Communications to the Editor

Shorter Nonbonded Than Bonded Contacts or Nonclassical Metal-to-Saturated Carbon Atom Interactions?

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Many important developments have recently taken place regarding the interaction and activation of nonmetal σ bonds with transition-metal centers, perhaps most notable being the discovery of complexes containing H_2 as an intact ligand.[1] Of course, analogous achievements for C−C bonds would be of particular importance. However, while a number of examples of C−C bond activation reactions have recently been reported,[2] such reactions remain very uncommon. In addition, to our knowledge there are no reported complexes in which a transition-metal center has been found interacting with saturated carbon−carbon bonds. Such species could provide important insight into the pathways by which C−C bonds may be selectively activated and functionalized by transition-metal centers. Herein, we report a reaction that generates an apparent electrophilic 14-electron titanium center in an environment which is shielded sterically from both C−H bonds and external coordinating agents, such that the metal can only make additional contacts with the accompanying C−C single-bonded framework. This situation has resulted in two remarkably short $Ti-C(sp^3)$ contacts—one even shorter than some clearly bonding Ti−C interactions. With the aid of theoretical studies, this has provided an opportunity to assess the extent and nature of these interactions.

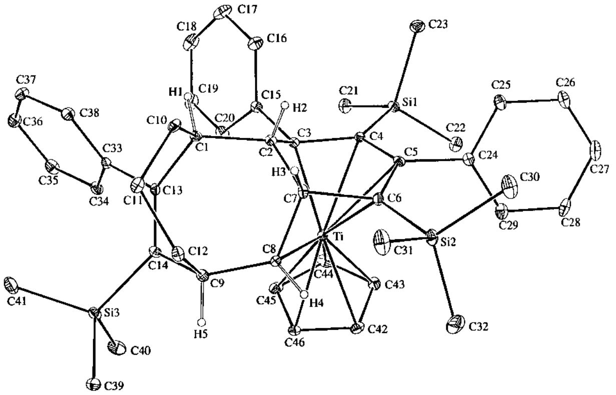
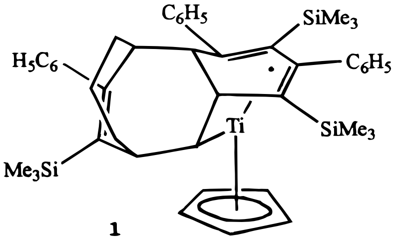


Figure 1. Solid-state structure of **1**. Additional bond distances: Ti−C(3,4,5,6,8) = 2.106(6), 2.299(6), 2.338(6), 2.214(6), 2.118(6) Å; C2−C3, 1.560(8) Å; C2−C7, 1.518(9) Å; C7−C8, 1.531(9) Å.



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The reaction of $Ti(C_5H_5)(C_8H_{11})(PEt_3)$ (C_8H_{11} = cyclooctadienyl) with excess $C_6H_5C_2SiMe_3$ led to the incorporation of 3 equiv of the alkyne, in contrast to a related reaction for the 2,4-dimethylpentadienyl analogue, for which only two alkyne equivalents were taken up.[2d] The somewhat air-sensitive product (**1**) has been routinely characterized, and its structure revealed by a low-temperature X-ray diffraction study (Figure 1).[3] The formation of complex **1** seems straightforwardly to have resulted from one alkyne first coupling between the dienyl ends, C(1,9). Subsequently, the other two alkynes coupled, phenyl-substituted ends first, to two of the remaining three dienyl positions, C(2,7), so that a Ti−C single bond remained involving the final, uncoupled dienyl carbon atom (C8). The resulting $Ti(C_5H_5)$(diene)(R) complex has a formal 14-electron count, Ti being too distant from the remaining olefin (C13,14) and any C−H bonds. However, close contacts of 2.579(7) and 2.293(7) Å are made with the saturated atoms C(2) and C(7)—the latter value being shorter than those for the bound C(4,5) or even any of the C_5H_5 carbon atoms![4] To deny the presence of a bonding interaction would thus require having a nonbonding contact shorter than a bonded one, clearly undermining the fundamental concepts of bonded and nonbonded radii; furthermore, the bonding parameters do not reveal any indication of severe strain in the arrangement. Under these circumstances, one must consider the possibility that a bonding interaction could occur between the titanium and saturated carbon atoms. In fact, in a complex containing an agostic (C−Si)→Ti interaction, a Ti−C distance of 2.52 Å was observed, and a theoretical study indicated that an analogous (C−C)→Ti interaction, although weaker, would be possible.[5] Given the presence of a long (1.596(8) Å) C6−C7 bond in the present case, there would be reason to suspect similar interactions here, particularly since in H_2 complexes a wide range of H−H distances has been observed.[6]

To assess the nature and degree of the possible agostic (C−C)→Ti interactions, DFT calculations[3,7] (hybrid method Becke

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(3) See the Supporting Information.

(4) In an electron-deficient iridium complex which undergoes a C−C activation reaction, a close contact of 2.71 Å is present between Ir and a saturated carbon atom.[2b] This is still ca. 0.5−0.6 Å longer than accompanying Ir−C bonding interactions, however, again supporting the idea of favorable interactions for **1**.

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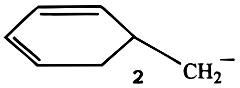
Table 1. Comparison of $^{13}C-^{13}C$ Couplings with Theoretical Results

donor NBO coupling	decrease of occupancy in **1a**	$\Delta E_{i,j}$ (kcal/mol)	$J(^{13}C-^{13}C)$ (Hz)
C6−C7	0.035	20.2	17.9
C3−C2	0.028	14.3	24.8
C7−C8	0.021	12.2	21.4
C7−C2	0.014	10.3	29.6
C7−H3	0.037	6.2	
C8−H4	0.012	5.1	
C2−H2	0.009	3.9	

3LYP[8]) have been carried out with extended all-electron basis sets of triple-ζ quality[9] for a simplified version of **1** containing Ti, C_5H_5, and a C_7H_9 ligand. The C_7H_9 fragment is composed of the 5-methylene-1,3-cyclohexadiene anion (**2**), derived from the C(2−8) fragment by replacement of all other non-hydrogen substituents by hydrogen atoms. To delineate the stabilizing interactions, a set of natural atomic orbitals (NAOs) and natural bond orbitals has been constructed.[10] Upon joining the $Ti(C_5H_5)^+$ and $C_7H_9^-$ fragments, one does observe significant occupancy decreases of four C−C and three C−H bonds (Table 1). Notably, the greatest decreases are observed for the C7−H3 and the long C6−C7 bond, and the second-order perturbative estimate of the stabilizing energy, ΔE_{ij}, for the donor−acceptor interactions between the four C−C bonds and Ti, 57 kcal/mol, appears remarkable.[3] Although this value is not a quantitative determination of the binding energy, a value of such magnitude makes it clear that something substantial is occurring, especially since use has been made of triple-ζ basis sets for all atoms.



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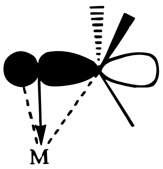
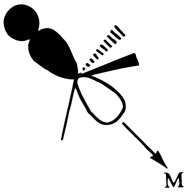
In fact, spectroscopic data further substantiate the presence of these interactions. Besides some unusual chemical shifts and $J(^{13}C-H)$ coupling constants (e.g., 149 Hz for C7), remarkably low $^{13}C-^{13}C$ coupling constants are present (as low as 17.9 Hz vs 30−39 Hz for the other C−C single bonds, see Table 1), and these correlate reasonably well with the calculated stabilizations. Together these data provide a compelling case for four significant agostic (C−C)→Ti interactions. Except for the C2−C7 bond, these interactions are analogous to the C−H counterparts in agostic $M-CH_3$ complexes.

Somewhat weaker interactions are found with three C−H bonds, one in the normal "agostic" mode (below, left), while in the other two the metal interacts with the C−H bonding orbital from the opposite side (below, right).[11] As a result of the various Ti−C interactions, a significant overlap-weighted NAO bond order is observed for Ti−C7 (0.168, cf., 0.182−0.209 for Cp's, C4 and C5), while that for Ti−C2 is half as large (0.082).





The encapsulation of an electrophilic, formally 14-electron titanium center in an environment isolated from all other likely donors but saturated carbon atoms has provided an opportunity to examine potential nonclassical M−C interactions. The presence of surprisingly short metal-to-saturated carbon atom contacts, accompanied by substantial orbital overlap, electron transfer, bond enthalpy, and supporting spectroscopic data testify strongly for agostic (C−C)→Ti bonding. Notably, other coupling reactions have led to further related species, suggesting that such species might be not uncommon.[3] In any event, the presence of these M−C interactions could well explain the facile C−C bond activation reactions that some coupling products undergo.[2d,3,12] Additional studies are underway to achieve a better understanding of these systems. Of course, it can be expected that zirconium analogues should lead to even stronger interactions,[12] and efforts to exploit this are underway.

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Supporting Information Available: Synthetic, spectroscopic, structural, and additional theoretical details for **1** (41 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) (a) A complex with a B−C bond in close proximity to a zirconium center has been observed; the presence of "pentavalent carbon" has been claimed.[12b] (b) Spence, R. E. v. H.; Parks, D. J.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J.; Rettig, S. J. *Angew. Chem., Intl. Ed. Engl.* **1995**, *34*, 1230. (c) These species bear significant similarities to carboranes, in which electrophilic boron centers may interact with, and rearrange, C−C bonds. It may also prove possible to design new ligands which could promote formation of similar agostic interactions.