

C–C Coupling Constants, J_{CC} , Are Reliable Probes for α -C–C Agostic Structures

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Received October 16, 2008

Summary: In contrast to structural parameters extracted from X-ray diffraction experiments, CC coupling constants (J_{CC}) prove to be reliable and sensitive probes of α -C–C agostic character.

Ever since the concept of agostic bonding first emerged, reliable experimental means of characterizing these intrinsically weak interactions have been sought.¹ The poor ability of X-rays to locate hydrogens makes this technique inherently unsuitable for probing the interaction between a C–H bond and a metal center, and as a result it is the distortion of the carbon backbone of the agostic group that is the key structural diagnostic of an agostic interaction in the solid state. In α -C–H agostic species even the structure of the carbon backbone is of limited use in this respect, as distortions of M–C–C angles are typically small. In view of the limitations of crystallography, the $^1J_{CH}$ coupling constants measured by NMR spectroscopy have emerged as the most useful and widely applicable experimental probe and the lowering of $^1J_{CH}$ is now considered to be the signature of agostic bonding. Complications can still arise in dynamic systems where thermal averaging of agostic and nonagostic C–H bonds can lead to apparently normal values of $^1J_{CH}$.^{1a,b} Nevertheless, NMR coupling constants have emerged as a sensitive and, importantly, readily acquired indicator of C–H agostic bonding.

In the past few years, a number of cases of C–C, as distinct from C–H, agostic structures have been reported in the literature,^{2–4} including several belonging to a family of metallocyclobutane complexes.^{2e,5,6} In many of these cases C–H bonds are also present and apparently accessible, making the adoption of a C–C agostic structure all the more remarkable because the metal apparently interacts with the most sterically shielded part of the molecule. The link between agostic interactions and C–H bond activation has long been recognized,⁷ and it is possible that these rare examples of C–C agostic interactions represent an early stage in cleavage of the more hindered C–C bonds, an area of much current interest.⁸ The development of reliable experimental probes of C–C agostic interactions is therefore a high priority. In principle, X-ray diffraction is more appropriate for the study of C–C agostic interactions than their C–H counterparts because two heavy atoms are involved, but the characteristic elongation of the C–C bond is often rather small. By analogy to C–H agostic interactions, the measurement of J_{CC} is an attractive alternative, but its use has been limited by the low natural abundance of ^{13}C and/or high cost of ^{13}C -labeled compounds.^{2e,f,6} In this paper we show that these J_{CC} values can be measured using the INADEQUATE sequence and that they are much more sensitive probes of the electronic density in the cyclopropyl group than the corresponding structural data.

It is important at this point to differentiate clearly the consequences of an agostic interaction (i.e. the deformation of the alkyl backbone and the lowering of $^1J_{CH}$ for a C–H agostic interaction) from their underlying cause. The classical model of agostic bonding invokes donation of a pair of electrons from a C–H bond to an electron-deficient metal center, resulting in a three-center–two-electron bond.^{1a} However, we and a number of other groups have argued that, in complexes of the rather electropositive early transition metals, direct interactions be-

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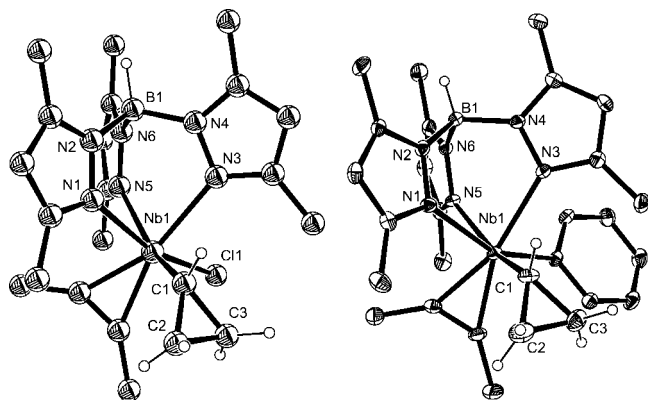


Figure 1. Plots of the molecular structures of **1** (left) and **2** (right). For **2**, the original numbering scheme for the cyclopropyl carbons has been changed to be consistent with that of **1**.

tween the C–H bonding electrons and the metal are minimal.^{9–11} The distortion of the appended alkyl group is instead driven by the high polarity of the M–C bond, which causes a canting at the α -carbon, such that the M–C bonding electrons are strongly delocalized. In light of these conflicting views as to the origin of the agostic bond, we adopt the phenomenological definition proposed by Scherer, McGrady, and co-workers, who suggest that the presence of an agostic distortion is defined by the experimental observables, irrespective of the electronic mechanism that drives them.^{1c} Thus, in this work we regard the reduction of the carbon–carbon coupling constants, J_{CC} , from their characteristic nonagostic values as being indicative of an “agostic interaction” and reserve comment on the precise origin of this reduction for the concluding remarks.

The X-ray crystal structures of $\text{Tp}^{\text{Me}_2}\text{NbX}(\text{c-C}_3\text{H}_5)(\text{MeCCMe})$ ($\text{X} = \text{Cl}$ (**1**), Ph (**2**)) have been reported previously,^{3,12} and key structural parameters are summarized in Figure 1 and Table 1. The overall geometries are very similar in both **1** and **2**, particularly with respect to the orientation of the cyclopropyl group relative to the niobium and the ancillary ligands. The structure of **1** shows clear evidence for the presence of an α -C–C agostic interaction, most notably in the tilt of the cyclopropyl group toward the metal center and the obtuse $\text{C}_\alpha\text{–Nb–Cl}$ angle. The two $\text{C}_\alpha\text{–C}_\beta$ bond lengths are consistent with this proposal, with the bond oriented toward Nb ($\text{C}(1)\text{–C}(3)$) 0.049 Å longer than the other ($\text{C}(1)\text{–C}(2)$). Although the difference is only ca. 3%, it lies well beyond the 3σ threshold and so is statistically significant. Although the tilting of the cyclopropyl group toward the Nb center is also apparent in the phenyl complex, **2**, and the mean value for $\text{C}(1)\text{–C}(3)$ is still marginally (0.014 Å) greater than that for $\text{C}(1)\text{–C}(2)$, this difference lies within 3σ and so is not statistically significant. The case for an α -C–C agostic interaction is therefore not as clear cut in **2** as it is in **1**. This may indicate that the coligand exerts an influence on the strength of the agostic bond but may equally simply reflect the fact that the magnitude of the changes lies close to the detection limits of the experiment. In order to

explore this issue further, we have synthesized the analogous methyl complex $\text{Tp}^{\text{Me}_2}\text{NbMe}(\text{c-C}_3\text{H}_5)(\text{MeCCMe})$ (**3**), but the structure of this complex is disordered, and no reliable metric data could be extracted from the refinement. We have also synthesized and structurally characterized an iron cyclopropyl complex, $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{c-C}_3\text{H}_5)$ (**4**),^{13,14} where the 18-electron count blocks any direct interaction between the metal center and the electrons in the C–C bonds. The molecular structure of **4** as determined by X-ray diffraction is shown in Figure 2 and is similar to those of other $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{alkyl})$ complexes,¹⁵ although there are some conformational side effects due to the cyclopropyl group itself.¹⁶ Most importantly, there is no distortion of any kind in the cyclopropyl ring: all C–C–C angles are 60°, and the C–C bond lengths (Table 1) are equal (within 3σ) at 1.49 Å.

In light of the inconclusive structural evidence for **2**, and the complete absence of data for **3**, we have turned to NMR spectroscopy to shed light on C–C agostic bonding in these systems. The unambiguously nonagostic system **4** provides a logical reference point for the following discussion. Its solution-phase $^{13}\text{C}\{^1\text{H}\}$ INADEQUATE spectrum exhibits a doublet for each of the three carbons of the cyclopropyl group, with J_{CC} values of 11 Hz (see the Supporting Information). It should be emphasized that the appearance of the signals as doublets indicates that the two coupling constants associated with each carbon center (for example, J_{C1C2} and J_{C1C3} for C(1)) must be identical, within the 2 Hz line width. The value of 11 Hz is very similar to the 12.4 Hz observed for cyclopropane itself,¹⁷ confirming the absence of any significant perturbation due to the metal center.

In contrast to experiments on **4**, our initial attempts to measure J_{CC} for complexes **1–3** by solution NMR with INADEQUATE sequences were frustrated by several anticipated difficulties, and no signal for the key C_α and C_β carbons of the cyclopropyl group was detected in ca. 0.5 M solutions in dichloromethane- d_2 on a Bruker Avance 500, even after 60 h. Pleasingly, however, the huge enhancement of the signal-to-noise ratio resulting from the use of a cryoprobe on a Bruker Avance 600 allowed reasonable INADEQUATE spectra for compound **1**, as well as for **2** and **3**, to be recorded over a ca. 6 h timespan. The data for all four complexes are gathered in Table 1. For **2**, full assignments of ^1H and ^{13}C NMR signals are based on HSQC and ROESY spectra.¹² A typical INADEQUATE spectrum (that of complex **3**) is reproduced in Figure 3, showing characteristic resonances for the two β -carbons C(2) and C(3)¹⁸ in the regions of δ 20 and 10, respectively. Resonances occur in similar regions for **1** and **2**.

For complex **3**, the resonance for C(2) consists of two well-resolved doublets with J_{CC} values of 9 and 15 Hz, values not dissimilar to those of **4** or indeed of cyclopropane itself. C(3), in contrast, appears as a doublet with $J_{CC} = 15$ Hz, which allows

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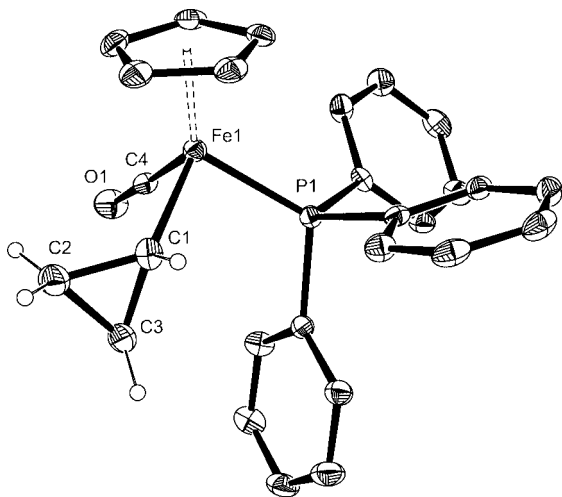
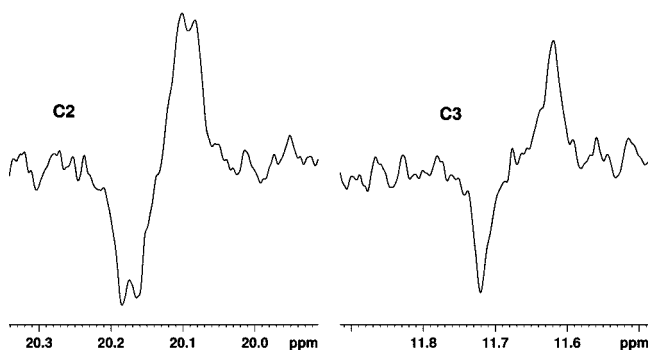
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Table 1. Experimental and Calculated Bond Lengths and Coupling Constants for 1–4 and Computed Data for 5–8

	C(1)–C(2)				C(1)–C(3)				C(2)–C(3)			
	$d(\text{C}–\text{C})/\text{\AA}$		J/Hz		$d(\text{C}–\text{C})/\text{\AA}$		J/Hz		$d(\text{C}–\text{C})/\text{\AA}$		J/Hz	
	exptl	calcd	exptl ^a	calcd	exptl	calcd	exptl ^a	calcd	exptl	calcd	exptl ^a	calcd
1	1.490(4)	1.50	11	9.8	1.539(4)	1.53	<3	–1.3	1.478(5)	1.49	15	14.3
2	1.509(5)	1.51	n.o. ^b	7.0	1.523(6)	1.53	<3	–2.1	1.482(6)	1.49	15	14.1
3		1.51	9	6.4		1.53	<3	–1.7		1.49	15	14.3
4	1.491(4)	1.51	10/11 ^c	9.4	1.478(4)	1.50	11/12 ^c	11.8	1.489(4)	1.50	12/10 ^c	10.8
5		1.50		8.2		1.53		–2.3		1.49		14.1
6		1.50		7.1		1.53		–4.0		1.49		14.6
7		1.49		8.7		1.54		–6.5		1.49		14.0
8		1.51		5.3		1.52		1.8		1.49		13.4

^a Line width at half-height: 3 Hz for **1–3**, 2 Hz for **4**. ^b Not observed. Only a doublet is observed for C(2); see text. ^c Definitive assignment not possible; see text.

**Figure 2.** Plot of the molecular structure of **4**.**Figure 3.** Expansion plots of the ¹³C INADEQUATE spectrum (150 MHz) for **3**.

us to assign J_{C2C3} as 15 Hz and therefore J_{C1C2} as 9 Hz. The fact that the intensity of the C(3) doublet is similar to that of each of the two doublets observed for C(2) is critical, because it indicates that the other coupling involving C(3), J_{C1C3} , must be less than the line width at half-height, ca. 3 Hz. We were unable to confirm the low value of J_{C1C3} by observing the signal for the α -carbon, C(1), as no INADEQUATE signal was detected for this nucleus due to quadrupolar relaxation and line broadening. We can, however, eliminate the alternative scenario, that a single doublet arises for C(3) because $J_{\text{C1C3}} \approx J_{\text{C1C2}}$ (as is the case for **4**), because in such circumstances the intensity should be twice that of each of the doublets for C(2). Moreover, such a large reduction in J_{CC} is not unprecedented: similarly low values have also been inferred in 1-silylcyclopropenes.¹⁹

In the absence of an X-ray crystal structure for **3**, the small value of J_{C1C3} is the key observation that suggests the presence of a CC agostic interaction.

For complex **1**, the INADEQUATE signal for C(2) again appears as a pair of doublets with J_{CC} values of 11 and 15 Hz, values rather similar to those of **3**. Moreover, in this case a single doublet ($J_{\text{CC}} = 11$ Hz) was detected for the α -carbon C(1), allowing us to assign $J_{\text{C1C2}} = 11$ Hz and therefore $J_{\text{C2C3}} = 15$ Hz. Unfortunately the signal for C(3) was obscured by the methyl carbons of Tp^{Me2} , precluding a reliable determination of J_{C1C3} , but it is clear from the appearance of C(1) as a doublet with intensity similar to each of the doublets of C(2) that J_{C1C3} must again be smaller than the line width of ca. 3 Hz. The data for **2** are of lower quality than for **1** or **3**, and as a result the INADEQUATE signal for C(2) appears as a broad featureless doublet with $J_{\text{CC}} \approx 15$ Hz, rather than as two distinct doublets as in **1** and **3**. As was the case for **3**, a signal for C(1) was not observed due to quadrupolar relaxation, but we were able to detect a signal for C(3), again as a single doublet, with $J_{\text{CC}} \approx 15$ Hz. The intensity of this signal is significantly lower than that of the broad doublet due to C(2), suggesting that the latter arises from the overlap of two distinct doublets of similar intensity with similar but not identical values of J_{CC} . On this basis, we can therefore again assert that $J_{\text{C1C3}} < 3$ Hz.

Our assignments of the signals observed in the INADEQUATE spectra of **1–4** indicate that an α -C–C agostic interaction is present in **1–3** but not in **4**. Moreover, the value of J_{CC} appears to be a much more sensitive probe of the presence or absence of agostic character than the structural data. In light of the difficulties experienced in collecting the INADEQUATE data, and in particular the absence of signals for some of the key carbon nuclei, we have turned to computation to provide support for our assignments. In a recent paper we showed that density functional theory is capable of reproducing not only the geometries of C–H agostic complexes of Nb but also the trends in coupling constants, J_{CH} .⁹ With this in mind, we have optimized the geometries of the Nb complexes **1–3**, as well as that of the nonagostic reference compound **4**, using the PBE1PBE functional.²⁰ The results, laid out in Table 1, show a remarkable level of agreement with the experimental data, both structural and spectroscopic. Considering first the C–C bond lengths, we note that while the three computed values for **4** are almost identical at 1.50 Å, a small but distinct elongation

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(ca. 0.02 Å) of the C(1)–C(3) bond relative to C(1)–C(2) emerges in **1–3**. Thus, the computed structures are consistent with the presence of a C–C agostic interaction in all three cases. It is important to emphasize that the computed elongation of C(1)–C(3) is very small and could easily be obscured in the solid state, as appears to be the case in **2**. Turning to the computed coupling constants, J_{CC} , we immediately note that the values for J_{C1C3} are uniformly low and are well below the ca. 3 Hz line width of the experiment. This offers strong support for our assignment of $J_{C1C3} < 3$ Hz for each of **1–3** on the basis of the experimental data. Trends within the other coupling constants are also well reproduced: for the nonagostic reference **4**, the computed values of 12, 9, and 11 Hz are in excellent agreement with experimental values of 10–12 Hz. Even the splitting of the two doublets for C(2) in the spectra of **1** and **3** is modeled adequately, with computed values of J_{C2C3} and J_{C1C2} in the region of 14 and 6–10 Hz, respectively, compared to experimental values of ~15 and ~10 Hz.

Our experimental results summarized in the preceding paragraphs confirm that, despite difficulties due to intrinsically low values of J_{CC} in the cyclopropyl ring, a distinct lowering of J_{CC} for the C(1)–C(3) bond is apparent in **1–3**. The low value of J_{C1C3} can only be inferred indirectly from the spectra through the absence of signals corresponding to this coupling, but our assignment is strongly supported by computation, which confirms a dramatic difference between J_{C1C3} and the remaining two coupling constants. These data are consistent with the presence of an α -C–C agostic structure in each of **1–3**, but the rather similar values of J_{C1C3} suggest that the strength of this interaction is largely independent of the identity of the X ligand, at least within the series X = Cl, Ph, Me. In order to establish whether this is the case across a more electronically diverse range of ligands, we have computed the structures and coupling constants for the complexes $\text{Tp}^{\text{Me}_2}\text{NbX}(\text{c-C}_3\text{H}_5)\text{-(MeCCMe)}$ (X = F (**5**), SiH_3 (**6**), H (**7**), NH_2 (**8**)), none of which have yet been synthesized. The results, summarized in Table 1, confirm that the values for J_{C1C3} are always smaller than those for free cyclopropane, indicating that agostic interactions are present in all cases. Moreover, the range of values is much wider in the series **5–8**, varying from –6.5 Hz for compound **7** (X = H) to 1.8 Hz for compound **8** (X = NH_2), confirming that the “agosticity” of the cyclopropyl ligand can indeed be tuned by the electronic properties of the other ligands. The agostic interaction is clearly stronger for strong σ -donors such as silyl and especially hydride, leading to negative values of J_{C1C3} . In contrast, the strong π -donor amido ligand gives a rather larger value of J_{C1C3} , suggesting that Nb–X π bonding increases the electron density at the metal center, thereby reducing the strength of the agostic interaction. Interestingly, the trends in computed J_{CC} values are mirrored in the structural data, where the C(1)–C(3) bond length increases in the order **8** < **5** = **6** < **7**. The differences in the structural parameters are, however, of the order of a few hundredths of an angstrom and will likely remain beyond the limits of detection of X-ray diffraction.

The previous paragraphs have established that an α -C–C agostic interaction, as defined by the reduction of J_{CC} from ~12 Hz to <3 Hz, is present in the niobium complexes **1–3** but not the electronically saturated iron species **4**. The underlying origin of these trends is rather difficult to establish because, unlike the C–H spin–spin coupling constants $^1J_{CH}$, J_{CC} values in any cyclopropyl complex are inherently a combination of one-bond

and two-bond coupling pathways. Indeed, the origin of the low values in cyclopropane itself, along with related highly strained molecules, has been the subject of debate.²¹ It is generally agreed that the Fermi contact term dominates the coupling in cyclopropanes and that simple interpretations relating the magnitude of J_{CC} with the s (or p) character of the CC bond must be used with caution. To the best of our knowledge, there have been no other reports of J_{CC} values for organometallic derivatives of cyclopropane, agostic or otherwise, but the influence of the substituent on J_{CC} in organic cyclopropanes²² is known to be rather small, with the general trend that the J_{CC} value increases with the electronegativity of the substituent. The effect is rather more dramatic in the 1-silylcyclopropenes that were noted previously, but in this case J_{CC} is substantially reduced for both the C–C and C=C bonds,¹⁹ whereas only one bond, that adjacent to the metal center, is affected in **1–3**. A simplistic interpretation of the trends in J_{CC} for **1–4** is that electronic saturation of the metal center blocks the donation of electrons from a C–C bonding orbital in the iron complex **4** but not in **1–3**. However, our recent work on α -C–H agostic distortions in niobium complexes suggests that the agostic interaction arises not through donation of C–H bonding electrons to the metal center but rather through a partial delocalization of the HOMO, which has dominant Nb–C σ bonding character, onto the π^* orbitals of the neighboring alkyne ligand.⁹ The driving force for this delocalization is the energy mismatch between the lone pair on the formally anionic alkyl ligand and the d orbitals on the electropositive niobium, which results in a highly polar Nb–C bond. This energy mismatch is likely to be equally important in the cyclopropyl complexes **1–3**, and delocalization of the Nb–C bonding electrons into the low-lying C–C antibonding orbitals of the cyclopropyl unit (negative hyperconjugation) may be responsible for the dramatic reduction in J_{CC} . If this interpretation is correct, it is the more covalent nature of the Fe–C bond rather than the electronic saturation of the metal center that prevents the adoption of an agostic structure in **4**. We are currently undertaking a detailed exploration of the electron densities of these species in an attempt to distinguish the different possible electronic mechanisms.

Acknowledgment. M.E. thanks the Agence Nationale de la Recherche (ANR) for support (Grant No. BLAN07–2_182861). J.E.M. and D.A.P. acknowledge the EPSRC for financial support (EP/C534425/2). A.L., F.B., and F.M. thank the Spanish MICINN (projects CTQ2008-06866-CO2-02/BQU and Consolider Ingenio 2010, Grant CSD 2006-0003) and the ICIQ Foundation for financial support.

Supporting Information Available: Text and tables giving experimental details for the synthesis and characterization of **4**, computational details, and Cartesian coordinates of all computed structures and a CIF file giving crystallographic data for **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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