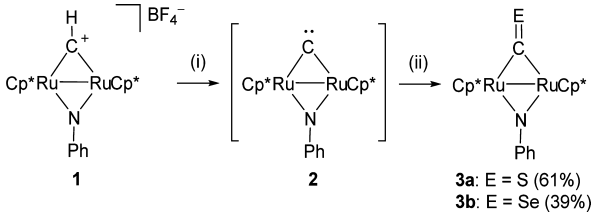
Scheme 1. Generation and Trapping of 2[a]



[a]Reagents and conditions: (i) $KN(SiMe_3)_2$, THF, −90 °C to −70 °C; (ii) $1/8S_8$ or Se, THF, −90 °C to r.t.

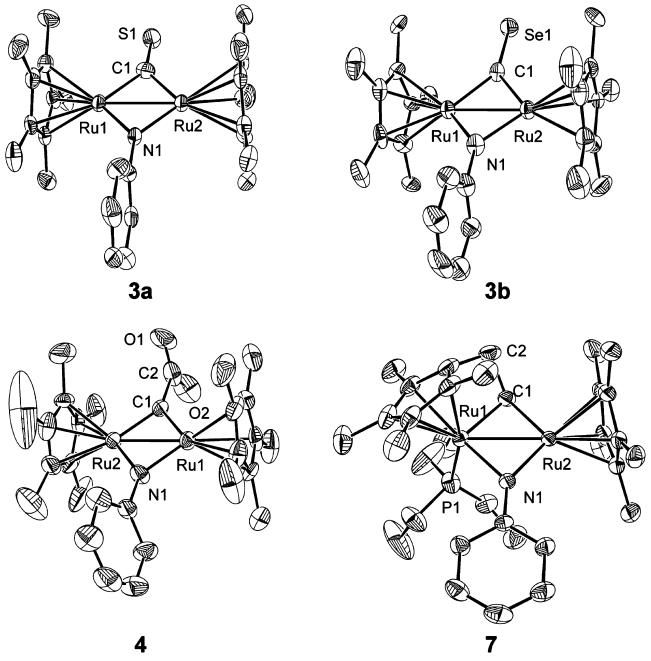


Figure 2. ORTEP drawings of **3a**, **3b**, **4**, and **7** with thermal ellipsoids drawn at the 30% probability level and all hydrogen atoms omitted for clarity.

The trapping reactions in Scheme 1 suggest that the target μ-carbido complex **2** is generated by deprotonation of **1** and behaves like a nucleophilic singlet carbene. Encouraged by these results, we next examined the direct observation of **2** by ^{13}C NMR spectroscopy. As shown in Figure 3, when the ^{13}C-enriched and THF-soluble μ-methylidyne complex $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-}^{13}CH)][B(C_6F_5)_4]$ (**1′**) was treated with 1 equiv of $KN(SiMe_3)_2$ (as 0.5 M toluene solution) in THF at −90 °C in an NMR tube, the signal of the μ-^{13}CH ligand in **1′** at δ = 379 ppm disappeared and a new signal appeared at δ 675 ppm, which is assignable to the μ-^{13}C ligand in $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-}^{13}C)]$ (**2′**).[17,18] The observed chemical shift for this carbon nucleus shows good agreement with a computed value of 702 ppm obtained from a GIAO calculation on a full structural model of **2**.[15] Although the magnitude of the downfield shift on going from μ-^{13}CH in **1′** to μ-^{13}C in **2′** is extremely large, the same trend is known for NHCs and corresponding imidazolium salts.[19] The chemical shift assigned to the μ-carbido ligand in **2′** is more downfield than any reported chemical shifts for carbido ligands,[20] the most downfield one being reported for $[Tp^*W(CO)_2CLi]$ (δ = 556 ppm; Tp* = hydrotris(dimethylpyrazol-1-yl)borate).[21] For reference, the essentially linear and tetravalent μ-carbido ligands of the types Ru═C═Ru[22] and Ru−C≡Ru[23] resonate at δ 430 and 414 ppm, respectively. The extremely downfield resonance for the μ-carbido ligand in **2′** compared to these values might be due to the bent and divalent nature of this carbon center.

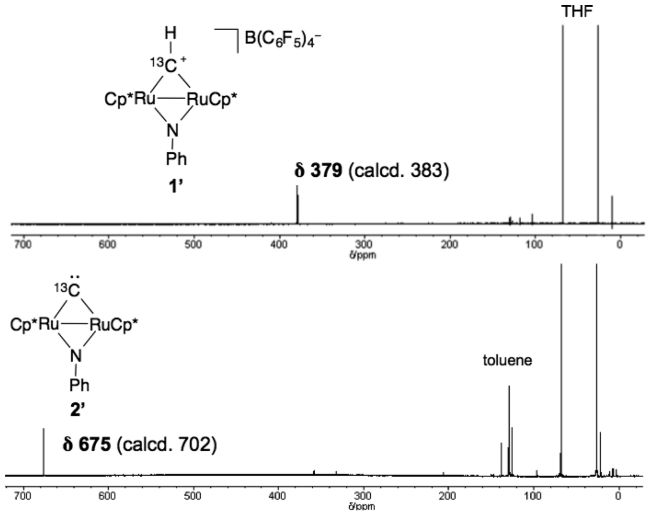
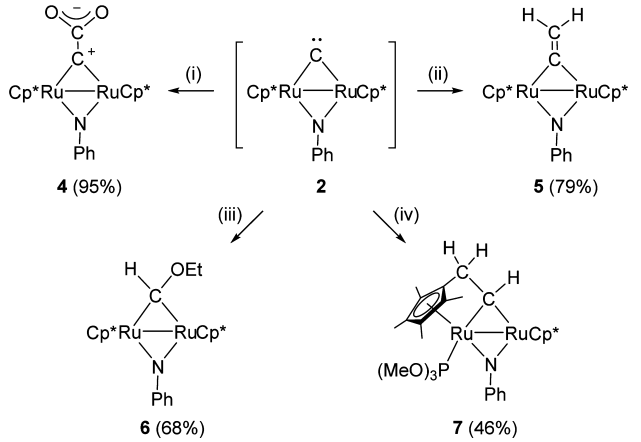


Figure 3. $^{13}C\{^1H\}$ NMR spectra for the reaction of **1′** with $KN(SiMe_3)_2$ (0.5 M in toluene) in THF. The spectrum on the top was recorded at 20 °C and that on the bottom at −80 °C.

Scheme 2. Reactivity of 2[a]



[a]Reagents: (i) CO_2; (ii) $Ph_2S^+CH_2^-$; (iii) EtOH; (iv) $P(OMe)_3$.

Having gathered evidence for the formation of **2**, we next examined the reactivity of this species, which is summarized in Scheme 2. The nucleophilic nature of **2** was demonstrated by its reaction with CO_2, which produced the formally zwitterionic μ-C−CO_2 adduct $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-}CCO_2)]$ (**4**) in 95% yield. A preliminary X-ray analysis for **4** revealed that the CO_2 unit in **4** is bent at a bond angle of 130(2)° and perpendicular to the Ru−C−Ru plane (Figure 2).[15] The $^{13}C\{^1H\}$ NMR spectrum of **4** displayed resonances assignable to the μ-CCO_2 ligand at δ 379 (C_α) and 175 (C_β) ppm. The former is consistent with the μ-alkylidyne character of this carbon,[12] while the latter is slightly more deshielded than those found in NHC−CO_2 adducts (149−159 ppm).[24] Complex **2** also reacted with the nucleophilic ylide $Ph_2S^+CH_2^-$, which produced the known μ-vinylidene complex $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-}CCH_2)]$ (**5**)[12] in 79% yield. Although the initial attack of the methylide carbon may occur at either a Ru or the μ-carbido center, this reaction is formally a reaction of the μ-carbido ligand in **2** with a nucleophile. Thus, these two reactions

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demonstrate the ambiphilic nature of the μ-carbido ligand in **2** consistent with its formulation as a singlet carbene-like carbon.

We also observed O−H and C−H activation reactions that provided additional support for the singlet-carbene-like reactivity of **2** (Scheme 2). Treatment of **2** with EtOH resulted in the O−H activation at the μ-carbido center in **2** to give the μ-ethoxycarbene complex $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-CH(OEt)})]$ (**6**) in 68% yield. The reaction is obviously analogous to the 1,1-addition of alcohol O−H bonds to NHCs.[25] Treatment of **2** with slight excess of $P(OMe)_3$ resulted in the intramolecular C−H bond activation of a Cp* methyl group at the μ-carbido carbon center to yield the product **7**, which was identified crystallographically (Figure 2).[15] The C−H insertion reaction is relatively uncommon for nucleophilic NHCs[26] but fairly common for ambiphilic singlet carbenes,[5a,27] where the lone-pair and the empty 2p orbitals on the carbene center can interact simultaneously with the C−H σ^* and σ orbitals, respectively, to facilitate the C−H bond activation. It seems likely that the intramolecular C−H insertion that furnished **7** proceeded via the intermediate $P(OMe)_3$ adduct of **2** whose μ-carbido center would behave like an ambiphilic singlet carbene to induce the intramolecular C−H insertion.

To gain insights into geometric and electronic structure of **2**, we performed a DFT calculation (B3LYP/6-31G(d,p)+SDD level), where a singlet state was considered according to the experimental results. The optimized geometry of **2** is shown in Figure 4a. It contains a planar NRu_2C core analogous to those

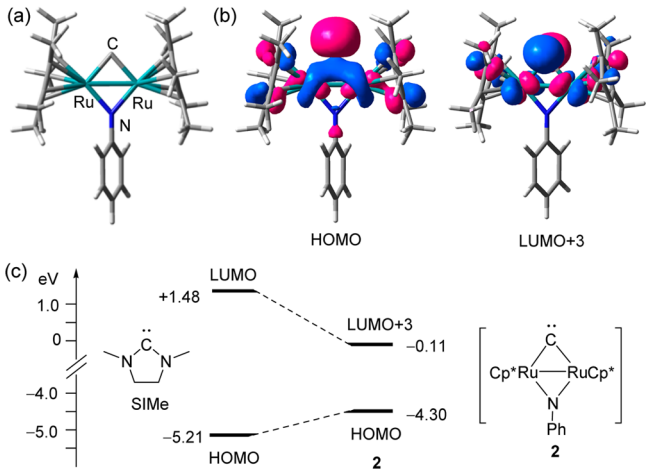

Figure 4. (a) Optimized structure of **2**. Selected distances (Å) and angle (deg): Ru−C = 1.915 (av), Ru-*N* = 1.924 (av), Ru−Ru = 2.530, Ru−C−Ru = 82.64. (b) HOMO (left) and LUMO + 3 (right) of **2**. (c) Frontier orbital energies of **2** and SIMe.

found in complexes of the type $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-L})]$.[12] The Ru−C bond distances for the μ-carbido ligand in **2** were calculated to be 1.915 (av) Å. These distances are slightly longer than those calculated for the μ-CH ligand in the protonated precursor $[(Cp^*Ru)_2(\mu\text{-NPh})(\mu\text{-CH})]^+$ (1.899 (av) Å), similarly to NHC/NHC-H^+ pairs.[28] However, the computed Ru−C distances in **2** are still short enough to suggest Ru−C multiple bond character. Further insights into the bonding and electronic structure of **2** were obtained by molecular orbital analysis. HOMO of **2** is a σ-type orbital that is predominantly localized on the μ-carbido carbon center and represents the nonbonding electron pair on this atom (Figure 4b). The LUMO of **2** (not shown)[15] is a π-type orbital that is mainly centered on the Ru_2N unit with Ru−N π-antibonding character and may explain Lewis acidic behavior of the Ru centers. An orbital that predominantly represents the empty π-type orbital on the μ-carbido carbon center is found at LUMO +3. This orbital has Ru−C π-antibonding character and indicates that the Ru fragments serve as π-donors to the carbon center to destabilize the empty carbon 2p orbital and reduce the electrophilicity of this carbon. The HOMO and LUMO + 3 of **2** demonstrate that the μ-carbido carbon center in **2** has a singlet-carbene-like electronic structure with the Ru units acting as π-donor substituents. To evaluate the donor ability the of Ru substituents, the energies of HOMO and LUMO+3 in **2** were compared with the energies of the corresponding orbitals of an NHC, namely 4,5-dihydro-1,3-dimethylimidazol-2-ylidene (SIMe). As shown in Figure 4c, the HOMO of **2** is higher than that of SIMe, which represents predominantly the nonbonding carbon sp^2 orbital. On the other hand, the LUMO + 3 of **2** is lower than the corresponding empty carbon $2p_z$ orbital of SIMe (LUMO). These data suggest that the Ru substituents in **2** has a stronger σ-donor and weaker π-donor ability than the amino substituents in SIMe.

In summary, deprotonation of the cationic μ-methylidyne complex **1** at low temperature produces the μ-carbido complex **2** as evidenced by trapping experiments and ^{13}C NMR observation. The reactivity of **2** toward electrophile, nucleophile, and O−H/C−H bonds is consistent with its formulation as a singlet carbene with considerable nucleophilicity and electrophilicity. The present study demonstrates for the first time that transition metal fragments can be used as heteroatom substituents on a carbene carbon center, and the Ru substituents in **2** appear to be stronger σ-donor and weaker π-donor compared to amino substituents in NHCs. Further studies will be directed toward elucidating the ability of **2** as ligands for metal complexes as well as the design and synthesis of other types of transition-metal-substituted carbenes.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(17) A low-temperature ^{1}H NMR spectrum of in situ generated **2′** is given in the Supporting Information (Figure S5).

(18) Variable-temperature NMR monitoring of this reaction mixture showed that **2′** began to decompose at about −60 °C and completely disappeared above −30 °C. See Supporting Information for details.

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