ORGANOMETALLICS

Article

Cite This: *Organometallics* 2019, 38, 4578−4584

pubs.acs.org/Organometallics

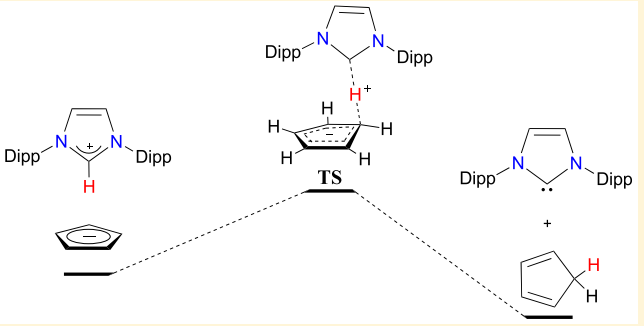
Labile Imidazolium Cyclopentadienides

Yuzhong Wang, Yaoming Xie, Holli L. Threlkeld, Pingrong Wei, Henry F. Schaefer, III, and Gregory H. Robinson*

Department of Chemistry and the Center for Computational Chemistry, The University of Georgia, Athens, Georgia 30602-2556, United States

Supporting Information

ABSTRACT: A series of imidazolium-based synthetic routes to imidazolium cyclopentadienides are reported. The 2:1 reaction of imidazolium (**1**) with $[Cp_2Ti^{III}Cl]_2$ gives $[NHC^{Dipp}H]^+[Cp_2Ti^{III}Cl_2]^-$ (NHC^{Dipp} = 2,6-diisopropylphenyl-substituted N-heterocyclic carbene) (**2**). The "inverse sandwich" imidazolium cyclopentadienide (**3**) is obtained as a crystalline solid via reaction of **1** with both $[Cp_2Ti^{III}Cl]_2$ and cyclopentadienyllithium (CpLi) (in a molar ratio of 2:1:1) in THF/toluene at elevated temperature. Notably, the 1:1 reaction of **1** with CpLi leads to the isolation of "multidecker" **4** in the solid state, while the corresponding 1:2 reaction of **1** with CpLi gives the crystals of CpLi-bound cyclopentadienyl-imidazolium complex **5**. While compounds **3**, **4**, and **5** have been structurally characterized using single-crystal X-ray diffraction, in solution these complexes dissociate due to the conversion of $[NHC^{Dipp}H]^+[Cp]^-$ to both cyclopentadiene and NHC^{Dipp} through intramolecular proton transfer. The equilibrium of the acid−base conversion between $[NHC^{Dipp}H]^+Cp^-$ and the 1:1 mixture of NHC^{Dipp} and cyclopentadiene is probed by theoretical methods.

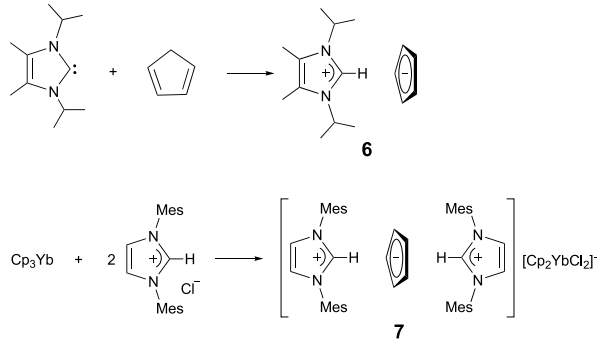


INTRODUCTION

Kealy and Pauson's seminal synthesis of ferrocene nearly seven decades ago,[1] along with its iconic "sandwich" molecular structure,[2] posited a new research vista for organometallic chemistry.[3−5] Multitudes of metallocenes have subsequently been synthesized and extensively utilized in a number of disparate fields.[3−8] The metal−cyclopentadienyl ligand bonding interactions in metallocenes usually possess both covalent and electrostatic characteristics.[3,9−11] In addition to its diverse "spectator ligand" applications in transition-metal chemistry, the cyclopentadienyl moiety has also been reported to exist as an unbound, or loosely bound (via hydrogen bonds), anion in a number of complexes.[12−25] The formation of complexes containing a Cp^- anion via the Cp-loss reactions of metal cyclopentadienyl complexes has been well reported.[13,15,16,18,19,25] The cyclopentadienyl anion may also be obtained by reactions of alkali-metal cyclopentadienides with cationic metal complexes,[14] ammonia,[23] and ammonium and phosphonium halides.[21,22] Moreover, the Cp^- species can also be produced from reactions of cyclopentadiene or its derivatives with a tris(dimethylamino)sulfonium (TAS^+) salt,[20] the Wittig reagent,[22] and an N-heterocyclic carbene (NHC).[24]

The chemistry of imidazolium cyclopentadienides has garnered only tepid attention.[24,25] Compounds **6** and **7** are rare examples of imidazolium-Cp^- (i.e., $C_5H_5^-$) complexes (Scheme 1). While **6** was prepared by direct combination of NHC^{iPr} (i.e., $\{(Me)CN(i\text{-}Pr)\}_2C$: with cyclopentadiene,[24] **7** was unexpectedly prepared via a $[NHC^{Mes}H]^+Cl^-$-mediated Cp-loss reaction of Cp_3Yb.[25] Notably, previous attempts to synthesize sterically demanding imidazolium ($[NHC^{Mes}H]^+$ or $[NHC^{Dipp}H]^+$ (**4**)) cyclopentadienides at room temperature were reportedly unsuccessful.[24] Herein, we report the syntheses,[26] molecular structures,[26] and computations[26] of "inverse sandwich" (**3**), "multidecker" (**4**), and CpLi-bound (**5**) cyclopentadienyl imidazolium complexes. Interestingly, while compounds **3**, **4**, and **5** can be isolated as crystalline solids at room temperature,[26] these complexes dissociate in solution (THF, toluene, or benzene) due to the conversion of

Scheme 1. Syntheses of Previously Reported Imidazolium $C_5H_5^-$ Complexes 6 and 7



Received: August 28, 2019
Published: November 27, 2019

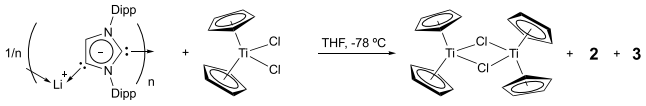
DOI: 10.1021/acs.organomet.9b00589
Organometallics 2019, 38, 4578−4584

$[NHC^{Dipp}H]^+[Cp]^-$ to the 1:1 mixture of NHC^{Dipp} and cyclopentadiene (through intramolecular proton transfer).[26] This acid–base conversion is reversible. In contrast, the recently reported imidazolium cyclopentadienide **6** (Scheme 1) does not demonstrate such labile behavior.[24]

RESULTS AND DISCUSSION

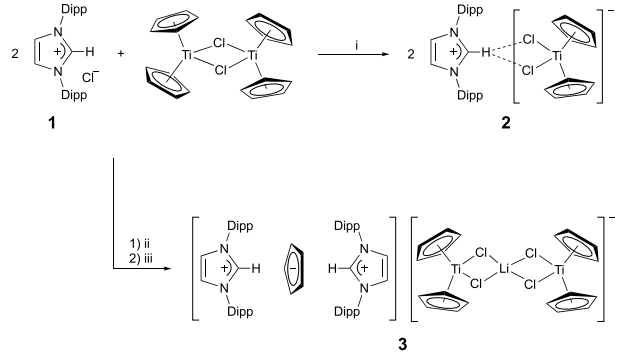
The anionic diisopropylphenyl-substituted N-heterocyclic dicarbene $NHDC^{Dipp}$ (Scheme 2), reported by this laboratory,[27] has proven to be a versatile synthetic platform from which a variety of abnormal carbene-based complexes, poly-NHCs, NHDC-based binuclear complexes, main-group dithiolene radicals,[28,29] and C4-functionalized NHCs may be accessed.[30−34] Notably, our synthetic efforts regarding the low-temperature reaction of $NHDC^{Dipp}$ with $Cp_2Ti^{IV}Cl_2$ in THF and subsequent workup in toluene did not afford the expected C4-titanocenyl-substituted N-heterocyclic carbene. Instead, **2**, **3**, and $[Cp_2Ti^{III}Cl]_2$ were isolated from the resulting mixture (Scheme 2). The formation of **3** involves not only the reduction of titanocene dichloride but also cyclopentadienyl extrusion. Indeed, our fortuitous preparation of compound **3** from this system initiated our interest in the possibility of a more targeted synthetic route to **3**.

Scheme 2. Reaction of $NHDC^{Dipp}$ with $Cp_2Ti^{IV}Cl_2$



Combination of the imidazolium salt **1** with paramagnetic $[Cp_2Ti^{III}Cl]_2$[35] (in a 2:1 molar ratio) affords **2** (5.4% yield) as amber crystals (Scheme 3), along with a considerable amount of unreacted **1**. Compound **3** is isolated as pale green crystals (49.3% yield) through the reaction of **1** with both $[Cp_2Ti^{III}Cl]_2$ and CpLi (in a molar ratio of 2:1:1) in THF/toluene mixed solvent, which is heated until a homogeneous solution is obtained (Scheme 3). While **7** was obtained via a Cp-loss reaction (Scheme 1), the formation of **3** may involve capturing the Cp^- anion and Li^+ cation by the cationic imidazolium and anionic $[Cp_2Ti^{III}Cl_2]^-$ moieties, respectively. Our efforts to prepare the analogue of **3** containing a Cl^- counterion, by combining **1** with CpLi (in 2:1 molar ratio) in THF, were unsuccessful, affording a mixture containing both **1** and **4**—a consequence of the extremely poor solubility of both **1** and **4** in THF. The direct combination of **1** and **4** in CH_2Cl_2 did not give the expected "inverse sandwich" imidazolium cyclopentadienide salt; instead, a complicated mixture resulted due to decomposition. It appears that $[Cp_2Ti^{III}Cl]_2$ plays a key role in the synthesis of the "inverse sandwich" imidazolium cyclopentadienide.

Scheme 3. Syntheses of 2 and 3[a]



[a]Dipp = 2,6-diisopropylphenyl. Legend: (i) THF; (ii) 1 equiv of CpLi, THF/toluene, Δ; (iii) crystallization.

An X-ray structural analysis[26] of **2** (Figure 1a) reveals that the hydrogen atom at the C2 carbon of the imidazolium fragment, located in the difference Fourier map, is oriented toward the area between the two chlorine atoms of the anionic $[Cp_2Ti^{III}Cl_2]^-$ moiety (which should be ascribed to the

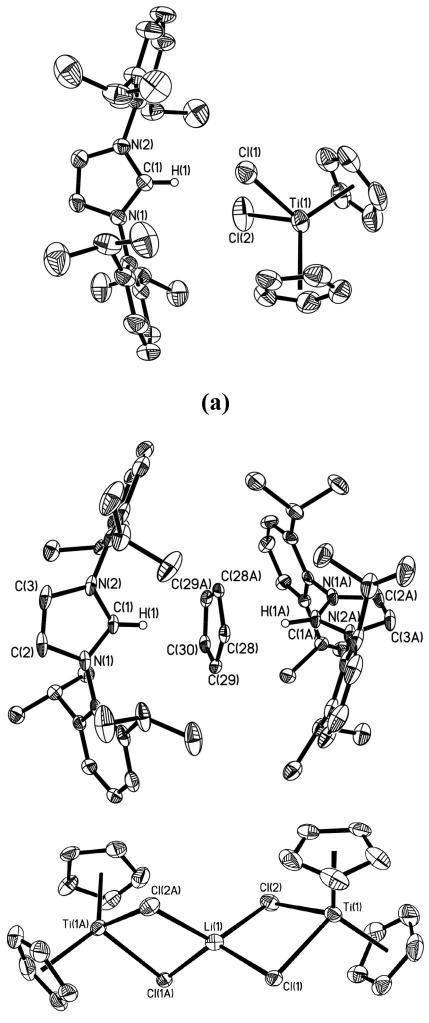


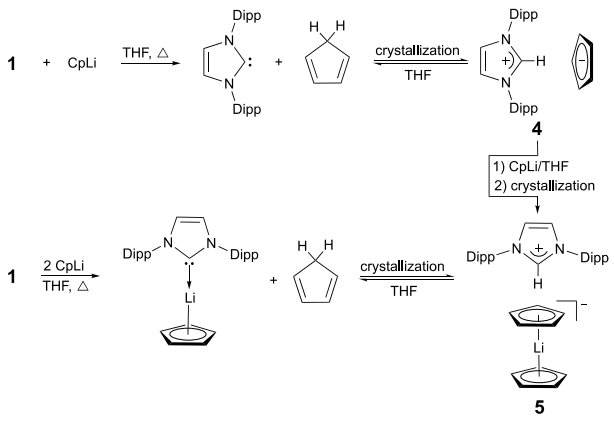
Figure 1. Molecular structures of **2** (a) and **3** (b). Thermal ellipsoids represent 30% probability; except for those residing at C2 carbons, hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **2**: C(1)–H(1) 0.919(17), C(1)–N(1) 1.329(3), C(1)–N(2) 1.323(3), Ti(1)–Cl(1) 2.5094(10), Ti(1)–Cl(2) 2.5114(9), Cl(1)–Ti(1)–Cl(2) 84.20(3). Selected bond distances (Å) and angles (deg) for **3**: C(1)–H(1) 0.931(16), C(1)–N(1) 1.333(3), C(1)–N(2) 1.331(3) C(28)–C(28A) 1.407(5), C(28)–C(29) 1.393(4), C(29)–C(30) 1.389(4), Ti(1)–Cl(1) 2.5336(8), Ti(1)–Cl(2) 2.5299(9), Li(1)–Cl(1) 2.326(3), Li(1)–Cl(2) 2.358(3); Cl(1)–Ti(1)–Cl(2) 84.19(3), Cl(1)–Li(1)–Cl(2) 92.89(2), Li(1)–Cl(1)–Ti(1) 89.37(11), Cl(1)–Li(1)–Cl(2A) 110.74(3).

DOI: 10.1021/acs.organomet.9b00589
Organometallics 2019, 38, 4578−4584

presence of C−H···Cl hydrogen bonds:[36] $d_{H(1)\cdots Cl(1)}$ = 2.538 Å, $\theta_{C(1)-H(1)\cdots Cl(1)}$ = 159°; $d_{H(1)\cdots Cl(2)}$ = 2.90 Å, $\theta_{C(1)-H(1)\cdots Cl(2)}$ = 125°). Notably, the anionic $[Cp_2Ti^{III}Cl_2]^-$ unit is usually observed in bimetallic complexes such as $[Cp_2Ti^{III}\{\mu\text{-}Cl\}_2]_2Zn$.[37,38] In the solid state,[26] compound **3** (Figure 1b) exists as an ion-separated salt. The anionic moiety of **3** reveals that two $[Cp_2Ti^{III}Cl_2]^-$ anions are bridged by one four-coordinate lithium cation in a distorted-tetrahedral geometry. The Ti−Cl (2.532 Å (av)) and Li−Cl (2.342 Å (av)) bond distances in **3** compare well with those (d_{Ti-Cl} = 2.543 Å (av), d_{Li-Cl} = 2.325 Å (av)(for neutral $[Cp_2Ti^{III}\{\mu\text{-}Cl\}_2Li(THF)_2]$.[39] Similar to **7**,[25] the cationic fragment of **3** demonstrates an "inverse sandwich" structure: two cationic imidazolium species residing on either side of a planar anionic Cp^- ring and adopting a staggered orientation due to the steric bulk (Figure 1). Similar to the interaction between the TAS^+ cations and Cp^- anion in $[(TAS)_2Cp]^+[Cp]^-$,[20] the interaction between two cationic imidazolium species and the central Cp^- anion in **3** is largely dominated by electrostatic forces. The C−C bond distances (1.389(4)−1.407(5) Å) of the Cp^- ring in **3** are similar to those in the model $[\mathbf{3}]^+$ [26] (1.413−1.416 Å) and in $[(TAS)_2Cp]^+[Cp]^-$ (1.385(3)−1.396(4) Å).[20] Similar to that in **2**, the H(1) atom in **3** (and **4** and **5**) was also located in the difference Fourier map. The imidazolium protons (i.e., H(1) for **3** and **5**; both H(1) and H(3AA) for **4**), pointing to the Cp^- ring, may involve C−H···Cp^- hydrogen bonding.[22,25] The H(1)···$Cp_{centroid}$ distance (2.171 Å) and C(1)−H(1)···$Cp_{centroid}$ angle (172.98°) in **3** are somewhat larger than those for the model $[\mathbf{3}]^+$ ($d_{H(1)\cdots Cp(centroid)}$ = 1.965 Å, C(1)−H(1)···$Cp_{centroid}$ angle = 160.74°).[26] Compound **3** has a shorter H···$Cp_{centroid}$ distance (2.171 Å) but larger C_{NHC}−H···$Cp_{centroid}$ angle (172.98°) in comparison to those for **7** ($d_{H\cdots Cp(centroid)}$ = 2.295(9) Å, C_{NHC}−H···$Cp_{centroid}$ angle = 162.4(5)°).[25]

The 1:1 mixture of **1** with CpLi in THF was heated until a homogeneous solution was obtained. The subsequent room-temperature crystallization gives **4** as a crystalline solid (Scheme 4). The crystallization rate depends on the concentration of the reactants. The high concentration of the reactants affords crystallization of **4** (from THF) at room temperature (over hours). Low-temperature crystallization (at −45 °C) gives a higher yield of **4** (84.1% yield). Alternatively, **4** may also be synthesized by the room-temperature reaction of NHC^{Dipp} with freshly prepared cyclopentadiene[40] (Scheme 4).

Scheme 4. Syntheses of 4 and 5[a]



[a]Dipp = 2,6-diisopropylphenyl.

X-ray-quality single crystals of **4** can be obtained by recrystallization in THF at room temperature. Essentially, these experimental observations would appear to be at odds with the conclusion drawn by Schäfer et al. (i.e., that compound **4** cannot be synthesized by reacting NHC^{Dipp} with cyclopentadiene at room temperature).[24] An X-ray structural analysis[26] reveals that the 1:1 adduct **4** does not exist as an isolated "half-sandwich" molecule but rather as a supramolecular "multidecker" polymeric chain (Figure 2a), in

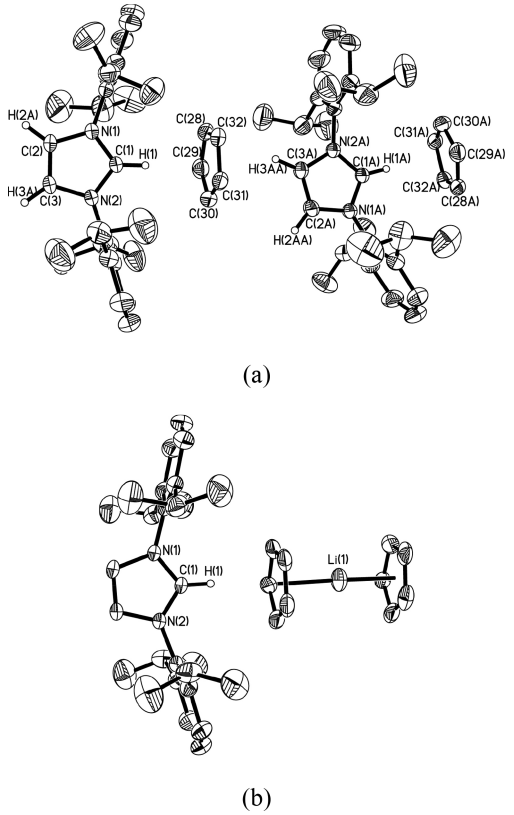


Figure 2. Molecular structures of **4** (a) and **5** (b). Thermal ellipsoids represent 30% probability; except for those residing at imidazole carbons (for **4**) and the C2 carbon (for **5**), hydrogen atoms are omitted for clarity. Selected bond distances (Å) for **4**: C(1)−H(1) 0.930(13), C(1)−N(1) 1.3266(18), C(1)−N(2) 1.3250(17), C(28)−C(29) 1.380(9), C(29)−C(30) 1.392(12), C(30)−C(31) 1.366(12), C(31)−C(32) 1.409(8). Selected bond distances (Å) and angles (deg) for **5**: C(1)−H(1) 0.938(18), C(1)−N(1) 1.326(4), C(1)−N(2) 1.318(4), C−C(Cp rings) 1.42, Li−C(Cp rings) 2.217(9)−2.442(8); $Cp_{centroid}$−Li(1)−$Cp_{centroid}$ 169.60.

which an imidazolium cation directs both the C2/proton unit (i.e., C(1)−H(1)) and the C4/proton unit (i.e., C(3A)−H(3AA)) toward two neighboring Cp^- rings, respectively. The cyclopentadienyl rings in **4** are crystallographically disordered. Consequently, for clarity, only one set of structural parameters of the Cp^- ring is illustrated in Figure 2. In **4**, the H(1)···$Cp_{centroid}$ distance (2.210 Å) is ca. 0.125 Å shorter than the H(3AA)···$Cp_{centroid}$ distance (2.335 Å). However, both of them are shorter than the C_{NHC}-H···$Cp_{centroid}$ distance in **6** (2.387−2.468 Å).[24] The C(1)−H(1)···$Cp_{centroid}$ angle (167.9°) in **4** is between those for **3** (173.0°) and **6** (151.4−156.2°).[24] By comparison with the gas-phase $[\mathbf{3}^+]$ and solid-state **3**, **4**, and **6**, our DFT computations[26] (M06-2X[41]/6-311G**[42]) suggest that gas-phase monomeric **4** demonstrates the shortest H···

DOI: 10.1021/acs.organomet.9b00589
Organometallics 2019, 38, 4578−4584

$Cp_{centroid}$ distance (1.923−1.938 Å) and most acute C_{NHC}−H···$Cp_{centroid}$ angle (143.2−146.4°).[26] The 1:2 mixture of **1** with CpLi in THF was heated until a homogeneous solution was obtained. The resulting solution was stored in a dry ice/acetone bath (−78 °C) over 2 h, giving **5** in 74.4% yield (Scheme 4). Compound **5** may also be prepared (80.7% yield) by combining **4** with CpLi in THF (in a 1:1 molar ratio). The anionic $[Cp_2Li]^-$ fragment in the X-ray structure of **5** (Figure 2b) exhibits structural parameters similar to those in $R^+[Cp_2Li]^-$ (R^+ = Ph_4P^+,[43] TAS^+ (tris(dimethylamino)-sulfonium)[44]). For instance, while being somewhat longer than that in polymeric CpLi (1.969 Å),[45] the Li−$Cp_{centroid}$ distances in **5** (1.998 and 2.017 Å) are similar to those in $Ph_4P^+[Cp_2Li]^-$ (2.008 Å) and in $TAS^+[Cp_2Li]^-$ (1.979 Å, av).[43,44] Among **3**−**5**, compound **5** has the longest H(1)···$Cp_{centroid}$ distance (2.223 Å) and largest C_{NHC}−H···$Cp_{centroid}$ angle (175.3°).

In contrast to **6**, which is stable in benzene solution (as confirmed by resonances at 6.17 ppm for imidazolium and 6.44 ppm for Cp^- proton),[24] the ^{1}H NMR spectrum of **4** (in THF-d_8 or C_6D_6) shows that **4** is converted to a 1:1 mixture of NHC^{Dipp} and cyclopentadiene in solution due to Cp^- anion mediated intramolecular deprotonation of the imidazolium moiety in **4** (Scheme 4).[26] Compound **5** displays similar behavior in THF, giving a 1:1 mixture of cyclopentadiene and NHC^{Dipp}:LiCp (due to NHC^{Dipp} in situ binding to LiCp) (Scheme 4).[26] The existence of the NHC^{Dipp}:LiCp complex in a THF solution of **5** is confirmed by comparing both the ^{1}H and ^{13}C NMR spectra of **5** with those of NHC^{Dipp}:LiCp, which is synthesized via a 1:1 reaction of NHC^{Dipp} with LiCp in THF.[26]

The X-ray structure of NHC^{Dipp}:LiCp (Figure 3) shows that the C_{NHC}−Li (2.104 Å, av) and Li−$Cp_{centroid}$ (1.845 Å, av)

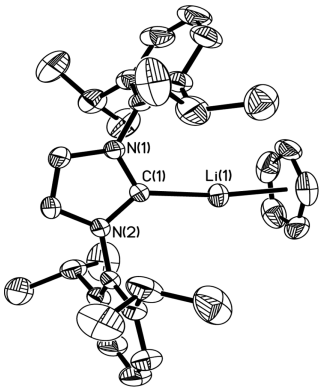


Figure 3. Molecular structure of NHC^{Dipp}:LiCp. Thermal ellipsoids represent 30% probability, hydrogen atoms are omitted for clarity, and bonding parameters of one of three molecules in one asymmetric unit are shown in the caption. Selected bond distances (Å) and angles (deg): C(1)−Li(1) 2.094(4), Li(1)−C(Cp rings) 2.156(5)−2.177(5), Li(1)−$Cp_{centroid}$ 1.841; C(1)−Li(1)−$Cp_{centroid}$ 171.51.

distances of NHC^{Dipp}:LiCp are shorter than those ($d_{C(NHC)-Li}$ = 2.155(4) Å, $d_{Li-Cp^*(centroid)}$ = 1.90 Å) of NHC^{tBu}:LiCp* (Cp* = 1,2,4-tris(trimethylsilyl)cyclopentadienide).[46] The conversion between this 1:1 mixture of NHC^{Dipp}:LiCp and C_5H_6 and **5** is also reversible (Scheme 4). Crystals of **3** are insoluble in toluene. The ^{1}H NMR spectroscopic study of **3** in THF-d_8 confirmed its dissociation by observing the resonances for both NHC^{Dipp} and cyclopentadiene (1:1 ratio). Furthermore, addition of toluene to a THF solution of **3** (volume ratio of toluene to THF 6:1) may result in the isolation of **2·toluene** crystals. It is noteworthy that **7** was also reported to decompose rapidly in coordinating solvents.[25]

To further study the reversible conversion between **4** and the cyclopentadiene−NHC^{Dipp} (acid−base) pair, computations related to the dissociation pathway of the monomeric model **4** (Figure 4) were probed using two different functionals

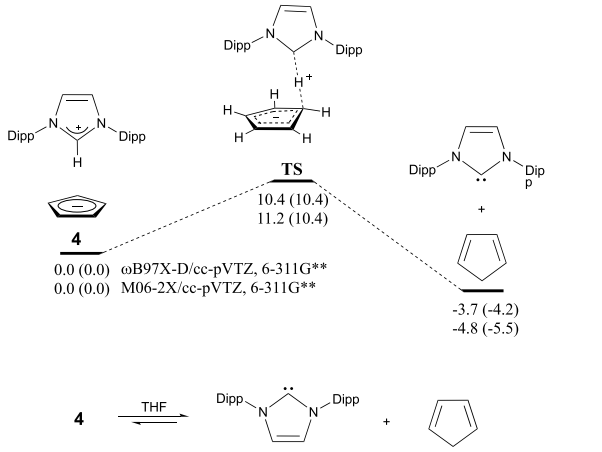


Figure 4. Theoretical Gibbs free energy profiles (in kcal/mol) for the proton-transfer in **4** predicted by two DFT methods (ωB97X-D[47] and M06-2X[41]), along with 6-311G**[42] and cc-pVTZ[48] basis sets. The data in parentheses are based on the 6-311G** basis set.

(ωB97X-D[47] and M06-2X[41]) and two basis sets (6-311G**[42] and cc-pVTZ[48]). This dissociation reaction involves the intramolecular proton transfer from the C2 carbon of the imidazolium moiety to the anionic Cp^- ring in **4** via a transition state (TS) with an energy barrier of 10.4 or 11.2 kcal/mol, depending upon the theoretical method utilized (Figure 4).[26] By comparison with those for **4** model[26] ($d_{C(NHC)-H}$ = 1.089−1.093 Å; the shortest C_{Cp}···H distance is 2.161−2.190 Å), in the TS, the C_{NHC}···H^+ distance is elongated to 1.449−1.490 Å, while the corresponding C_{Cp}···H^+ distance is shortened to 1.361−1.371 Å. In contrast to the strongly exergonic (ΔG^{298} = −83.5 kcal/mol) reaction of NHC^{iPr} with C_5H_6 (resulting in **6**),[24] the reaction Gibbs free energy of **4** in the range of −3.7 to −5.5 kcal/mol somewhat favors the conversion of **4** to the neutral NHC^{Dipp} ligand and cyclopentadiene in the gas phase. This is also consistent with the behavior of **4** in organic solvents (i.e., THF, toluene, and benzene). The absence of observable ^{1}H NMR resonances of **4** in a dilute THF-d_8 solution (Figure S1) suggests that the equilibrium (in Figure 4) dramatically shifts to the right. By comparison, the ^{1}H NMR spectrum of the saturated solution of **4** in THF-d_8 (Figure S2) exhibits not only the resonances of the 1:1 mixture of NHC^{Dipp} and C_5H_6 but also a group of broadened signals for **4**. The integral ratio of C_5H_6 to $C_5H_5^-$ (ca. 5:1) suggests that 16.7% of **4** exists in the saturated THF solution. While the ^{1}H NMR resonance of $C_5H_5^-$ in **4** is observed as a broad singlet at 4.84 ppm (Figure S2), the corresponding resonance for the imidazolium-H (i.e., NC(H)-N) is obscured due to the signal broadening caused by fast proton transfer. Variable-temperature (VT) ^{1}H NMR experiments of **4** in THF-d_8 were also performed. However, a substantial amount of **4**, as a crystalline solid, deposited on the walls of the NMR tube, obviously decreasing the resolution of

DOI: 10.1021/acs.organomet.9b00589
Organometallics 2019, 38, 4578−4584

the ^{1}H NMR signals, when the temperature was decreased to −20 °C. Consequently, the expected imidazolium proton resonance of **4** was not observed. This may be partially ascribed to the low solubility of **4** in THF, especially at low temperature. Additional attempts to conduct VT-^{1}H NMR studies of **4** in CD_2Cl_2 were unsuccessful due to decomposition. On the basis of our experimental observations, both low temperature and high concentration favor the formation of **4**, due to an equilibrium shift to the left (Figure 4).

CONCLUSION

Compounds **3**, **4**, and **5** were prepared at room temperature and structurally characterized using single-crystal X-ray diffraction studies. Notably, these complexes are inclined to dissociate in solution due to the conversion of $[NHC^{Dipp}H]^+[Cp]^-$ to both cyclopentadiene and NHC^{Dipp} through intramolecular proton transfer. The small (−3.7 to −5.5 kcal/mol) Gibbs free energy of **4**, coupled with 10.4−11.2 kcal/mol transition state energy, supports the existence of an equilibrium between **4** and the 1:1 mixture of CpH and NHC^{Dipp}. Both low temperature and high concentration favor the formation of **4** due to the equilibrium in Figure 4 shifting to the left.

EXPERIMENTAL SECTION

General Considerations. The syntheses of air-sensitive compounds were performed under purified argon using Schlenk techniques and an inert-atmosphere drybox (M-Braun LabMaster SP). Chemicals were purchased from Aldrich and Strem and used as received. The solvents were dried and distilled under argon from Na/benzophenone prior to use. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer. The VT-^{1}H NMR experiments were conducted on a Varian Unity Inova 500 MHz spectrometer in a temperature range from +20 to −20 °C. X-ray intensity data for **2·toluene**, **4**, **5·THF**, and NHC^{Dipp}:LiCp were collected at room temperature on a Bruker D8 Quest PHOTON 100 CMOS X-ray diffractometer system with Incoatec Microfocus Source (IμS) monochromated Mo Kα radiation (λ = 0.71073 Å, sealed tube) using φ- and ω-scan techniques. The X-ray intensity data for **3·toluene** were measured at 100 K on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-scan technique.

Compound 2. A 10 mL portion of THF was placed in a Schlenk tube containing both **1** (1.991 g, 4.68 mmol) and $[Cp_2TiCl]_2$ (1.000 g, 2.34 mmol) at room temperature, and this mixture was then stirred overnight. After the volatile materials were removed in vacuo, the residue was extracted using 20 mL of toluene. After toluene was removed from the filtrate in vacuo, the resulting residue was dissolved in the THF/toluene (a volume ratio of 1/6) mixed solvent, inducing the formation of **2·toluene** as amber crystals (0.186 g, 5.4% yield). Mp of **2·toluene**: gradually decomposed (>128 °C) and melted (>166 °C). Crystal data for **2·toluene**: $C_{44}H_{55}Cl_2N_2Ti$, fw = 730.70, monoclinic, $P2_1/n$, a = 12.7334(5) Å, b = 13.9889(5) Å, c = 24.0779(10) Å, β = 100.837(1)°, V = 4212.4(3) Å^3, Z = 4, R1 = 0.0597 for 6280 data ($I > 2\sigma(I)$), wR2 = 0.1808 (all data).

Compound 3. A 10 mL portion of THF was placed in a Schlenk tube containing both **1** (1.000 g, 2.35 mmol) and $[Cp_2TiCl]_2$ (0.502 g, 1.18 mmol), and this mixture was stirred at room temperature for 2 h. The addition of CpLi (0.085 g, 1.18 mmol) to the mixture in the Schlenk tube resulted in an immediate color change from dark brown to green. After this mixture was stirred for 1 h, 5 mL of toluene was added and then the mixture was stirred another 1 h. The resulting slurry was heated until a homogeneous solution was achieved. X-ray-quality pale green crystals of **3·toluene** were obtained through concentrating the solution under reduced pressure, which was collected and subsequently rinsed using toluene (0.835 g, 49.3% yield). Mp of **3·toluene**: decomposed (>123 °C) and melted (at 181 °C). Crystal data for **3·toluene**: $C_{86}H_{107}Cl_4LiN_4Ti_2$, fw = 1441.28, monolinic, $P2/n$, a = 15.2148(10) Å, b = 14.0833(9) Å, c = 19.2093(12) Å, β = 96.7680(10)°, V = 4087.4(5) Å^3, Z = 2, R1 = 0.0454 for 4832 data ($I > 2\sigma(I)$), wR2 = 0.1077 (all data).

Compound 4. An 8 mL portion of THF was placed in a Schlenk tube containing both **1** (1.000 g, 2.35 mmol) and CpLi (0.170 g, 2.36 mmol). The mixture was heated until a homogeneous solution was achieved, which was then stored at −45 °C over 4 days. After filtration, a crystalline solid of **4** (0.900 g, 84.1% yield) was collected. X-ray-quality single crystals of **4** were obtained through recrystallization of **4** in THF at room temperature. Mp: gradually decomposed (>170 °C) and melted (215−216 °C). ^{1}H NMR (400.14 MHz, THF-d_8) (note: the saturated solution of **4** in THF-d_8 gives an equilibrium mixture containing **4**, NHC^{Dipp}, and cyclopentadiene; see Figure S2): for **4**, δ 1.07 [bm, 12H, $CH(CH_3)_2$], 1.29 [bm, 12H, $CH(CH_3)_2$], 2.31 [bm, 4H, $CH(CH_3)_2$], 4.84 (bs, 5H, Cp), 7.17−7.47 (bm, 8H, Ar-*H* and NC*H*); for cyclopentadiene, δ 2.93 (s, 10H), 6.40−6.42 (m, 10H), 6.51−6.52 (m, 10H); for NHC^{Dipp}, δ 1.17 [d, 60H, $CH(CH_3)_2$], 1.20 [d, 60H, $CH(CH_3)_2$], 2.82 [m, 20H, $CH(CH_3)_2$], 7.17 (s, 10H, NC*H*), 7.26 [d, 20H, Ar-*H*), 7.35 [t, 10H, Ar-*H*). Crystal data for **4**: $C_{32}H_{42}N_2$, fw = 454.67, monoclinic, $C2/c$, a = 24.9929(10) Å, b = 16.7920(6) Å, c = 18.3899(13) Å, β = 129.3380(10)°, V = 5969.2(5) Å^3, Z = 8, R1 = 0.0563 for 3832 data ($I > 2\sigma(I)$), wR_2 = 0.1593 (all data).

Compound 5. A 6 mL portion of THF was placed in a Schlenk tube containing both **1** (1.000 g, 2.35 mmol) and CpLi (0.340 g, 4.72 mmol). The mixture was heated until a homogeneous solution was achieved, which was then stored at −78 °C for 2 h. After filtration, a crystalline solid of **5·THF** (1.049 g, 74.4% yield) was collected. X-ray-quality single crystals of **5·THF** were obtained through recrystallization of **5·THF** in THF at room temperature. Mp: gradually decomposed (>187 °C) and melted (>286 °C). ^{1}H NMR (400.14 MHz, THF-d_8): (note: **5·THF** dissociates in THF-d_8, resulting in a 1:1 mixture of NHC^{Dipp}:LiCp and cyclopentadiene) for cyclopentadiene, δ 2.93 (s, 2H), 6.40−6.41 (m, 2H), 6.51−6.52 (m, 2H); for NHC^{Dipp}:LiCp, δ 1.17 [d, 12H, $CH(CH_3)_2$], 1.19 [d, 12H, $CH(CH_3)_2$], 2.75 [m, 4H, $CH(CH_3)_2$], 5.54 (s, 5H, Cp), 7.20 (s, 2H, NC*H*), 7.26 [d, 4H, Ar-*H*), 7.37 [t, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (100.63 MHz, THF-d_8): for cyclopentadiene, δ 42.3, 133.1, 133.8; for NHC^{Dipp}:LiCp, δ 24.0, 25.0 [$CH(CH_3)_2$], 29.4 [$CH(CH_3)_2$], 103.6 (Cp), 122.9, 124.1, 129.5, 139.4, 146.9 (Ar-*C* and imidazole-*C*). Crystal data for **5·THF**: $C_{41}H_{55}LiN_2O$, fw = 598.81, monoclinic, $P2_1/m$, a = 11.1108(6) Å, b = 15.1463(8) Å, c = 12.5385(7) Å, β = 114.491(2)°, V = 1920.22(18) Å^3, Z = 2, R1 = 0.0882 for 2868 data ($I > 2\sigma(I)$), wR2 = 0.2276 (all data).

Compound NHC^{Dipp}:LiCp. A 5 mL portion of THF was placed in a Schlenk tube containing both NHC^{Dipp} (0.400 g, 1.03 mmol) and CpLi (0.074 g, 1.03 mmol). After the mixture was stirred for 1 h, the volatiles were removed in vacuo, giving a raw material of NHC^{Dipp}:LiCp in a quantitative yield. X-ray-quality single crystals of NHC^{Dipp}:LiCp were obtained by recrystallization from THF/toluene mixed solvent. Mp: gradually decomposed (>240 °C) and melted (286−288 °C). ^{1}H NMR (400.14 MHz, THF-d_8): δ 1.16 [d, 12H, $CH(CH_3)_2$], 1.18 [d, 12H, $CH(CH_3)_2$], 2.77 [m, 4H, $CH(CH_3)_2$], 5.64 (s, 5H, Cp), 7.19 (s, 2H, NC*H*), 7.26 [d, 4H, Ar-*H*), 7.37 [t, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (100.63 MHz, THF-d_8): δ 24.0, 25.0 [$CH(CH_3)_2$], 29.4 [$CH(CH_3)_2$], 103.5 (Cp), 122.9, 124.1, 129.5, 139.5, 146.9 (Ar-C and imidazole-C). Crystal data for NHC^{Dipp}:LiCp: $C_{32}H_{41}LiN_2$, fw = 460.61, orthorhombic, *Pbca*, a = 19.0298(10) Å, b = 18.3538(9) Å, c = 51.678(3) Å, V = 18049.7(16) Å^3, Z = 24, R1 = 0.0729 for 9983 data ($I > 2\sigma(I)$), wR2 = 0.1917 (all data).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00589.

Details of syntheses, computations, and X-ray crystallography (PDF)

DOI: 10.1021/acs.organomet.9b00589
Organometallics 2019, 38, 4578−4584

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1943558−1943561 and 1947403 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail for G.H.R.: robinson@uga.edu.

ORCID

Yuzhong Wang: 0000-0003-3557-5085

Henry F. Schaefer, III: 0000-0003-0252-2083

Gregory H. Robinson: 0000-0002-2260-3019

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation for support: (CHE-1565676 and CHE-1855641 to G.H.R. and Y.W.; CHE-1661604 to H.F.S.).

REFERENCES

(1) Kealy, T. J.; Pauson, P. L. A New Type of Organo-Iron Compound. *Nature* **1951**, *168*, 1039−1040.

(2) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. The Structure of Iron Bis-cyclopentadienyl. *J. Am. Chem. Soc.* **1952**, *74*, 2125−2126.

(3) *Metallocenes: Synthesis Reactivity Applications*; Wiley-VCH: Weinheim, 1998.

(4) Jutzi, P.; Burford, N. Structurally Diverse π-Cyclopentadienyl Complexes of the Main Group Elements. *Chem. Rev.* **1999**, *99*, 969−990.

(5) *Ferrocenes: Ligands, Materials and Biomolecules*; Wiley: Chichester, 2008.

(6) Coville, N. J.; Duplooy, K. E.; Pickl, W. Monosubstituted Cyclopentadienyl Half-Sandwich Transition-Metal Complexes. *Coord. Chem. Rev.* **1992**, *116*, 1−267.

(7) Poli, R. Monocyclopentadienyl Halide-Complexes of the d-Block and f-Block Elements. *Chem. Rev.* **1991**, *91*, 509−551.

(8) Paz-Sandoval, M. A.; Rangel-Salas, I. I. Half-Open Metallocenes with Heterodienyl Ligands and Related Compounds. *Coord. Chem. Rev.* **2006**, *250*, 1071−1106.

(9) Swart, M. Metal-Ligand Bonding in Metallocenes: Differentiation between Spin State, Electrostatic and Covalent Bonding. *Inorg. Chim. Acta* **2007**, *360*, 179−189.

(10) Rayon, V. M.; Frenking, G. Bis(benzene)chromium Is a δ-Bonded Molecule and Ferrocene Is a π-Bonded Molecule. *Organometallics* **2003**, *22*, 3304−3308.

(11) Fernandez, I.; Cerpa, E.; Merino, G.; Frenking, G. Structure and Bonding of $[E\text{-}Cp\text{-}E']^+$ Complexes (E and E' = B-Tl; Cp = Cyclopentadienyl). *Organometallics* **2008**, *27*, 1106−1111.

(12) Mcdonald, R. N.; Chowdhury, A. K.; Setser, D. W. Gas-Phase Ion−Molecule Reactions of Cyclopentadienyl Anion ($c\text{-}C_5H_5^-$). *J. Am. Chem. Soc.* **1981**, *103*, 7586−7589.

(13) Casey, C. P.; Oconnor, J. M.; Haller, K. J. Interconversion of η^5-C_5H_5, η^1-C_5H_5, and Ionic "η^0"-C_5H_5 Rhenium Compounds - X-Ray Crystal-Structure of $[Re(No)(CH_3)(PMe_3)_4]^+[C_5H_5]^-$. *J. Am. Chem. Soc.* **1985**, *107*, 1241−1246.

(14) Lilga, M. A.; Sohn, Y. S.; Ibers, J. A. Some Chemistry of Alkyl Complexes of Bis(1,2-Bis(Diphenylphosphino)Ethane)Iridium(I). *Organometallics* **1986**, *5*, 766−771.

(15) Anderson, G. K.; Cross, R. J. Generation of Sigma-Bonded and Ionic C_5H_5 Complexes from η^5-Cyclopentadienyl-Palladium and η^5-Cyclopentadienyl-Platinum Precursors and Their Involvement in Hydrogen-Deuterium Exchange Phenomena. *J. Chem. Soc., Chem. Commun.* **1986**, *0*, 1502−1504.

(16) Anderson, G. K.; Cross, R. J.; Fallis, S.; Rocamora, M. Reversible Formation of η^1- and η^0-Cyclopentadienyl Complexes by Treatment of $[M(C_6H_4N{=}NC_6H_4R)(\eta^5\text{-}C_5H_5)]$ (M = Pd, Pt) with Tertiary Phosphines. *Organometallics* **1987**, *6*, 1440−1446.

(17) Marder, T. B.; Williams, I. D. Facile Displacement of an η^5-Indenyl Ligand - Crystal Structure of the $[Rh(Me_2PCH_2CH_2PMe_2)_2]^+$ Salt of the Naked Indenyl Anion. *J. Chem. Soc., Chem. Commun.* **1987**, 1478−1480.

(18) Kakkar, A. K.; Taylor, N. J.; Marder, T. B. Synthesis and Structure of the $[Rh_2(dmpe)_4(\mu\text{-}dmpe)]^{2+}$ Salt of the Naked Cyclopentadienyl Anion - a Comparison of the Reactivity of $[(\eta\text{-Indenyl})Rh(\eta\text{-}C_2H_4)_2]$ and $[(\eta\text{-}C_5H_5)Rh(\eta\text{-}C_2H_4)_2]$. *Organometallics* **1989**, *8*, 1765−1768.

(19) Butts, M. D.; Bergman, R. G. Mechanistic Investigations of Cp-Loss Reactions in an Early-Late Heterobimetallic Complex - Isolation of a Cationic Tantalum Palladium Compound with a Free Cyclopentadienyl Counteranion. *Organometallics* **1994**, *13*, 1899−1910.

(20) Wessel, J.; Behrens, U.; Lork, E.; Mews, R. Tris(Dimethylamino)Sulfoniumcyclopentadienide $[Tas]^+[C_5H_5]^-$ and Tris(Dimethylamino)Sulfoniumpyrrolide $[Tas]^+[C_4H_4N]^-$ - Two Isostructural Salts with "Naked" Anions A^- and the "Inverse" Sandwich-Cations $[\{(Me_2N)_3S)\}_2A]^+$ (A = $C_5H_5^-$, $C_4H_4N^-$). *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 443−446.

(21) Harder, S.; Prosenc, M. H.; Rief, U. Syntheses and X-ray Structures of Anionic Sodocene Sandwiches. *Organometallics* **1996**, *15*, 118−122.

(22) Harder, S. Can C-H···C(π) Bonding Be Classified as Hydrogen Bonding? A Systematic Investigation of C-H···C(π) Bonding to Cyclopentadienyl Anions. *Chem. - Eur. J.* **1999**, *5*, 1852−1861.

(23) Michel, R.; Herbst-Irmer, R.; Stalke, D. Unprecedented CpLi Ammoniacates. *Organometallics* **2010**, *29*, 6169−6171.

(24) Bischoff, I. A.; Müller, C.; Huch, V.; Zimmer, M.; Schäfer, A. Imidazolium Cyclopentadienide Salts and their Use as Cp-Transfer Reagents. *Eur. J. Inorg. Chem.* **2019**, 1941−1944.

(25) Abernethy, C. D.; Macdonald, C. L. B.; Clyburne, J. A. C.; Cowley, A. H. A Persistent C-H···C(π) T-Stacked Cation. *Chem. Commun.* **2001**, 61−62.

(26) See the Supporting Information for synthetic, computational, and crystallographic details.

(27) Wang, Y.; Xie, Y.; Abraham, M. Y.; Wei, P.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. A Viable Anionic N-Heterocyclic Dicarbene. *J. Am. Chem. Soc.* **2010**, *132*, 14370−14372.

(28) Wang, Y.; Hickox, H. P.; Xie, Y.; Wei, P.; Blair, S. A.; Johnson, M. K.; Schaefer, H. F., III; Robinson, G. H. A Stable Anionic Dithiolene Radical. *J. Am. Chem. Soc.* **2017**, *139*, 6859−6862.

(29) Wang, Y.; Xie, Y.; Wei, P.; Blair, S. A.; Cui, D.; Johnson, M. K.; Schaefer, H. F., III; Robinson, G. H. Stable Boron Dithiolene Radicals. *Angew. Chem., Int. Ed.* **2018**, *57*, 7865−7868.

(30) Ghadwal, R. S. Carbon-Based Two Electron σ-Donor Ligands beyond Classical N-Heterocyclic Carbenes. *Dalton Trans.* **2016**, *45*, 16081−16095.

(31) Nasr, A.; Winkler, A.; Tamm, M. Anionic N-Heterocyclic Carbenes: Synthesis, Coordination Chemistry and Applications in Homogeneous Catalysis. *Coord. Chem. Rev.* **2016**, *316*, 68−124.

(32) Waters, J. B.; Goicoechea, J. M. Coordination Chemistry of Ditopic Carbanionic N-Heterocyclic Carbenes. *Coord. Chem. Rev.* **2015**, *293*, 80−94.

(33) Nesterov, V.; Reiter, D.; Bag, P.; Frisch, P.; Holzner, R.; Porzelt, A.; Inoue, S. NHCs in Main Group Chemistry. *Chem. Rev.* **2018**, *118*, 9678−9842.

(34) Uzelac, M.; Hevia, E. Polar Organometallic Strategies for Regioselective C-H Metallation of N-Heterocyclic Carbenes. *Chem. Commun.* **2018**, *54*, 2455−2462.

DOI: 10.1021/acs.organomet.9b00589
Organometallics 2019, 38, 4578−4584

(35) Green, M. L. H.; Lucas, C. R. Some d^1 Bis-π-Cyclopentadienyl Titanium Complexes with Nitrogen or Phosphorus Ligands. *J. Chem. Soc., Dalton Trans.* **1972**, 1000−1003.
(36) Aakeroy, C. B.; Evans, T. A.; Seddon, K. R.; Palinko, I. The C-H···Cl hydrogen bond: Does It Exist? *New J. Chem.* **1999**, *23*, 145−152.
(37) Coutts, R. S. P.; Wailes, P. C. *Advances in Organometallic Chemistry*; Academic Press: New York, 1970; Vol. *9*.
(38) Salzmann, J. J. A New Organometallic Titanium-Zinc Compound. *Helv. Chim. Acta* **1968**, *51*, 526−529.
(39) Baum, E.; Matern, E.; Pikies, J.; Robaszkiewiez, A. Oxidative Dimerisation of Phosphanes and Indications for the Intermediate Presence of (^{t}Bu$_2$P)−P in Reactions of [(η^5-C$_5$H$_5$)$_2$TiCl$_2$] and [(η^5-C$_5$H$_5$)(η^5-C$_5$Me$_5$)TiCl$_2$] with (^{t}Bu$_2$P)−P(SiMe$_3$)Li and ^{t}Bu$_2$P−P(Li)−P^{t}Bu$_2$. Formation of Titanium(III) Fulvalene Complexes. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1090−1095.
(40) Dickson, R. S.; Dobney, B. J.; Eastwood, F. W. Preparation of Cyclopentadiene from Its Dimer. *J. Chem. Educ.* **1987**, *64*, 898−898.
(41) Zhao, Y.; Truhlar, D. G. Comparative DFT Study of Van der Waals Complexes: Rare-Gas Dimers, Alkaline-Earth Dimers, Zinc Dimer, and Zinc-Rare-Gas Dimers. *J. Phys. Chem. A* **2006**, *110*, 5121−5129.
(42) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. XX. a Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72*, 650−654.
(43) Harder, S.; Prosenc, M. H. The Simplest Metallocene Sandwich - the Lithocene Anion. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744−1746.
(44) Wessel, J.; Lork, E.; Mews, R. Alkali Metallocene Anions - Syntheses and Structures. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2376−2378.
(45) Dinnebier, R. E.; Behrens, U.; Olbrich, F. Solid State Structures of Cyclopentadienyllithium, -Sodium, and -Potassium. Determination by High-Resolution Powder Diffraction. *Organometallics* **1997**, *16*, 3855−3858.
(46) Arduengo, A. J.; Tamm, M.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. Carbene-Lithium Interactions. *Chem. Lett.* **1999**, *28*, 1021−1022.
(47) Chai, J. D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom-Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.
(48) Dunning, T. H. Gaussian-Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

DOI: 10.1021/acs.organomet.9b00589
Organometallics 2019, 38, 4578−4584