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Synthesis and Structural Features of Arduengo Carbene Complexes of Group 4 Metallocene Cations

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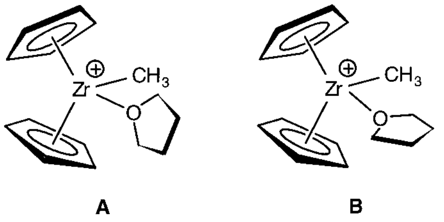
Treatment of [$Cp_2TiCH_3(thf)^+$] (**5**, with [BPh_4^-] anion) with 1,3-diisopropylimidazol-2-ylidene (**4**) at ambient temperature resulted in a rapid displacement of the thf ligand by the stable heterocyclic carbene to yield the Arduengo carbene methyltitanocene cation complex **6a** (>90% isolated). The X-ray crystal structure analysis of **6a** showed that the heteroatom-stabilized carbene ligand [d(Ti−C(carbene) = 2.289(2) Å, d(Ti−CH_3) = 2.178(3) Å] was bonded to titanium in an orientation where the imidazol-2-ylidene ring lies in the major σ-ligand plane of the bent metallocene moiety. A DFT calculation of **6a** and a series of related model compounds has revealed that the Arduengo carbene serves as a pure σ-donor ligand to the titanocene moiety. The observed favored "*in-plane*" orientation of the ligand is steric in origin. Consequently, complex **6a** attains an analogous C_s-symmetric structure in solution, featuring symmetry-equivalent Cp rings and a pair of diastereotopic isopropyl substituents as well as chemically differentiated imidazol-2-ylidene $C^4H{=}C^5H$ groups. The reaction of the ion pair [$(Cp_2ZrCH_3)^+(CH_3B(C_6F_5)_3^-)$] (**7**) with **4** gave the analogous Arduengo carbene zirconocene cation complex **6b** (>95% isolated, with [$CH_3B(C_6F_5)_3^-$] anion).

Introduction

Alkyl group 4 metallocene cations [e.g., $^RCp_2TiCH_3^+$] play an important role as the active species, or the immediate precursors, respectively, of homogeneous Ziegler−Natta catalysts.[1] Their donor ligand-stabilized derivatives [e.g., $^RCp_2TiCH_3(thf)^+$] have contributed significantly to the development of the organometallic bent metallocene cation chemistry.[2] Typical donor ligands used include organic nitriles,[3] pyridine derivatives,[4] and occasionally a phosphine,[5] but the most often used stabilizing donor group is probably the tetrahydrofuran ligand. It can act as a strongly stabilizing four-electron donor ligand in some of its zirconocene cation chemistry,[6] but in most cases it simply serves as a two-electron donor.[7] Structurally, the former situation is indicated by a "perpendicular" arrangement of the idealized tetrahydrofuran ligand plane[6] with regard to the major σ-ligand plane of the bent metallocene (formula A in Chart 1), which allows a significant dative ligand-to-metal interaction in the metallocene σ-plane.[8] The alternative two-electron interaction usually results in an "*in-plane*" orientation of the thf ligand, as depicted in formula B in Chart 1, which appears to represent the sterically least demanding situation.

Chart 1



A

B

Arduengo carbenes (see Chart 2) are very strong σ-donor ligands, which due to their specific electronic features are almost completely lacking additional π-donor or π-acceptor properties.[9,10] In combination with

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† X-ray crystal structure analysis.

‡ Quantum chemical calculations.

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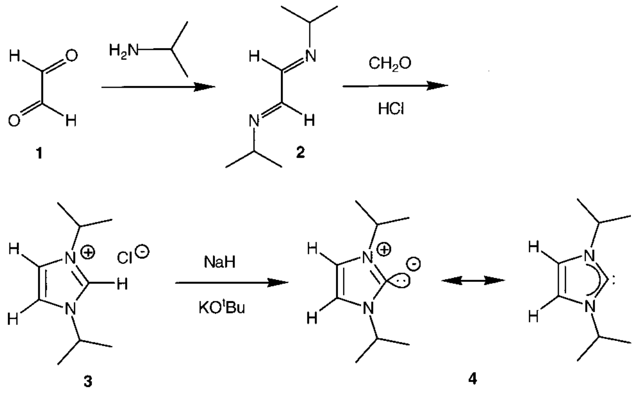
Chart 2



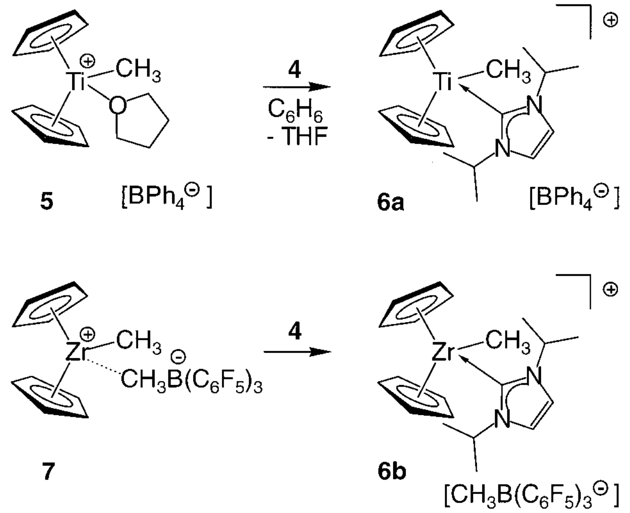
their adjustable steric bulk, which can be easily controlled via their established synthetic entries, they should serve as suitable stabilizing σ-donor ligands in group 4 metallocene cation chemistry, leading to a detailed ligand control of the reactivity of these important organometallic complexes. To the best of our knowledge, the synthesis of Arduengo carbene complexes of the alkyl group 4 metallocene cations and their structural characterization has not previously been described in the literature.[11] We, therefore, wish to describe here the first examples of such compounds in this article, where we have attached the readily available 1,3-diisopropylimidazol-2-ylidene ligand (see Chart 2)[12] at the respective $[Cp_2M^{IV}CH_3]^+$ cations.

Results and Discussion

Experimental Investigations. The synthesis of the methyltitanocene (1,3-diisopropylimidazol-2-ylidene) cation complex **6a** was carried out by treatment of the tetrahydrofuran-stabilized $[Cp_2TiCH_3(thf)^+][BPh_4^-]$ salt **5**[7] with the Arduengo carbene **4**[9,13] in benzene solution at ambient temperature. Under these conditions the thf ligand is rapidly displaced from the titanium center and the donor ligand **4** added to it. The corresponding 1:1 adduct **6a** was isolated as its tetraphenylborate salt in >90% yield (see Scheme 1).

Single crystals of complex **6a** were obtained from dichloromethane. The X-ray crystal structure analysis of **6a** revealed the presence of separate, independent cations and $[BPh_4^-]$ anions in the crystal plus a disordered molecule of CH_2Cl_2. The titanium atom in the cation of **6a** is pseudotetrahedrally coordinated by two η^5-Cp rings (with Ti−C(Cp) distances ranging between 2.361(2) and 2.410(2) Å and a Cp(centroid)−Ti−Cp(centroid) angle of 134.5°), a methyl group, and the Arduengo carbene ligand. The $Ti-CH_3$ bond length (Ti−C22) amounts to 2.178(3) Å, which is a typical value for a titanium−methyl σ-bond. The connecting bond between the titanium center and the carbene ligand carbon atom C2 is only slightly longer at d(Ti−C2) = 2.289(2) Å. The C2−N1 (1.357(3) Å) and C2−N5 (1.363(3) Å) bond lengths inside the planar five-membered heterocycle are practically identical in length with the related stable free carbene 1,3-di-*tert*-butylimidazol-2-ylidene (**4′**: C2−N1/5 1.362 Å),[14] whereas the N1−C2−N5 angle in the coordination compound **6a** (103.6(2)°) is slightly larger than in the reference **4′** (102.0°). This small increase is typically observed upon coordination of an Arduengo carbene to a transition metal center.[10b]

Scheme 1



The N1−C5 and N3−C4 bond lengths amount to 1.379(3) and 1.384(3) Å, respectively. The remaining C4−C5 bond length inside the imidazolylidene moiety is slightly shorter at 1.328(3) Å. The bond lengths inside the N_2C_3 heterocyclic ligand core in **6a** probably indicate a considerable degree of π-delocalization[15] (reference values of **2**: d(C=N) = 1.267(1) Å, $d[C(sp^2)-C(sp^2)]$ = 1.463(2) Å).

A characteristic feature of the structure of complex **6a** is the conformational arrangement of the σ-bonded imidazolylidene ligand at the group 4 bent metallocene framework. The planar five-membered heterocycle is located in plane with the Cp−Ti−Cp bisecting major σ-ligand plane of the metallocene. The corresponding dihedral angles C22−Ti−C2−N1 and C22−Ti−C2−N3 amount to 176.7(2)° and −6.5(2)°. The planar arrangement extends even to the sec-carbon centers of the N-bonded isopropyl substituents (θTi−C2−N1−C6 −0.7(3)°, Ti−C2−N3−C9 2.3(3)°). The central C22−Ti−C2 angle between the σ-ligands at the front side of the bent metallocene wedge amounts to 104.6(1)°. This leaves

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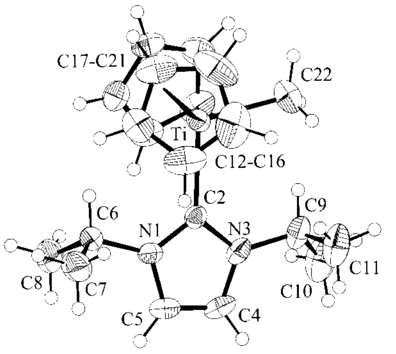


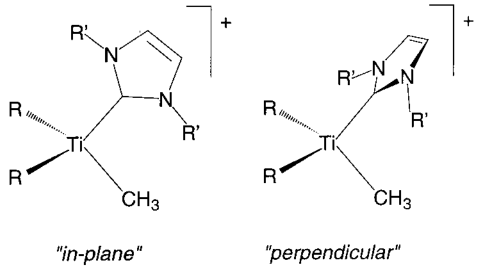
Figure 1. Molecular structure of **6a** (top view of the cation only). Selected bond lengths (Å) and angles (deg): Ti−C2 2.289(2), Ti−C22 2.178(2), Ti−C_{Cp} 2.383(3), N1−C2 1.357(2), C2−N3 1.363(3), N3−C4 1.384(3), C4−C5 1.328(3), C5−N1 1.379(3), N1−C6 1.477(3), C6−C7 1.530(3), C6−C8 1.523(3), N3−C9 1.476(3), C9−C10 1.531(3), C9−C11 1.523(3); C2−Ti−C22 104.6(1), Ti−C2−N1 128.3(1), Ti−C2−N3 128.1(1), N1−C2−N3 103.6(2), C2−N1−C5 111.4(2), C2−N1−C6 126.8(2), C2−N3−C4 110.9(2), C2−N3−C9 125.8(2), C6−N1−C5 121.7(2), C9−N3−C4 123.2(2), N1−C5−C4 107.0(2), N3−C4−C5 107.1(2).

room enough between the σ-ligands to allow for a nonconstrained arrangement in the σ-ligand plane. Consequently, the typical bonding parameters around the proximal nitrogen center N1 and the distal nitrogen atom N3 are practically identical in complex **6a** (e.g., the bond angles Ti−C2−N1 and Ti−C2−N3 amount to 128.3(1)° and 128.1(1)°, respectively). Figure 1 depicts a top view of the structure of the cation of **6a**.

Complex **6a** exhibits an analogous structure in solution. This has become evident from the typical appearance of its ^1H and ^{13}C NMR spectra. In CD_2Cl_2 solution (600 MHz) at ambient temperature complex **6a** exhibits a single ^1H NMR resonance of the pair of symmetry-equivalent Cp ligands at δ 6.29 (^{13}C NMR signal at δ 115.6). There is a Ti−CH_3 resonance at δ 0.80 (^1H) (^{13}C: 64.9). Complex **6a** exhibits a pair of isopropyl NMR resonances originating from the proximal [N^1-*CH*Me_2: δ 3.02 (^1H), δ 51.4 (^{13}C)] and the distal [N^3-*CH*Me_2: δ 3.05 (^1H), δ 51.3 (^{13}C)] N-$CHMe_2$ moieties (orientation relative to the adjacent Ti−CH_3 vector). The correct relative assignment was based on an $^1H\{NOE\}$ experiment, where irradiation at the Ti−CH_3 signal resulted in a response at the δ 3.02 resonance of the proximal N^1-isopropyl group. The 4-H/5-H ^1H NMR resonances of **6a** are observed as an AB pattern at δ 7.07 (4-H) and 7.03 (5-H). The differentiation between the two symmetry-related halves of the 1,3-diisopropylimidazol-2-ylidene ligand persisted upon increasing the monitoring temperature of the ^1H NMR experiment until decomposition of the complex was observed. We have, thus, found no indication for rapid rotation of the carbene ligand around the Ti−C2 linkage in solution on the ^1H NMR time scale. The C2 ^{13}C NMR resonance of **6a** was located at δ 178.2, which is typically shifted to a smaller δ-value by ca. $\Delta\delta$ 30 ppm relative to the free carbene ligand.[9,10b]

The related zirconium complex **6b** was prepared by a slightly different route. In this case we used the donor ligand-free methylzirconocene cation (**7**)[16,17] as the starting material. This precursor was generated in this case simply by treatment of dimethylzirconocene with the strong organometallic Lewis acid $B(C_6F_5)_3$.[18] The resulting $[(Cp_2ZrCH_3^+)(CH_3B(C_6F_5)_3^-)]$ ion pair (**7**) was readily cleaved when treated with the neutral free Arduengo carbene **4** at room temperature in benzene solution. The resulting salt **6b** was isolated in ca. 95% yield (see Scheme 1).

Scheme 2



6a - R = Cp, R' = iPr
6c - R = Cp, R' = H
6d - $R_2 = (\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_4)$ (*ansa*), R' = iPr
8a - R = H, R' = H
8b - R = H; R' = iPr

The NMR analysis of **6b** revealed a structure similar to that of **6a** in solution characterized by an *in-plane* orientation of the imidazolylidene ligand. Its specific symmetry features result in the observation of a single Cp resonance [δ 6.36 (^1H in CD_2Cl_2), δ 115.5 (^{13}C)] and the signals of two inequivalent pairs of isopropyl substituents (for details see the Experimental Section and the Supporting Information). Complex **6b** also features an AB pattern of the 4-H/5-H protons of the imidazolylidene ligand. The coordinated "carbene" ^{13}C NMR resonance of **6b** occurs at δ 178.0, and the Zr-CH_3 ^{13}C NMR signal is found at δ 46.9 (^1H: δ 0.57). Again, there is no indication for rapid rotation of the σ-bound 1,3-diisopropylimidazol-2-ylidene ligand at Zr in complex **6b**.

Theoretical Studies. The typical bonding features and the analysis of the conformational properties of the Ti−carbene linkage were studied by means of DFT calculations.[19] These calculations were carried out on the experimentally investigated titanium system **6a** (see above), for the model complexes **6c**, **8a**, and **8b**, and for the ansa-compound **6d** (Scheme 2).

1. Optimized Geometries and Relative Stabilities. We first wanted to estimate the relative stabilities of the *in-plane* versus the *perpendicular* conformations of the various cationic titanium complexes **6a**,**c**,**d** and **8a**,**b**. The two prominent conformations of **6c** are depicted in Figure 3 in geometries as they were obtained by the DFT optimizations.

Selected optimized geometric parameters together with the relative energies of all the calculated complexes

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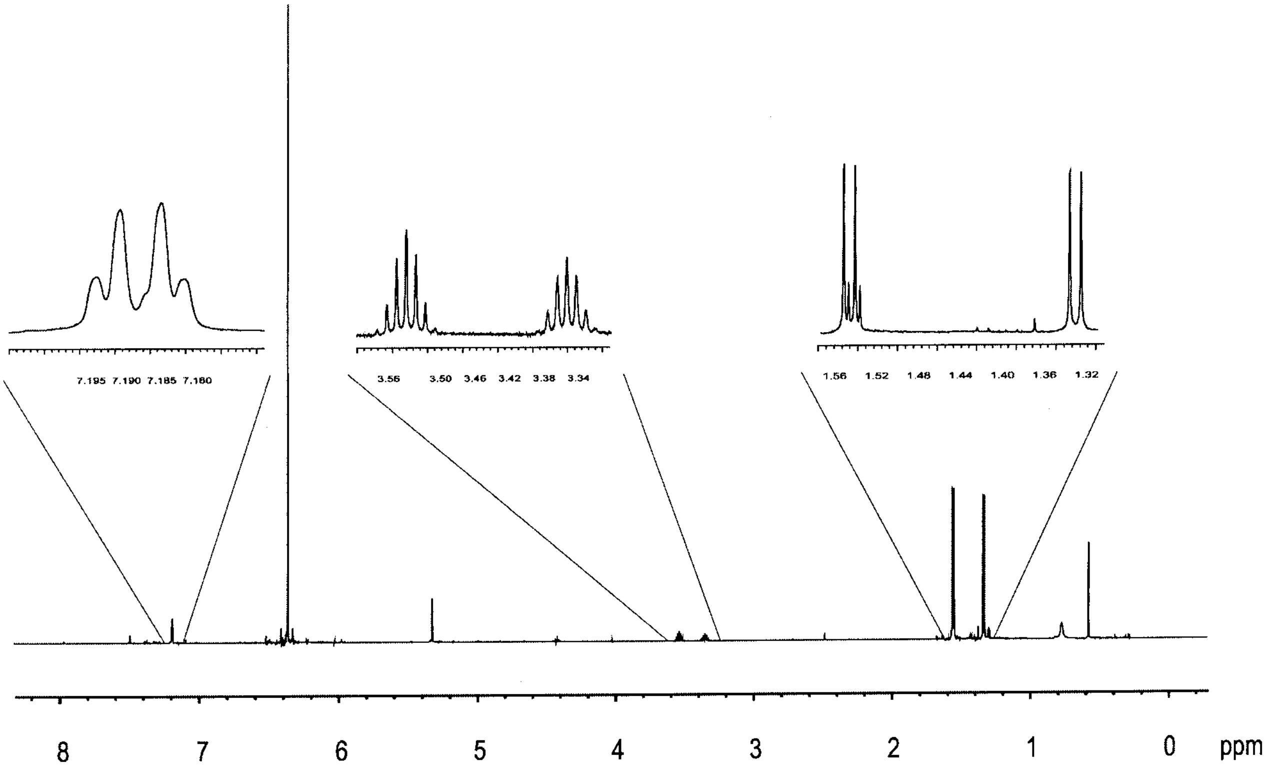

Figure 2. ^1H NMR spectrum of complex **6b** in CD_2Cl_2 solution (600 MHz, ambient temperature).

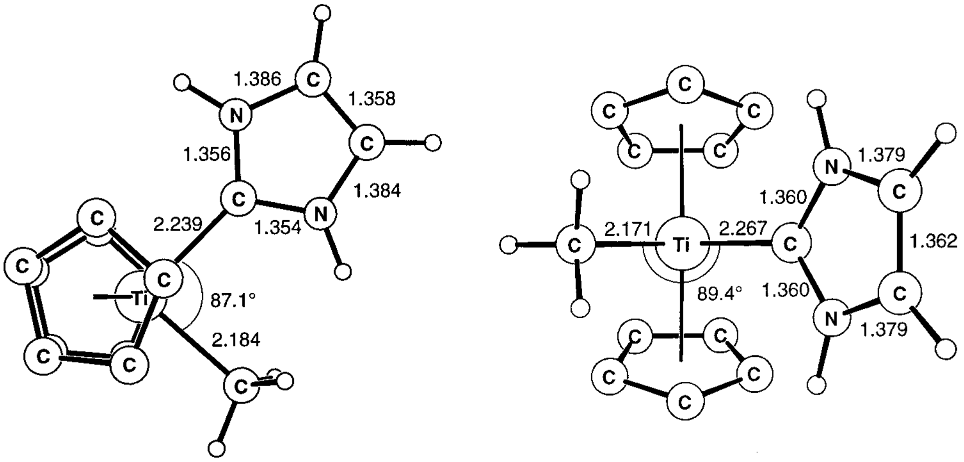

Figure 3. Optimized conformational geometries for complex **6c**: *in-plane* (left) and *perpendicular* (right).

are presented in Table 1. For the model compounds **8a**, **8b**, and **6c**, the *in-plane* and *perpendicular* conformations are relatively close in energy ($\Delta E = +0.2$, $+0.7$, and $+2.8$ kcal/mol). The overall geometric parameters of both conformations do not show great differences. This also means that in these model compounds the rotation of the carbene around the Ti–C bond does not significantly influence the coordination mode of the other ligands.

On the contrary, the presence of bulky isopropyl groups and the cyclopentadienyl ligands in the cation **6a** (Figure 4) and the ansa-system **6d** leads to a clear preference for the *in-plane* conformation ($\Delta E = +19.7$ and $+12.0$ kcal/mol). In addition there is a spectacular increase of the Ti–C2 bond length by $\Delta d = +0.25$ Å from the *in-plane*-**6a** conformation to the *perpendicular*-**6a** isomer, demonstrating the effect of strong steric repulsions between the isopropyl and the cyclopentadienyl groups. For similar reasons the Cp(centroid)–Ti–Cp(centroid) angle is decreased from 135.8° in the *in-plane* to 127.2° in the *perpendicular* conformation of **6a**. The conformational preference and the Cp/isopropyl repulsion is also seen in the DFT results for the ansa-metallocene complex **6d**. A substantially lowered energy difference between both conformations ($\Delta E = +12.0$ kcal/mol) was found, as well as lower values for the Cp(centroid)–Ti–Cp(centroid) angles of the *in-plane* (120.7°) and *perpendicular* (116.8°) conformations. In comparison with **6a** the ansa-system shows lower values for the carbene rotational barrier and the change of the angle of the two Cp planes since the ansa link of the Cp rings a priori reduces the bending back.

2. Frontier Orbital Analysis of Complex 6c. The electronic interaction between the neutral imidazol-2-ylidene and the cationic metal complex unit $Cp_2TiCH_3^+$ has been studied considering a fragmental approach in

Table 1. Selected Optimized Parameters[a] and Relative Energies[b] for the DFT Calculated C_s-Symmetric Arduengo Carbene−Transition Metal Complexes 6a, the Model Complexes 6c, 8a, and 8b, and the ansa-Compound 6d

complex	R	R′	α[c]	Ti−$C_{(CH3)}$	Ti−$C_{(carbene)}$	$C_{(carbene)}$−N	C=C	$C_{(CH3)}$−Ti−$C_{(carbene)}$	X−Ti−X[d]	N−$C_{(carbene)}$−N	Δ*E*
8a	H	H	0 (∥ planes)	2.036	2.208	1.359	1.363	110.6	111.0	103.1	+0.2
	H	H	90 (⊥ planes)	2.030	2.204	1.358	1.364	111.3	115.2	103.1	0.0
8b	H	^{i}Pr	0	2.047	2.175	1.365−1.366	1.369	117.8	110.1	105.0	+0.7
	H	^{i}Pr	90	2.039	2.177	1.363	1.368	109.5	114.6	105.2	0.0
6c	Cp	H	0	2.184	2.239	1.354−1.356	1.358	87.1	135.8	102.9	0.0
	Cp	H	90	2.171	2.267	1.360	1.362	89.4	133.8	102.0	+2.8
6a	Cp	^{i}Pr	0	2.211	2.319	1.365−1.370	1.356	109.3	135.3	103.8	0.0
	Cp	^{i}Pr	90	2.182	2.569	1.386	1.352	84.8	127.2	101.7	+19.7
6d	ansa-CH_2	^{i}Pr	0	2.195	2.327	1.368−1.370	1.357	108.0	120.7	103.5	0.0
	ansa-CH_2	^{i}Pr	90	2.174	2.448	1.381	1.354	85.9	116.8	102.2	+12.0

[a] DFT calculated distances in Å, and angles in deg. [b] DFT calculated energy differences in kcal/mol. [c] Angle between the planes defined by the N-heterocyclic carbene and the atoms Ti, $C_{(CH3)}$, and $C_{(carbene)}$. [d] X = H for **8a** and **8b**, and X = Cp(centroid) (the geometric center of the cyclopentadienyl rings) for complexes **6** (see Scheme 2 for the definition of the substitution pattern).

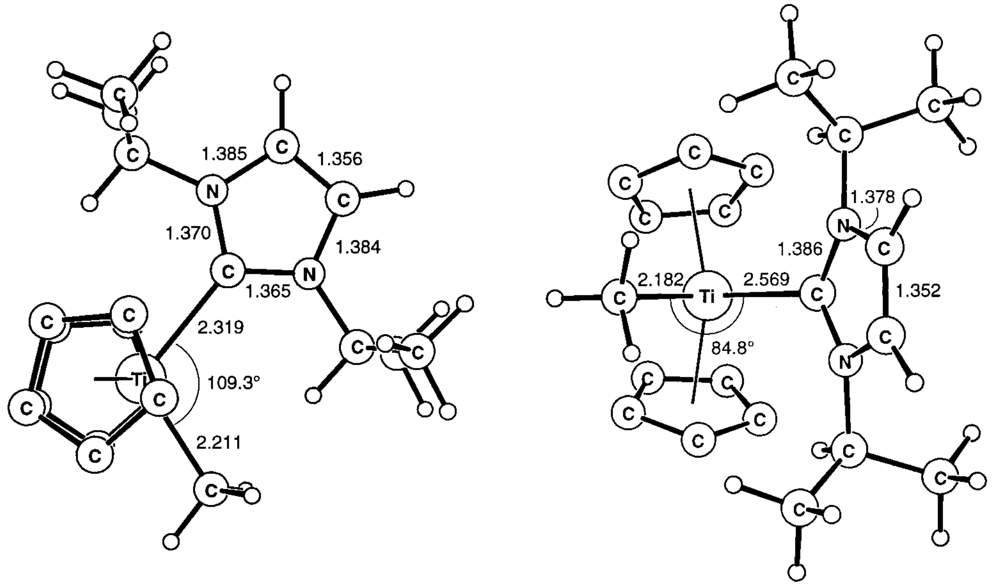

Figure 4. Calculated optimized conformations for the experimentally investigated titanocene cation complex **6a**: depicted are the *in-plane* conformation (left), representing the global minimum, and the less favored *perpendicular* orientation (right).

which the complex has C_s-symmetry. Figure 5 shows the orbital interaction diagram of the model complex **6c** in the *in-plane* conformation.

The highest occupied molecular orbital 10a′ (HOMO) of the diaminocarbene is mainly composed of the donating lone pair of the carbene center. The two electrons are only marginally delocalized into the five-membered cycle. The bonding interaction of the carbene lone pair with the two lowest lying unoccupied orbitals of the Cp_2TiMe^+ fragment (17a′ and 18a′ in C_s-symmetry) leads to a low-lying metal−carbon σ-orbital 23a′ (Figure 6), indicating a strong bond. In addition an almost purely metal oriented vacant orbital 27a′ (LUMO) of the complex results. This latter orbital is normally identified in d^0 Cp_2ML_2 systems as the low-lying "a_1".[20] Thus the overall bonding situation of the carbene ligand does not correspond to the one generally observed for Fischer-type carbene complexes, where we have significant σ- and π-bonding contributions.

The Mulliken charges for the complex **6a** and the model complex **6c** are given in Table 2. The charge distribution within the complexes is not really affected by the change from the *in-plane* to the *perpendicular* conformation. The positive charge at the carbene carbon atom is relatively constant in **6c** (0.21*e* for *in-plane* and 0.22*e* for *perpendicular*), while the long distance Ti−C in the *perpendicular*-**6a** conformation due to the steric interactions induces a smaller positive charge on this carbon atom (+0.12*e* vs +0.20*e*) and a larger one on the metal (+1.00*e* vs +0.93*e*). As to the strong electronegative N centers, they exhibit no change at all during the rotation of the carbene. Consequently, these charges confirm the σ-orbital character of the metal−carbene bond and the lack of π-bonding contributions.

The only interaction, which can be identified as carbene back-donation, is almost negligible. It occurs by an about 2% admixture of the empty 5a″ orbital of the carbene fragment into an appropriate ligand oriented Cp-Ti function. The HOMO 17a″ is also mainly of Cp-Ti π-bonding character, which is at an unusually high energy due to small antibonding interactions with carbene-type functions (for further details see the Supporting Information).

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(20) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

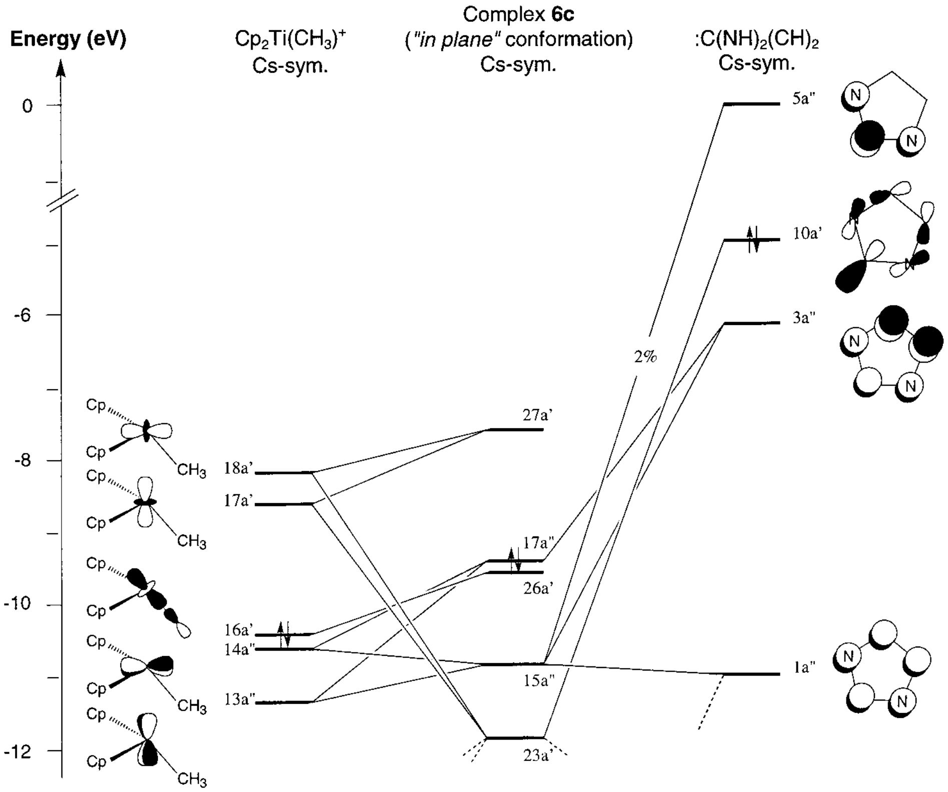

Figure 5. Orbital interaction diagram of the model complex **6c** in the *in-plane* conformation.

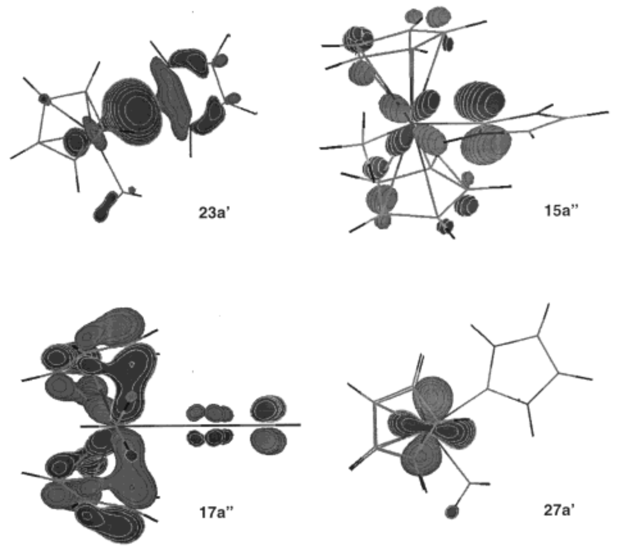

Figure 6. Molecular orbitals 23a′, 15a″, 17a″ (HOMO), and 27a′ (LUMO) of the model complex **6c** in the *in-plane* conformation.

Table 2. Mulliken Charges of 6a and 6c

	6a		6c	
atom	in-plane	perpendicular	in-plane	perpendicular
Ti	+0.93	+1.00	+1.02	+1.04
CH_3	−0.49	−0.44	−0.50	−0.45
C2	+0.20	+0.12	+0.22	+0.21
N1/3	−0.47	−0.46	−0.41	−0.40
C4/5	+0.20	+0.22	+0.19	+0.20
R/R′(C_α)	−0.25	−0.24		

Conclusions

Our study shows that the Arduengo carbene complexes **6** can readily be prepared from suitable alkyltitanocene and -zirconocene cation precursors. The resulting bond between the group 4 metal cation center and the carbene carbon atom is strong, as judged from the structural features of **6a** and the fact that the stable carbene **4** easily displaces coordinated tetrahydrofuran from the methyltitanocene(thf) cation **5**. The observed conformational orientation of the carbene ligand in the metallocene σ-plane that bisects the Cp(centroid)−M−Cp(centroid) angle indicates that the Arduengo carbene ligand acts primarily as a pure (and strong) σ-donor ligand at these very electrophilic group 4 metallocene complexes.[21,22] This is confirmed by the results of the theoretical investigation carried out in the course of our study that has identified steric influences as being decisive for the observed conformational preference in complex **6a**. This study also demonstrates that Arduengo carbenes seem to be suitable strongly stabilizing σ-donor ligands at group 4 metallocene systems and, therefore, likely to be of use in developing the organometallic chemistry of such systems further.

Experimental Section

General Information. Organic and inorganic starting materials (e.g., isopropylamine, 40 wt % glyoxal solution in water) were used as purchased. Solvents were dried and distilled under argon prior to use. The syntheses of the stable carbenes (**4**) and the metal−carbene complexes (**6**) were carried out under argon using a modified Schlenk technique or in a

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(21) For a rare example of a Fischer-type zirconium carbene complex see: Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 178.

(22) For examples of nucleophilic Schrock-type group 4 metallocene carbene complexes and related compounds, see e.g.: Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583. Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336. Review: Beckhaus, R. *Angew. Chem.* **1997**, *109*, 694; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686.

glovebox (atmosphere containing less than 1 ppm oxygen and water, respectively). The metal complexes were stored at −37 °C to prevent decomposition. The compounds **2**−**4**, **5**, and **7** were prepared according to literature procedures.[7,9,13,16]

Bis(η^5-cyclopentadienyl)(1,3-diisopropylimidazol-2-ylidene)titanium Tetraphenylborate (6a). A solution of 13.0 mg (85.6 μmol) of 1,3-diisopropylimidazol-2-ylidene in 1 mL of benzene was added to a suspension of 50.0 mg (85.6 μmol) of bis(η^5-cyclopentadienyl)(tetrahydrofuran)titanium tetraphenylborate in 1 mL of benzene. The suspension was stirred for 10 min, and the solvent was then decanted from the precipitate. The solid was washed with 3 mL of benzene, the solvent was again decanted off, and the product was dried in vacuo to yield 53.0 mg (93%) of the bis(η^5-cyclopentadienyl)-(1,3-diisopropylimidazol-2-ylidene)titanium tetraphenylborate product **6a**, mp 150 °C (dec). Anal. Calcd for $C_{44}H_{49}BN_2Ti$ (664.6): C 79.52, H 7.43, N 4.22. Found: C 78.29, H 7.04, N 4.12. HRMS: Calcd for $C_{20}H_{29}N_2Ti^+$ 345.1812, found 345.1798. ^{1}H NMR (599.9 MHz, CD_2Cl_2): δ 7.07 (d, $^3J_{HH} = 2.0$ Hz, 1H, 4-H), 7.03 (d, $^3J_{HH} = 2.0$ Hz, 1H, 5-H), 6.29 (s, 10H, Cp-*H*), 3.05 (sept, $^3J_{HH} = 6.7$ Hz, 1H, 3-NC*H*), 3.02 (sept, $^3J_{HH} = 6.7$ Hz, 1H, 1-NC*H*), 1.41 (d, $^3J_{HH} = 6.7$ Hz, 6H, 1-NCH(CH_3)$_2$), 1.18 (d, $^3J_{HH} = 6.7$ Hz, 6H, 3-NCH(CH_3)$_2$), 0.80 (s, 3H, Ti-CH_3); [BPh_4^-]: 7.34 (m, 8H, *o*-H), 7.05 (m, 8H, *m*-H), 6.90 (m, 4H, *p*-H). ^{13}C{^{1}H} NMR (150.84 MHz, CD_2Cl_2): δ 178.2 (C2), 121.0 (C5), 120.9 (C4), 115.6 (Cp-*C*), 64.9 (Ti-*C*H$_3$), 51.4 (1-N*C*H), 51.3 (3-N*C*H), 23.8 (1-NCH(*C*H$_3$)$_2$), 23.5 (3-NCH(*C*H$_3$)$_2$); [BPh_4^-]: 164.4 (*ipso*-C), 136.3 (*o*-C), 126.0 (*m*-C), 122.1 (*p*-C). ^{11}B NMR (64.21 MHz, CD_2Cl_2): δ −11.9 (BPh_4^-). IR (KBr): $\tilde{\nu}$ 3119 (w), 3052 (w), 2968 (w), 1578 (w), 1478 (w), 1371 (w), 1262 (m), 1209 (m), 1102 (m), 1022 (m), 831 (s), 739 (s), 706 (s), 607 (m).

X-ray crystal structure analysis of 6a: formula $C_{20}H_{29}N_2$-$Ti \cdot C_{24}H_{20}B \cdot CH_2Cl_2$, $M = 749.49$, yellow crystal 0.35 × 0.20 × 0.05 mm, $a = 12.4995(2)$ Å, $b = 12.8593(2)$ Å, $c = 13.3636(2)$ Å, $\alpha = 80.884(1)°$, $\beta = 79.553(1)°$, $\gamma = 76.278(1)°$, $V = 2037.1(1)$ Å^3, $\rho_{calc} = 1.222$ g cm^{-3}, $\mu = 3.74$ cm^{-1}, empirical absorption correction via SORTAV ($0.880 \leq T \leq 0.982$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 23 709 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 9674 independent ($R_{int} = 0.047$) and 6196 observed reflections [$I \geq 2\sigma(I)$], 493 refined parameters, $R = 0.055$, $wR_2 = 0.118$, max. residual electron density 0.34 (−0.40) e Å^{-3}, the solvent molecule CH_2Cl_2 was refined with split positions (ratio 0.55(2):0.45) and restraints (SADI), hydrogens calculated and refined as riding atoms.

The data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, 1997).

Bis(η^5-cyclopentadienyl)(1,3-diisopropylimidazol-2-ylidene)methylzirconium Methyltris(pentafluorophenyl)-borate (6b). A solution of 41.0 mg (79.5 μmol) of tris(pentafluorophenyl)borane in 1 mL of benzene was added to 20.0 mg (79.5 μmol) of bis(η^5-cyclopentadienyl)dimethylzirconium. The solution was stirred for 5 min at room temperature. To this solution of the salt bis(η^5-cyclopentadienyl)-methylzirconium methyltris(pentafluorophenyl)borate **7** was added a solution of 12.0 mg (79.5 μmol) of 1,3-diisopropylimidazol-2-ylidene **4** in 0.5 mL of benzene. The product (**6b**) precipitated after 10 min at room temperature. The solvent was removed in vacuo, and the yellow oily product was dried in vacuo to yield 69.0 mg (95%) of **6b**. HRMS: Calcd for $C_{20}H_{29}N_2Zr^+$ *m/z* 387.1378, found *m/z* 387.1362. ^{1}H NMR (599.9 MHz, CD_2Cl_2): δ 7.19 (d, $^3J_{HH} = 2.1$ Hz, 1H, 5-H), 7.18 (d, $^3J_{HH} = 2.1$ Hz, 1H, 4-H), 6.36 (s, 10H, Cp-*H*), 3.53 (sept, $^3J_{HH} = 6.6$ Hz, 1H, 3-NC*H*), 3.34 (sept, $^3J_{HH} = 6.6$ Hz, 1H, 1-NC*H*), 1.55 (d, $^3J_{HH} = 6.6$ Hz, 6H, 3-NCH(CH_3)$_2$), 1.33 (d, $^3J_{HH} = 6.6$ Hz, 6H, 1-NCH(CH_3)$_2$), 0.77 (br s, 3H, CH_3-B(C_6F_5)$_3$), 0.57 (s, 3H, Zr-CH_3). ^{13}C{^{1}H} NMR (150.84 MHz, CD_2Cl_2): δ 178.0 (C2), 121.9 (C4), 121.4 (C5), 115.5 (Cp-*C*), 53.4 (3-N*C*H), 53.0 (1-N*C*H), 46.9 (s, 3H, Zr-*C*H$_3$), 23.84 (1-NCH(*C*H$_3$)$_2$), 23.77 (3-NCH(*C*H$_3$)$_2$), 10.5 (br s, 3H, *C*H$_3$-B(C_6F_5)$_3$); [−B(*C*$_6$F$_5$)$_3$]: δ 149.7, 148.1, 139.0, 137.8, 137.3, 136.2. ^{19}F NMR (564.3 MHz, C_6D_5Br): δ −131.9, −163.9, −166.5, (CH_3−B(C$_6$*F*$_5$)$_3$). IR (KBr): $\tilde{\nu}$ 3117 (w), 2964 (m), 2364 (w), 2295 (w), 1646 (m), 1514 (w), 1458 (m), 1378 (w), 1264 (m), 1089 (m), 1020 (w), 974 (w), 951 (w), 933 (w), 816 (m), 736 (w), 683 (w), 529 (w).

Computational Details. All DFT calculations were carried out using the Amsterdam Density Functional program package ADF, release 1999.01 and 2000.01.[19] Energies and geometries (all symmetrized according to C_s symmetry) were evaluated by using the local exchange−correlation potential of Vosko, Wilk, and Nusair[23] with the addition of gradient corrections due to Becke[24] for the exchange energy and Perdew[25] for the correlation energy. The standard double-ζ STO basis with one set of polarization functions was applied for H, C, and N atoms (ADF database III), while the standard triple-ζ basis sets were employed for the Ti atom (ADF database IV). The frozen-core approximation was applied for the 1s electrons of C and N atoms and for the 1s−3p electrons of the transition metal. The geometry optimizations were performed by minimizing the energy gradient by the BFGS formalism[26] until the required level of convergence was fulfilled. The numerical integration precision, based on a method developed by te Velde,[27] was set to 5.0, and final gradients were better than 0.002 hartree·Å^{-1}.

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Supporting Information Available: Further details of the X-ray crystal structure analysis of compound **6a** and additional synthetic and spectroscopic information. Additional DFT calculations and tables giving optimized geometries and final bonding energies for all calculated molecules.

OM020088K

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