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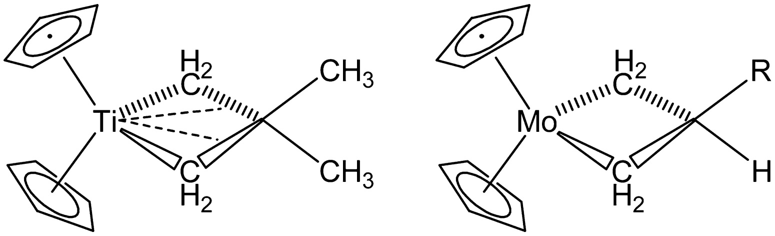

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Structural and Spectroscopic Demonstration of Agostic C−C Interactions in Electron-Deficient Metallacyclobutanes and Related Cage Complexes: Possible Implications for Olefin Polymerizations and Metatheses

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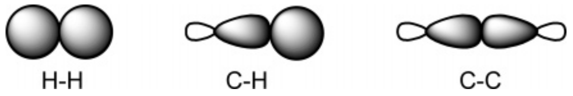
Abstract: The reaction of the half-open titanocene, Ti(C_5H_5)(c-C_8H_{11})(PMe_3) (c-C_8H_{11} = cyclooctadienyl), with two equivalents of PhC_2SiMe_3 leads to their incorporation and coupling to the dienyl fragment. One alkyne inserts into a C−H bond of the central CH_2 group of the c-C_8H_{11} ligand's edge-bridge, while the second undergoes a 5+2 coupling with the dienyl fragment, yielding coordinated σ-allyl and olefin fragments, as demonstrated by X-ray diffraction. Together with the C_5H_5 and PMe_3 coordinations, this leads to a 14-electron count. While the very electron-deficient titanium center passes up potential π coordination of the allyl fragment, it instead engages in interactions with one or two C−C bonds, and perhaps a C−H bond, as revealed from the structural and spectroscopic data. Similar interactions have been found in electron-deficient metallacyclobutane complexes of titanium and zirconium, but not in the 18-electron molybdenum and tungsten analogues. These and other observations may have implications relating to metatheses and polymerizations of olefins.

Introduction

The formal coordination of a σ bonding pair of electrons to an unsaturated metal center is a process of great importance chemically, as for example in an intermediate in oxidative addition, and theoretically. One can easily recognize the importance and enormity of this field by the recent publication of a book on this subject.[1] Perhaps the most commonly encountered examples of these interactions are the "agostic" (C−H) → M complexes, in which an additional connection (direct or indirect) exists between the carbon and metal atoms, and the M−(η^2-H_2) "σ complexes," which lack any sort of additional connection.

Given the existence of (C−H) → M and (H−H) → M interactions, it is naturally of interest to consider the possibility of similar (C−C) → M interactions, an understanding of which would certainly bear heavily on the important challenge of selective C−C bond activations.[2] The major impediment to such interactions is the more directional nature of carbon-centered bonds, which contain appreciable p orbital character, as below.[3]



Indeed, a trajectory mapping of (C−H) → M geometries in various complexes clearly demonstrates that the C−H interaction with the metal center initially involves the hydrogen atom almost exclusively.[4] Thus, metal centers will generally find it difficult to gain access to C−C σ bonding density, although an early theoretical study found that a favorable (C−C) → Ti interaction would be possible in a hypothetical complex related to a known (Si−C) → Ti agostic species.[5] Additionally, most often there will be other accompanying bonds, particularly C−H, that would be more disposed to agostic coordination. Nonetheless, it has been observed that cage-like arrays of carbon atoms may be generated around an electron-deficient metal center, such that the metal center lies in close proximity to C−C bonds, but not C−H bonds.[6] In such cases, C−C bond cleavage reactions have been observed,[6a] and even (C−C) → Ti agostic interactions have resulted.[6b] It would of course be more interesting to observe a situation in which a (C−C) → M interaction actually was favored on its own merits, rather than being to some extent forced to occur. We now report such a case; furthermore, we demonstrate that such species can be prepared from the designed generation of C−C bonds in the vicinity of a metal center. The

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Table 1. Crystallographic Data for $Ti(C_5H_5)(c\text{-}C_8H_{11})(PhC_2SiMe_3)_2PMe_3$ (**1**), $Mo(C_5H_5)_2(\mu\text{-}CH_2)_2C(H)(C_4H_7)$ (**7**), $W(C_5H_5)_2(\mu\text{-}CH_2)_2C(H)(C_3H_5)$ (**8**), $Ti(C_5Me_5)_2(\mu\text{-}CH_2)_2C(H)(i\text{-}C_3H_7)$ (**10**), and $Zr(C_5Me_5)_2(\mu\text{-}CH_2)_2C(H)(C_3H_5)$ (**11**)

formula	$C_{38}H_{53}PSi_2Ti$	$C_{17}H_{22}Mo$	$C_{16}H_{20}W$	$C_{26}H_{42}Ti$	$C_{26}H_{40}Zr$
formula wt	644.85	322.29	396.17	402.50	443.80
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
color	red-brown	orange	orange	red	yellow
a (Å)	11.1012(3)	6.0180(1)	9.7526(3)	9.3925(3)	14.9263(2)
b (Å)	8.5576(1)	12.2151(4)	11.0920(4)	14.7287(3)	11.1737(2)
c (Å)	38.4579(11)	19.3869(6)	12.3529(4)	16.6544(4)	14.9173(2)
β (deg)	97.6502(10)	92.6584(18)	92.3555(19)	96.6871(13)	109.4416(8)
temp (K)	150(1)	150(1)	150(1)	150(1)	150(1)
Z	4	4	4	4	4
R (2σ)	0.0468	0.0239	0.0229	0.0458	0.0259
wR2 (2σ)	0.0848	0.0558	0.0523	0.1046	0.0650
GOF	1.039	1.099	1.068	1.029	1.044

results obtained may provide useful insight into the processes of olefin metatheses and polymerizations.

Experimental Section

All synthetic procedures and handling of organometallic compounds were carried out under a nitrogen atmosphere, either in Schlenk apparatus or in a glovebox. Solvents were dried and deoxygenated either by distillation under nitrogen from benzophenone ketyl, or by passing through columns of activated alumina under nitrogen. Spectroscopic studies were carried out as previously described.[7] The ^{13}C NMR spectra were not precisely integrated, but numbers of carbon atoms are given in accord with their assignments. Analytical data were obtained from E&R Microanalytical Labs. $Ti(C_5H_5)_2(\mu\text{-}CH_2)_2CMe_2$,[8] $Ti(C_5Me_5)_2(\mu\text{-}CH_2)_2C(H)(i\text{-}C_3H_7)$,[9] and $Zr(C_5Me_5)_2(\mu\text{-}CH_2)_2C(H)(CH_2CHCH_2)$[10] were prepared as previously described.

Structural data for complex **1** have been previously deposited[6b] but were of marginal quality, possibly due to the tendency of the compound to undergo rearrangement to some blue species and the resulting need to bring about crystallization rapidly, leading to poor crystal quality. Later it was found that addition of PMe_3 appears to slow the rearrangement, which therefore allowed for crystallization to be carried out more slowly, resulting in better crystalline quality. Together with low temperature data collection, this led to a greatly improved structural result. Each of the X-ray crystal structures was initially solved using direct methods with the SIR 97 program, and any remaining atoms were then found from difference Fourier maps using the SHELX97 program package. All nonhydrogen atoms were refined anisotropically, while all hydrogen atoms were refined isotropically. Pertinent parameters for the data collection and structural results are provided in Table 1 (also see Supporting Information for additional bonding parameters).

Bis(phenyltrimethylsilylacetylene) Coupling Product with $Ti(C_5H_5)(c\text{-}C_8H_{11})(PMe_3)$, 1. A modification of a previously reported procedure was used for the preparation of this compound.[6b] To an orange-brown, magnetically stirred slurry of 0.60 g (2.0 mmol) of $Ti(C_5H_5)(c\text{-}C_8H_{11})(PMe_3)$ at −78 °C in 50 mL of pentane was added 0.70 g (4.0 mmol) of $PhCCSiMe_3$ via syringe. The reaction mixture instantly turned red with some solvation of the solid. After a few minutes at −78 °C, the flask was removed from the cold bath and allowed to warm to room temperature. As it warmed, a bright red solid precipitated which, as the solution approached room temperature, began to redissolve. Upon reaching room temperature, all volatiles were removed in vacuo over the course of ca. 2 h. The remaining powdery residue was triturated with 20 mL of pentane to produce a red slurry which was cooled to 0 °C, collected on a Schlenk frit, washed with 3 × 10 mL of cold pentane, and dried in vacuo. Yield: 480 mg (37%). The red product can be purified by recrystallization from ether, although care must be taken as the compound rearranges in solution at room temperature to a blue compound that remains uncharacterized. Crystals (mp 124−126 °C) for the X-ray study were grown by slow evaporation of a concentrated ether solution to which several equivalents of PMe_3 had been added. The solid is stable indefinitely under a nitrogen atmosphere in the absence of light. Analytical data have been deposited previously.[6b]

The ^1H NMR spectral data have been presented previously but are included here with their assignments which were made possible through multidimensional NMR methods. Resonances for the aromatic carbon atoms were obscured by the solvent peaks and have therefore been omitted. For the preparation of ^{13}C-labeled compound, $C_6H_5C^{13}CH$ (containing 15% $C_6H_5{}^{13}CCH$; Cambridge Isotope Labs) was converted to $C_6H_5C^{13}CSiMe_3$ via a published procedure,[11] and then used in the reaction above to prepare the labeled metal complex.

^1H NMR (benzene-d_6, ambient): δ 7.15−6.90 (m, 10H, Ph), 6.02 (s, 1H, H12), 5.81 (s, 5H, Cp), 4.97 (m, 1H, H1), 4.05 (dd, 1H, J = 8.7, 8.4 Hz, H3), 3.59 (m 1H, H2), 3.49 (m, 1H, H7), 3.08 (td, 1H, J = 8.3, 1.7 Hz, H4), 2.42 (m, 2H, H8a,b), 2.21 (m, 1H, H6a or H6b), 2.00 (m, 1H, H6a or H6b), 0.83 (tt, 1H, J = 6.3, 1.1 Hz, H5), 0.31 (d, 9H, J = 3.7 Hz, $P(CH_3)_3$), −0.050 (s, 9H, $Si(CH_3)_3$), −0.073 (s, 9H, $Si(CH_3)_3$).

^{13}C NMR (benzene-d_6, ambient): δ 167.3 (s, 1C, C9 or C11), 144.9 (s, 1C, C9 or C11), 124.8 (d, 1C, J = 131.4 Hz, C12), 118.5 (dt, 1C, J = 150.7, 8.5 Hz, C3), 105.6 (d of quintets, 5C, J = 170.1, 6.7 Hz, Cp), 105.0 (s, 1C, C10), 89.0 (d, 1C, J = 166.6 Hz, C4), 82.2 (d, 1C, J = 156.1 Hz, C2), 47.8 (d, 1C, J = 122.7 Hz, C1), 46.8 (t, 1C, J = 129.0 Hz, C8), 45.8 (d, 1C, J = 124.2 Hz, C7), 43.9 (t, 1C, J = 128.6 Hz, C6), 25.8 (dd, 1C, J = 130.7, 3.9 Hz, C5), 17.2 (q, 3C, J = 126.3 Hz, J_{C-P} = 13.1 Hz, $P(CH_3)_3$), 4.4 (q, 3C, J = 118.2 Hz, $Si(CH_3)_3$), 0.6 (q, 3C, J = 118.7 Hz, $Si(CH_3)_3$).

^{13}C INADEQUATE NMR (THF-d_8, ambient): C1−C2 (J = 41.8 Hz), C2−C3 (J = 52.6 Hz), C3−C4 (J = 42.8 Hz), C4−C5 (J = 31.3 Hz), C5−C6 (J = 30.5 Hz), C6−C7 (J = 34.8 Hz), C7−C8 (J = 34.0 Hz), C8−C1 (J = 29.1 Hz). From labeled compound, C5−C10 (J = 22.7 Hz). Some coupling constants were not observed due to the lack of any hydrogen atoms on at least one of the carbon atoms. These bonds, however, were inconsequential to the arguments at hand.

$Mo(C_5H_5)_2(\mu\text{-}CH_2)_2C(H)[CH_2C(Me)CH_2]$, 7. To a stirred slurry of 0.50 g (1.2 mmol) $Mo(C_5H_5)_2(C_3H_5)PF_6$[12] in ca. 30 mL of diethyl ether at 0 °C was added a slurry of ca. 0.28 g (2.4 mmol) of $ClMgCH_2C(Me){=}CH_2$ in 20 mL of diethyl ether. The slurry of methallyl Grignard reagent was prepared from a THF solution[13] of known concentration by removal of the solvent in vacuo, followed by addition of ether and

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vigorous stirring to produce the slurry. This step is necessary because the later reaction does not proceed in the presence of appreciable quantities of THF. After addition of the Grignard reagent, the mixture was allowed to warm to room temperature and stirred for 1 h. The initial suspension slowly converted to a red solution with a white precipitate. Upon completion of the reaction, the solvent was removed in vacuo to yield a red residue. Pentane (50 mL) was added to the flask, and the contents were vigorously stirred for 20 min to yield an orange-red solution with white precipitate. The mixture was filtered on a coarse Schlenk frit with a Celite pad, and the filtrate was concentrated to ca. 5 mL, followed by placement in a −30 °C freezer. A bright orange solid precipitated from the solution overnight to yield 200 mg of product (51%). Crystals suitable for a diffraction study were grown by slow crystallization of the product from a concentrated pentane solution at −30 °C.

^{1}H NMR (benzene-d_6, ambient): δ 4.99 (s, 1H, H16a), 4.98 (s, 1H, H16b), 4.26 (s, 5H, Cp), 4.13 (s, 5H, Cp), 2.66−2.58 (m, 1H, MCB−H$_\beta$), 2.25 (d, 2H, J = 6.6 Hz, H14a,b), 1.14 (t, 2H, J = 9.0 Hz, MCB−H$_\alpha$), 0.25 (t, 2H, J = 10.4 Hz, MCB−H$_\alpha$).

^{13}C NMR (benzene-d_6, ambient): δ 145.3 (s, 1C, C15), 110.7 (t, 1C, J = 153 Hz, C16), 88.6 (d, 5C, J = 177 Hz, Cp), 86.0 (d, 5C, J = 177 Hz, Cp), 57.4 (t, 1C, J = 123 Hz, C14), 50.4 (d, 1C, J = 124 Hz, MCB−C$_\beta$), 24.0 (q, 1C, 124 Hz, Me), −7.7 (t, 2C, 133 Hz, MCB−C$_\alpha$).

Anal. Calcd For $C_{17}H_{22}Mo$: C, 63.35; H, 6.88. Found: C, 63.17; H, 7.06.

Attempts to prepare $Mo(C_5H_5)_2(\mu\text{-}CH_2)_2C(H)(CH_2CHCH_2)$ by the reported reaction[14] of $Mo(C_5H_5)_2Cl_2$ with excess C_3H_5MgCl consistently led to an entirely different, though similarly colored, product $[Mo(C_5H_5)(\eta^{5,2}\text{-}C_5H_4C_3H_5)]$, in which allylation of one Cp ligand had taken place.

$[W(C_5H_5)_2(\eta^3\text{-}C_3H_5)]^+(PF_6)^-$. This compound was prepared in a manner similar to that previously reported.[14] $(W(C_5H_5)_2HLi)_4$ (1.0 g (0.78 mmol)) was suspended in ca. 25 mL of toluene and cooled to 0 °C. Freshly distilled allyl chloride (1 mL) was added, and the mixture was allowed to slowly warm to room temperature and was stirred for 1 h. The mixture gradually converted to a mostly clear orange solution and was then treated with 10 mL of deoxygenated water via syringe and stirred vigorously for 10 min. The toluene layer was separated via syringe, and the aqueous phase was washed with three 5-mL aliquots of toluene. The toluene fractions were collected together, and the solvent was removed in vacuo to yield a sticky red residue. The residue was extracted with four 20-mL aliquots of ca. 50 °C hexanes and filtered through a coarse Schlenk frit with a Celite pad. The filtrate was concentrated to ca. 10 mL from which a fair amount of pale yellow−orange solid precipitated, and the mixture was then placed in a −20 °C freezer for 2 h. The supernatant was separated from the precipitated Cp_2WH_2, concentrated to ca. 5 mL, and placed in a −60 °C freezer overnight to produce $W(C_5H_5)_2(C_3H_5)_2$ in ca. 40% yield as small orange crystals.

$W(C_5H_5)_2(C_3H_5)_2$ (0.40 g) was dissolved in 20 mL of deoxygenated acetone and was treated with 0.20 mL of a 60% HPF_6 solution in water, resulting in a change in color of the solution from red to pale orange. Deoxygenated water (7 mL) was added, and the solution was concentrated in vacuo until red, polycrystalline solid precipitated from the solution. The remaining nearly colorless aqueous supernatant was removed via syringe and the solid washed with three 5-mL aliquots of deoxygenated water and dried in vacuo for several hours to yield the cationic complex in ca. 90% yield. The solid can be recrystallized from acetone but was typically utilized in later preparations without further purification.

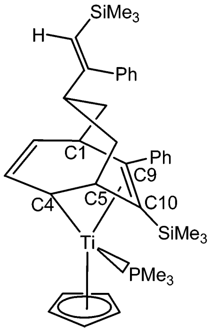
$W(C_5H_5)_2(\mu\text{-}CH_2)_2C(H)(CH_2CHCH_2)$, 8. This compound was prepared from $W(C_5H_5)_2(C_3H_5)_2$ as described in the literature.[14] The ^{1}H NMR spectral data differ somewhat from those previously published, while the ^{13}C NMR data had not been reported.

^{1}H NMR (benzene-d_6, ambient): δ 6.15−6.04 (m, 1H, H15), 5.19 (d, 1H, J = 17.5 Hz, H16a), 5.14 (d, 1H, J = 10.5 Hz, H16b), 4.22 (s, 5H, Cp), 4.09 (s, 5H, Cp), 2.33−2.22 (m, 1H, MCB−H$_\beta$), 2.08 (t, 2H, J = 6.8 Hz, H14a,b), 1.40 (t, 2H, J = 8.8 Hz, MCB−H$_\alpha$), 0.37 (t, 2H, J = 10.2 Hz, MCB−H$_\alpha$).

^{13}C NMR (benzene-d_6, ambient): δ 138.1 (d, 1C, J = 149 Hz, C15), 114.2 (t, 1C, J = 154 Hz, C16), 85.5 (d, 5C, J = 179 Hz, Cp), 82.5 (d, 5C, J = 180 Hz, Cp), 55.3 (t, 1C, J = 124 Hz, C14), 52.7 (d, 1C, J = 125 Hz, MCB−C$_\beta$), −23.7 (t, 2C, J = 130 Hz, MCB−C$_\alpha$).

Results and Discussion

$Ti(C_5H_5)(c\text{-}C_8H_{11})$:Alkyne Coupling Products. The reaction of $Ti(C_5H_5)(c\text{-}C_8H_{11})(PMe_3)$ ($c\text{-}C_8H_{11}$ = cyclooctadienyl) with $C_6H_5C_2SiMe_3$ led to the incorporation of two equivalents of the alkyne and formation of **1**, as opposed to the situation for the analogous PEt_3 complex, which incorporated three equivalents of the alkyne, yielding **2**. The replacement of PEt_3 by PMe_3 can be seen to have led to a markedly different product.



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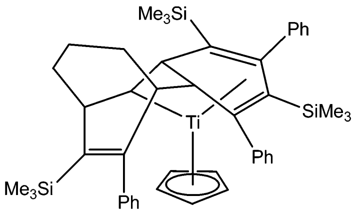

2

While one alkyne has undergone the expected coupling across the dienyl fragment's termini (C1, C5) in **1**, as also occurred for **2**, the second alkyne actually has become incorporated at the central carbon atom of the cyclooctadienyl ligand's trimethylene bridge. The presence of the more strongly bound PMe_3 (vs PEt_3) ligand can clearly be implicated for this unusual result. With phosphine dissociation inhibited for $Ti(C_5H_5)(c\text{-}C_8H_{11})(PMe_3)$ (**3**), the electron-deficient titanium center could undergo oxidative addition of one of the C−H bonds in the trimethylene bridge (Scheme 1). While attack at the central CH_2 group would provide the most direct route to the observed product, it is more likely that attack occurs instead at one of the CH_2 groups adjacent to the dienyl fragment. This seems more reasonable as quite severe distortion would be necessary to bring the central CH_2 group close to the metal, particularly since the other two CH_2 groups are themselves already bent substantially out of the dienyl plane in the ground state, and this becomes even more pronounced for the central CH_2 group, which is then located above the dienyl ligand, where a favorable C−H/π interaction may occur.[15] Thus, the C−H oxidative addition would likely generate an η^6-triene complex (**4**). In fact η^6 coordination by even an acyclic fragment to titanium has been observed.[16] Further support for this proposal comes from the fact that C−H bonds in related edge-bridges of various cyclic π ligands are notoriously prone to undergo C−H activation

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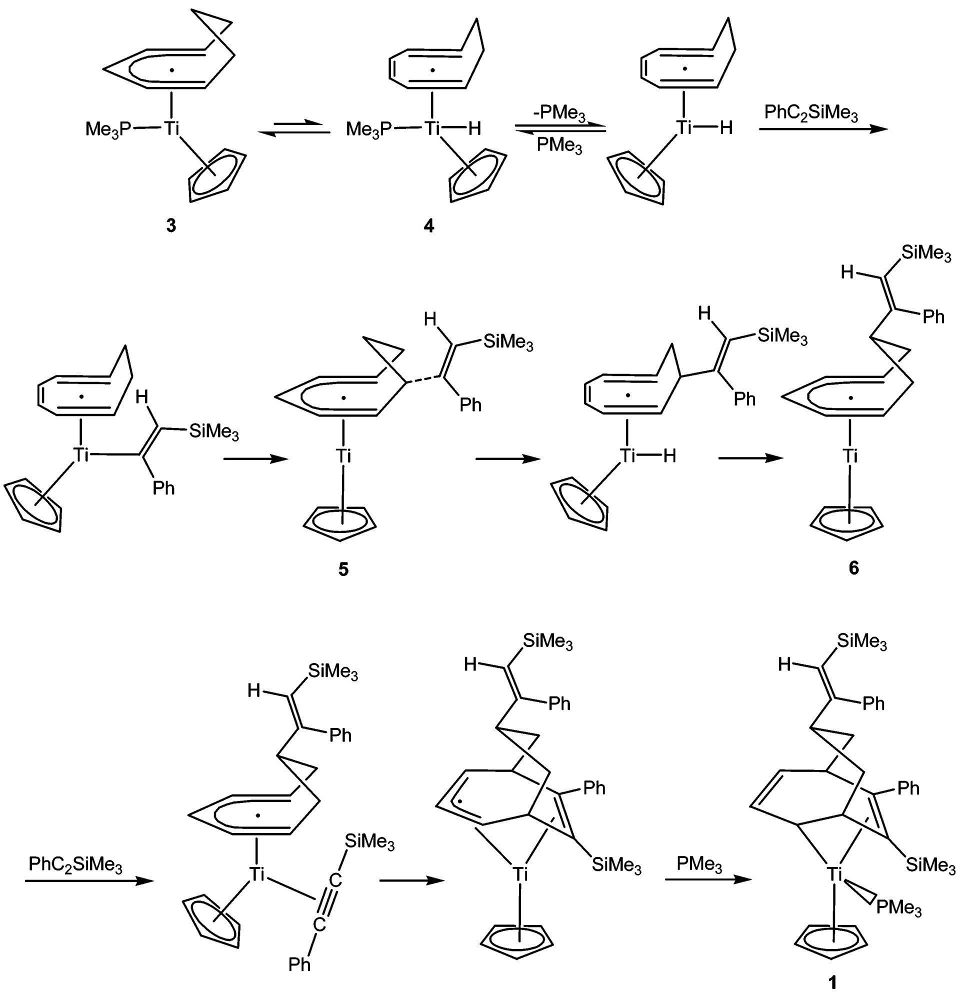
Scheme 1



reactions in electron-deficient complexes, even at low temperatures.[17] With the additional metal–ligand bonding and steric crowding in **4**, PMe$_3$ dissociation should be more favorable, which could be followed by alkyne coordination. At this point at least two pathways could be proposed for the incorporation of the substituted vinyl group on the edge bridge. The most likely possibility seems to be that the alkyne coordination results in a molecular arrangement in which the bulky Me$_3$Si group preferentially resides near the small hydride ligand, leading to hydride transfer to the Me$_3$Si-substituted carbon atom, followed by vinyl-triene coupling to yield **5**. A subsequent 1,6 hydride shift (shown as a formal C–H oxidative addition and subsequent reductive elimination) would then lead to the proper location of the substituted vinyl fragment, on the central methylene group (**6**). This location should be less sterically crowded than that in **5** and thus more stable. With the addition of the vinyl substituent, the edge-bridge should be resistant to further couplings, and the eventual coordination of the second alkyne equivalent would allow for a 5+2 ring-forming reaction (yielding the observed **1** after recoordination of the PMe$_3$) as has also been surmised for the initial coupling reaction undergone by Ti(C$_5$H$_5$)(*c*-C$_8$H$_{11}$)(PEt$_3$). An alternative to the above would involve direct coupling of one or both ends of the triene to the initially incorporated alkyne prior to hydride transfer, ultimately yielding **5**.

As a starting point for considering the bonding in **1** (Figure 1 and Supporting Information, Table 1), one can recognize coordination by C$_5$H$_5$, Me$_3$P, and an olefin (C9–C10). Additionally, there is a clear Ti–C4 interaction (2.172(3) Å), but the respective Ti–C3 and Ti–C2 distances, 2.388(3) and 2.604(3) Å, are significantly longer. As other metal centers have been found to be able to sustain $\eta^{2,3}$ coordination by similar cage

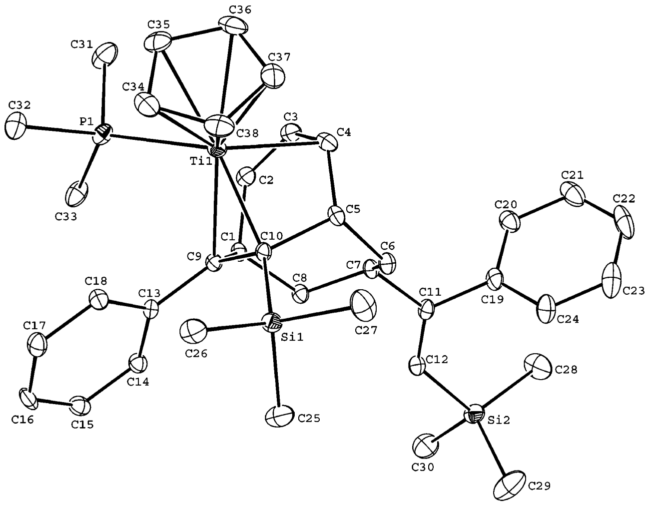


Figure 1. Solid-state structure of Ti(C$_5$H$_5$)(*c*-C$_8$H$_{11}$)(PhC$_2$SiMe$_3$)$_2$(PMe$_3$), **1**.

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[17] (a) Basta, R.; Arif, A. M.; Ernst, R. D. *Organometallics* **2003**, *22*, 812. (b) Herbert, B. J.; Baik, M.-H.; Green, J. C. *Organometallics* **2004**, *23*, 2658.

structures,[18] to a first approximation one can thus regard the C2−C4 fragment as an η^1-allyl ligand. This would then lead to a 14-electron configuration for the complex, which raises the question, why would there only be η^1-allyl coordination. Given that it has long been recognized that agostic coordination can be more favorable than olefin coordination,[19] the shift of the metal center toward C5 might be attributed to a (C−H) → Ti agostic interaction. However, the $J(^{13}C5-H)$ value of 131 Hz is clearly not decreased from the usual range of 125−130 Hz, as would have been expected were there such an interaction.[20] Furthermore, the Ti- -H5 separation of ca. 3.00 Å is very long compared to Ti- -C5 (2.539(3) Å) and hence also does not fit expectations for a (C−H) → Ti interaction.

Given the existence of agostic (C−C) → Ti interactions in **2**, their presence might be considered for **1**. Such interactions entail the formal donation (**12a**) of electron density from a σ-(C−C) bond to an empty orbital on the metal center as the likely dominant interaction, with the potential also for some back-bonding (**12b**) from a metal d orbital to the empty σ^*(C−C) orbital.

12a **12b**

To address this possibility, resort was first made to INADEQUATE NMR methods, which led to most $J(^{13}C-^{13}C)$ values but unfortunately did not yield that for the C5−C10 bond as a result of a rearrangement that the compound undergoes at room temperature. Through the use of appropriately labeled alkyne, the J(C5−C10) value was ultimately obtained and found to be quite low at 22.7 Hz. This is remarkably low for a C−C single bond, for which a value in the range of 30−39 Hz would be expected,[21] but it is quite comparable to those (17.9−29.6 Hz) found for the four C−C bonds in **2** which DFT calculations indicated were involved in (C−C) → Ti agostic interactions. Decreases of this magnitude are comparable to what is often found for (C−H) → M interactions. The structural and spectroscopic data therefore clearly demonstrate the presence of a (C5−C10) → Ti agostic interaction. Nonetheless, closer inspection of the data indicates that the present case actually is probably even more complicated. In particular, the presence of an agostic interaction between the metal center and the C5−C10 bond should lead to a significant increase in the C5−H coupling constant, as was found for **2** (149 Hz). The observed value, 131 Hz, does not show much of an increase, which can best be explained by assuming that there actually is an accompanying, weak (C5−H) → Ti agostic interaction after all (vide supra), which would be expected to provide an offsetting decrease in the coupling constant. Given the closeness of the Ti center to both C4 and C5, it seems possible, if not likely, that at least a weak (C4−C5) → Ti interaction is also present, particularly given the observation for **2** that a metal center may interact with four C−C bonds simultaneously. While the data at hand are not sufficient to answer this question, the observation of the reasonably normal J(C4−C5) value (31.3 Hz) would similarly be consistent with offsetting effects of the stronger C5−C10 coordination and a weaker C4−C5 coordination. Although one may fairly question why the metal center would generate a stronger interaction with the C5−C10 bond than with the C4−C5 bond, it has been demonstrated that close proximity of a C−C bond to a metal center is not sufficient to guarantee an agostic interaction;[22] the metal center must have available appropriate orbital(s) to interact with a given C−C bond. In any event, the structural and spectroscopic data for the C4−C5 and C5−C10 bonds consistently indicate a strong interaction only for the latter. Overall, then, one sees for complex **1** a likely total of three agostic interactions: two involving C−C bonds and one a C−H bond. Thus, as was found for **2**, it appears that when a metal center is sufficiently electron deficient to interact with a C−C bond, it will generally do so with any such bonds in its proximity.

Furthermore, an examination of the C2−C4 allyl fragment suggests that there actually is also a small partial contribution from a π-allyl resonance form. In particular, the C2−C3 and C3−C4 distances of 1.368(4) and 1.406(4) Å do not reflect pure C═C and C−C bonds, and the Ti−C4 distance is somewhat longer than that of a Ti−C single bond in **2** (2.118(6) Å). This is also illustrated by the respective C−C coupling constants of 52.6 and 42.8 Hz for the C2−C3 and C3−C4 bonds. Hence, the observed structural and spectroscopic parameters reveal an intriguing competition between π-allyl and agostic coordination. Certainly in general situations, orbital energies would make C═C bonds better donors and acceptors than C−C bonds, and olefin coordination would normally be further enhanced by the differences in σ and π orbital orientations, although this could be altered in the case of **1** to some extent by its cage geometry. It may then be that the remarkable ability of C−C agostic coordination to compete with that of an olefin results from the presence of several agostic interactions, which might be individually weaker than olefin coordination, but taken in sum could be stronger.

Although an individual (C−C) → Ti interaction may still be weaker than olefin coordination, it is nonetheless clear that, for **1**, the former is surprisingly competitive with the latter. Given the scarcity of simple olefin complexes of titanium, zirconium, and hafnium, and the current nonexistence of simple bis(olefin) complexes,[23] one would generally not expect that olefin coordination to these metal centers would be particularly favorable anyway. These considerations may factor into the high activities displayed by many of their complexes in olefin polymerizations. In particular, if one examines the migratory insertion step in the catalytic cycle (Scheme 2, upper), one may find the inclusion of quite complicated intermediates.[24] However,

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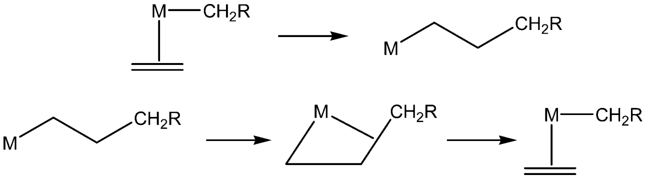
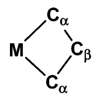
Scheme 2



the reverse process, involving C−C bond activation, would clearly require an intermediate species[25] with an agostic (C−C) → M interaction (Scheme 2: C−H agostic interactions may also be involved[26] but are not shown). This therefore also represents an intermediate in the forward direction. One can note that both the starting complex and the intermediate have one M−C σ bond. Conversion of the starting olefin complex to the intermediate species thus entails the replacement of olefin coordination by an agostic (C−C) → M interaction. If the agostic interaction can indeed be competitive with olefin coordination for these early metal centers, that could reduce the barrier for the insertion process and therefore lead to more active catalysts.[27]

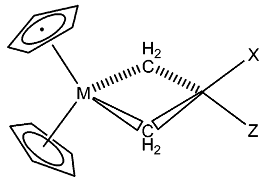
Metallacyclobutane Complexes. It is noteworthy that the alkyne coupling reactions leading to **1** and **2** both resulted in (C−C) → Ti agostic interactions, suggesting that these might not be uncommon in complexes of these early metals. Indeed, a third coupling product, in which four alkynes have been incorporated, also appears to have such interactions, while related zirconium reactions tend to lead to C−C or C−Si bond activations.[28] At least one other compound with a similar cage-like structure has been reported and has been formulated as having a (C−C) → Ti agostic interaction.[29] While many other variations of these alkyne coupling approaches could be employed (e.g., use of alternative dienyl ligands) to access additional agostic complexes, it would be of particular importance to be able to design specific compound types in which the (C−C) → M agostic interactions were clearly adopted as a matter of preference rather than potentially being a geometric artifact (e.g., **1** vs **2**). As the various complexes observed to date have all contained arrays of C−C single bonds in the vicinity of an electron-deficient metal center, it became of interest to design the simplest possible complexes in which such bonds could be in close proximity to a metal center. An especially promising possibility seemed to be metallacyclobutanes, **13**, for which two C−C bonds would be available for interaction with the metal center.



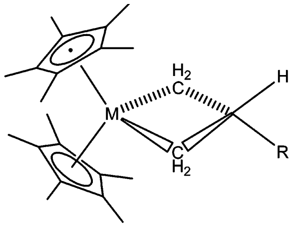
13

That this was a viable approach was suggested by the substantially different ^{13}C NMR shifts observed for C_α or C_β in bis(cyclopentadienyl) complexes of molybdenum vs zirconium (16 and 18 electrons, respectively).[14,30] Thus, for typical Mo and W complexes, the resonances for C_β were shifted over 50 ppm downfield of those for C_α, whereas for Ti, Zr, and Hf complexes, *upfield* shifts of ca. 60−80 ppm were observed. While chemical shifts are not always diagnostic of the presence of agostic interactions,[20a] the difference in these shifts, $\delta(C_\alpha) - \delta(C_\beta)$, has been proposed, in fact, to be a measure of the M- -C_β separation in metallacyclobutanes.[31] To date, structures of $M(C_5H_5)_2(\mu\text{-}CH_2)_2C(R)(R')$ complexes have been reported for titanium,[32] but not for zirconium,[33] hafnium, molybdenum, or tungsten. The titanium complexes indeed possessed short Ti−C(β) separations, as did an alkoxide-containing tungsten complex (active as an olefin metathesis catalyst).[34] The possibility of (C−C) → M agostic interactions in such species therefore becomes an important issue to address. Interestingly, if one considers the Ti−C(4,9,10) interactions in **1** as all involving Ti−C single bonds, by virtue of σ-allyl and titanacyclopropane resonance forms,[35] the Ti−C4−C5−C10 fragment in **1** would itself be a titanacyclobutane, although clearly very asymmetric in terms of its agostic interactions.

To assess the extent of any (C−C) → M interactions in electron-deficient metallacyclobutanes, detailed structural and spectroscopic studies of their $M(C_5H_5)_2$ and $M(C_5Me_5)_2$ derivatives have been carried out for titanium, zirconium, molybdenum, and tungsten complexes **7**, **8**, **10**, and **11** (Figures 2−5), and a comparison of pertinent parameters is summarized in Table 2, while additional structural data are presented in Supporting Information Tables 2−5. Both sets of data clearly demonstrate the existence of the agostic (C−C) → M interactions in the electron-deficient complexes only (i.e., M = Ti,



M = Mo; X = H; Z = $CH_2C(Me)CH_2$ (**7**)
M = W; X = H; Z = $CH_2C(H)CH_2$ (**8**)
M = Ti; X = Z = CH_3 (**9**)



M = Ti; R = i-C_3H_7 (**10**)
M = Zr; R = $CH_2C(H)CH_2$ (**11**)

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(24) (a) Structural representations of such intermediates have been depicted with as many as five dashed lines, for example: (b) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406.

(25) As pointed out by a reviewer, the agostic species would not necessarily be intermediates in that they do not need to be local minima in an energetic sense.

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(35) The presence of the phenyl and trimethylsilyl substituents would in fact stabilize a metallacyclopropane resonance contribution.

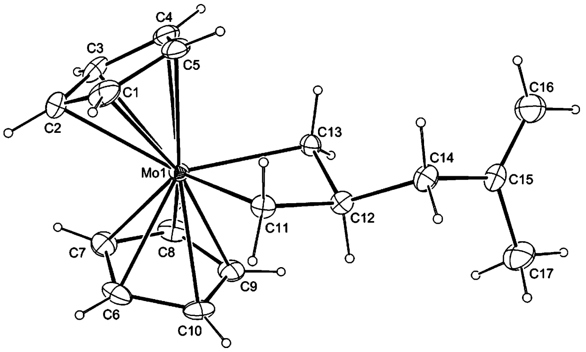

Figure 2. Solid-state structure of $Mo(C_5H_5)_2[(CH_2)_2C(H)C_4H_7]$, **7**.

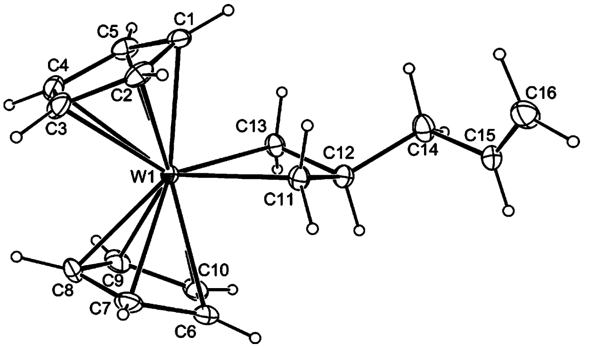

Figure 3. Solid-state structure of $W(C_5H_5)_2(CH_2)_2C(H)(C_3H_5)$, **8**.

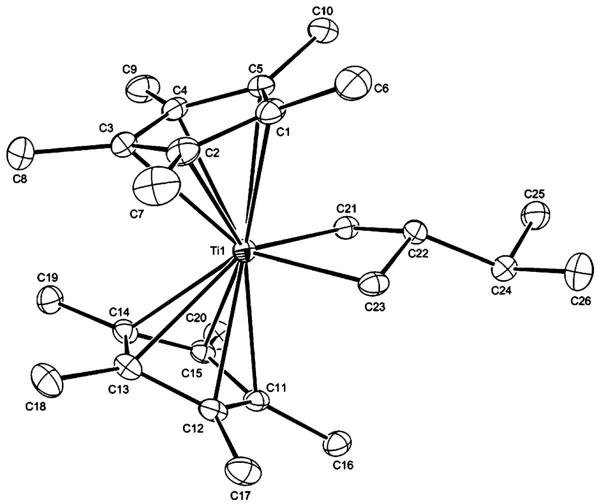

Figure 4. Solid-state structure of $Ti(C_5Me_5)_2(CH_2)_2C(H)(i\text{-}C_3H_7)$, **10**.

Zr, but not Mo, W). Thus, the $M-C_\alpha-C_\beta$ angles for the titanium and zirconium complexes are close to 10° smaller than those for the molybdenum and tungsten complexes, while just the opposite is observed for the $C_\alpha-M-C_\alpha$ and $C_\alpha-C_\beta-C_{\alpha'}$ angles. Interestingly, the angles for **1** are quite similar to those of **9**−**11**. The angular differences of these complexes relative to **7** and **8** lead to much shorter $M-C_\beta$ separations for the electron-deficient species (**1**, **9**−**11**). Hence, while the $Zr-C_\alpha$ distance is similar to those of the Mo and W complexes, the $Zr-C_\beta$ distance is ca. 0.20 Å shorter than the (Mo/W)-C_β distances. Further, the $C_\alpha-C_\beta$ bonds are consistently lengthened for **9**−**11**, vs those for **7** and **8**. The smallest increase, ca. 0.02 Å, is observed for **10**, a titanium complex with one hydrogen substituent on C_β. The presence of a $C_\beta-H$ bond can lead to a partial $(C_\beta-H) \rightarrow$ Ti agostic interaction, which would compete with the $(C-C) \rightarrow$ Ti interactions. Indeed, for titanacyclobutane complex **9**, which has no $C_\beta-H$ bonds, the $C_\alpha-C_\beta$ lengthening increases to ca. 0.05 Å. Similarly, for zirconacyclobutane **11**, having (as does **10**) one $C_\beta-H$ bond, a greater lengthening is also observed (vs that for **10**), ca. 0.04 Å. While these increases appear small relative to those in at least some C−H agostic complexes, an increase of only some 0.15 Å would result in a weakening of the C−C bond by ca. 50%;[36] furthermore, the agostic interaction is shared between two C−C bonds, thereby leading to a lesser degree of lengthening than one would see were there a single $(C-C) \rightarrow M$ interaction. In contrast, $(C-H) \rightarrow M$ interactions generally involve just one C−H bond. Considering these factors along with the previous results for a $(C-C) \rightarrow$ Ti agostic complex, and the more directional nature of C−C bonds, it seems likely that $(C-C) \rightarrow M$ agostic complexes will tend to show relatively small lengthenings of their C−C bonds. This would in fact be consistent with the trend for H_2 and C−H analogues, and specifically with the fact that some H_2 complexes exhibit over 50% elongations of their H−H bonds,[37] while C−H elongations are more modest. Although it is clear that agostic bonding would only occur for electron-deficient complexes, it can be noted that back-bonding interactions in 18-electron metallacyclobutanes have been proposed to play a role in their chemical transformations.[38]

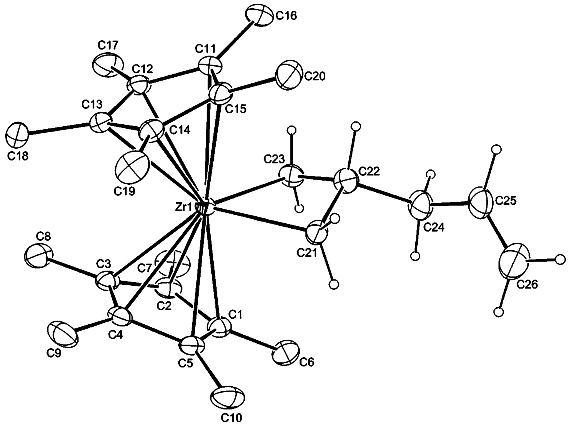

Figure 5. Solid-state structure of $Zr(C_5Me_5)_2[(CH_2)_2C(H)C_3H_5]$, **11**.

The spectroscopic data further confirm the presence of agostic $(C-C) \rightarrow M$ interactions for the electron-deficient species. Thus, while $^{13}C-^{13}C$ coupling constants of 30−39 Hz are the norm for typical single bonds (remaining in the 28−29 Hz range for cyclobutanes),[21] the values of $J(C_\alpha-C_\beta)$ for the electron-deficient complexes are obviously remarkably low, around 21−24 Hz. This may be compared to values in the range of 17.9−29.6 Hz observed for **2**, for which a molecular orbital study also provided clear support for the agostic interpretation.[6b] In contrast, the $C_\alpha-C_\beta$ coupling constants for the 18-electron complexes of molybdenum and tungsten fall in the normal range, at 31−32 Hz. The decrease of the $J(C-C)$ values for **9**−**11** by about a third is similar to observations for C−H agostic complexes.[20]

It should also be noted that the zirconacyclobutane fragment in **11** exists in a puckered orientation which seems to allow for a partial $(C_\beta-H) \rightarrow$ Zr agostic interaction in competition with the partial $(C-C) \rightarrow$ Zr interactions. In accord with this

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(36) Baldridge, K. K.; Kasahara, Y.; Ogawa, K.; Siegel, J. S.; Tanaka, K.; Toda, F. *J. Am. Chem. Soc.* **1998**, *120*, 6167.
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Table 2. Comparison of Pertinent NMR and Structural Parameters for Metallacyclobutanes

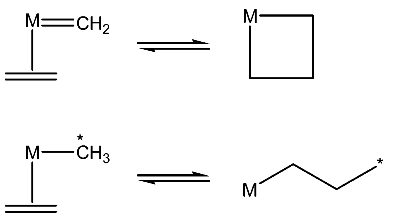
	cmpd				
	Mo (**7**)	W (**8**)	Ti (**9**,**10**)	Zr (**11**)	Ti (**1**)
			NMR Chemical Shifts (ppm) and Coupling Constants (Hz)		
$J(C_\alpha-C_\beta)$	32.1	31.2	22.0, 24.2	20.7	31.3, 22.7
$J(C_\alpha-H)$	133	130	137,[a] 134	129[b]	167
$J(C_\beta-H)$	124	125	−, 125	127[b]	131
$J(C_\beta-C_\gamma)$	n.d.[c]	30.2	34.8, 31.8	31.7	30.5
$\delta(C_\alpha)$	−7.7	−23.7	83.1, 71.9	60.4	89.0, 105.0
$\delta(C_\beta)$	50.4	52.7	5.2, 22.6	14.5	25.8
			Bond Distances (Å)		
$M-C_\alpha$	2.258(2)	2.244(2)	2.145(5), 2.156(2)	2.251(3)	2.172(3), 2.123(2)
$M-C_\beta$	2.849(2)	2.850(3)	2.600, 2.597(2)	2.649(2)	2.539(3)
$C_\alpha-C_\beta$	1.528(2)	1.532(4)	1.583(7), 1.552(2)	1.574(1)	1.540(3), 1.555(4)
$C_\alpha-H$	0.96	0.99	−, 0.91	0.97	0.92(3)
$C_\beta-H$	1.00(2)	0.98(5)	−, 0.95(2)	1.075(19)	0.97(2)
$M-H_\beta$	3.19(2)	3.30(5)	−, 2.98(2)	3.12(2)	3.00
M−C(Cp)	2.31	2.31	2.41, 2.45	2.56	2.40
			Angles (Deg)		
$M-C_\alpha-C_\beta$	95.7(1)	96.2(1)	87.1(3), 87.35(9)	85.8(2)	85.15(11)
$C_\alpha-M-C_{\alpha'}$	61.79(7)	62.99(13)	74.8(3), 71.43(8)	70.62(6)	74.15(10)
$C_\alpha-C_\beta-C_{\alpha'}$	98.75(15)	99.9(3)	110.9(6), 108.4(2)	111.51(14)	113.6(2)
fold angle[d]	28.9	22.4	4.2, 25.8	28.5	15.9
	20.2	19.5	26.1, 22.1	21.1	27.7
$Cp/MC_\alpha C_{\alpha'}$	20.9	22.3	24.2, 20.7	20.8	28.2

[a] See ref 8. [b] See ref 10. [c] Not determined. [d] This is the angle between the $MC_\alpha C_{\alpha'}$ and $C_\alpha C_\beta C_{\alpha'}$ planes.

proposition, the $C_\beta-H$ bond distance appears to be lengthened somewhat, at 1.075(19) Å, which may be compared to values in the range of 0.88(3)−1.05(2) Å for all the other 39 C−H bonds in the molecule, and to a value of 0.95(2) Å in **10**. The agostic interaction might be regarded as "inverted," since the M−C distance is shorter than the M−H distance, which indicates that the (C−H) → M agostic interactions are of secondary importance to the (C−C) → M interactions. It would in any case seem likely that even stronger (C−C) → M interactions would be present in complexes having no β-hydrogen atoms. This is supported by the fact that the $J(C_\alpha-C_\beta)$ value for **9** is 2.2 Hz lower than that for **10**. Likewise, as zirconium and hafnium tend to form stronger bonds than titanium,[39] their complexes should also lead to stronger agostic coordination, and more facile C−C bond activations, as in fact has been observed.[27,28] This expectation is also supported by the data, as the $J(C_\alpha-C_\beta)$ value for **11** is 3.5 Hz lower than that for **10** and the $M-C_\beta$ distance is only ca. 0.05 Å longer in **11** than in **10**, again indicating a stronger interaction for the heavier transition metal center. Hence, a hafnacyclobutane complex with no $C_\beta-H$ bonds should show an even smaller $J(C_\alpha-C_\beta)$ value than those observed here for titanium and zirconium.

Potential Implications for Olefin Metathesis. Some final consideration may be given to the possible role that (C−C) → M agostic interactions could play in the olefin metathesis process, for which metallacyclobutanes are present as intermediates (Scheme 3, top).[40] The conversion of the metallacyclobutane intermediate to a metal carbene complex and a coordinated olefin involves breaking one of the C(α)−C(β) bonds and the generation of a bond from the metal center to what had been the C(β) atom. Both of these are natural results of a C−C bond activation process (alternatively, this may be viewed as a combination of α- and β-eliminations, defined relative to each C_α atom[41]), which would be initiated by the agostic coordination of the C−C bond. As the synthetic and structural results have shown, these interactions can well be expected in electron-deficient metallacyclobutanes. One must then consider how the above discussion could relate to the actual types of complexes employed in olefin metathesis. For both the molybdenum- and ruthenium-based systems, metallacyclobutane intermediates exist which may be regarded as electron-deficient. In the case of ruthenium, the catalyst precursors are typically 16-electron complexes, and the presence of very bulky phosphine ligands, e.g., $P(c\text{-}C_6H_{11})_3$ can even lead to 14-electron intermediates.[42] A recent theoretical study has in fact provided support for this view,[43] while a low-temperature spectroscopic study of a 14-electron ruthenacyclobutane has revealed a very low J(C−C) value of 15.0 Hz and very high J(C−H) values (155, 165 Hz),[44]

Scheme 3



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(41) Note that the reversion of a metallacyclobutane to an olefin and a metal carbene has indeed produced the expected products of both an α and a β elimination.

nicely consistent with the presence of agostic (C−C) → Ru interactions. For the molybdenum complexes, however, there are no dissociable ligands, and it would be possible for all intermediates to attain an 18-electron configuration without an agostic interaction, by virtue of the presence of alkoxide ligands, which can serve as π-donors, even through both lone pairs (formal 5-electron donation).[45] However, a key feature of some of these catalysts is the presence of electron-withdrawing substituents on the alkoxide ligand,[34,46] which can reduce its donating ability, allowing for (C−C) → Mo agostic interactions to become energetically competitive.

Structural data for pertinent metallacyclobutanes provide helpful insight into the question of electron deficiency. To date, reported ruthenacyclobutane structures have all involved 18-electron complexes, and as expected, no evidence for Ru−C(β) interactions is seen, with the Ru−C(β) separations typically being ca. 0.5−0.6 Å longer than the Ru−C(α) bond distances.[31,47] A similar trend is seen for most molybdenum (and tungsten) analogues,[46,48] for which the M−C(β) separations tend to exceed the M−C(α) bond distances by ca. 0.6 Å. A very important exception is found for $W(NR)(OR')_2(CH_2CH_2CH_2)$ [$R = 2,6\text{-}C_6H_3(i\text{-}Pr)_2$; $R' = C(CF_3)_2(n\text{-}C_3F_7)$] and a related $OCMe(CF_3)_2$ complex.[34] These species, having the most electronegative groups attached to their alkoxide carbon atoms, have W−C(β) distances which are only 0.27−0.29 Å longer than the W−C(α) distances (cf., 0.60 Å for the 18-electron $W(C_5H_5)_2$ analogue in Table 2). These species also contain lengthened C(α)−C(β) bonds, averaging 1.616(11) Å for the more accurately characterized structure. A clear correspondence can be seen between these data and those for the electron-deficient complexes in Table 2. On the basis of the long $C_\alpha-C_\beta$ bond lengths, these species can also be expected to display very low $J(C_\alpha-C_\beta)$ values, due to the presence of (C−C) → W interactions. For the active metathesis catalysts with better donating alkoxide ligands, leading to a nonelectron-deficient ground state for the complex, a low energy excited state may be expected, perhaps accessed during certain molecular vibrations, in which at least a partial (C−C) → M agostic interaction is realized.

Conclusions

As a result of the directional nature of C−C bonds, and the rapid loss of C−C bond strength with increased C−C distance, C−C agostic interactions with metal centers tend to lead to fairly modest bond lengthenings, which may have impeded their recognition in earlier structural studies. It appears that modest lengthenings will prove to be the norm for such species, as could be expected on the basis of observations of C−H and H−H analogues. This work demonstrates that INADEQUATE NMR spectroscopy (and specifically the $^{13}C-^{13}C$ coupling constants that it provides) is clearly a powerful diagnostic tool, and most probably the method of choice, for revealing the presence of these interactions.[49] Good correlations have been observed between the $J(^{13}C-^{13}C)$ values and several geometric parameters, and both sets of data vary with the nature of the metal center and the metallacyclobutane substituents in a reasonably predictable fashion. In general cases, it appears likely that an isolated (C−C) → M interaction will not be present; rather, additional interactions with proximal C−H and/or C−C bonds will also be found, thereby further diluting any observable spectroscopic or structural change.[50] However, highly strained C−C bonds, as in cyclopropane, would have greatly enhanced donor and acceptor abilities by virtue of a decreased σ/σ^* energy separation, and thereby might lead to more localized (C−C) → M interactions. Such agostic complexes with the lithium cation[51] and a Nb(III) center[52] have been characterized structurally, although especially for transition metal complexes, one might again observe additional interactions, particularly with the C−H bonds.

Substantial evidence has already accumulated which implicates these interactions in polymerization processes, particularly chain transfer termination.[53] With the added observation that (C−C) → Ti agostic interactions may be competitive with olefin coordination, leading to especially low barriers for the insertion process, one finds an additional way in which these interactions may impact on olefin polymerizations, potentially contributing to the high activities of the early metal complexes as polymerization catalysts.

The presence of agostic (C−C) → M interactions in metallacyclobutanes also seems to be of some significance for olefin metathesis by initiating the cleavage of one of the C−C bonds on the way to expulsion of olefin. This process is actually quite similar to that involved in polymerization as the bond-activated

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(50) It is also to be expected that even in cases of interactions primarily involving C−H bonds, there could be weaker C−C interactions as well, in essence leading to a continuum of possibilities in which the relative C−H and C−C contributions vary. See, for example: Haaland, A.; Scherer, W.; Ruud, K.; McGrady, G. S.; Downs, A. J.; Swang, O. *J. Am. Chem. Soc.* **1998**, *120*, 3762.

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species for each contains a coordinated olefin.[54] In olefin metathesis, the olefin would be accompanied by a carbene ligand, whereas in the polymerization process the olefin would be accompanied by an alkyl ligand (Scheme 3). The participation of a (C−C) → M agostic interaction in the metathesis process nicely accounts for the dependence of the reactivity of certain Schrock catalysts on the electronic properties of their alkoxide ligands.

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Supporting Information Available: Tables containing additional bonding parameters and 2D NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(54) One can also observe some interesting analogies with H/H exchange processes in MH_3 units. See ref 1, pp 121−128, 188−194.