How Strong Is an Agostic Bond? Direct Assessment of Agostic Interactions Using the Generalized Compliance Matrix[†]

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The strength of an α-agostic bond in $CH_2{=}TiHF$ has been evaluated using the generalized compliance matrix from HF (Hartree−Fock), MP2 (second-order Møller−Plesset perturbation), CCSD(T) (coupled cluster theory with single and double substitutions with noniterative triple excitations), and several formulations of DFT (density functional theory) in combination with large all-electron basis sets. While HF underestimates the agostic interaction, both MP2 and the local spin density approximation (LSDA) dramatically overestimate the agostic Ti···H interaction strength. Hybrid DFT (B3LYP) and pure DFT (BLYP) are in line with the CCSD(T) level of theory. The DFT compliance constants and their coupling values are further used to characterize the agostic C−H···W interaction in $[W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)]$ (**1**; dmpe = (dimethylphosphino)ethane). The strength of this agostic bond is analyzed as a function of the metal atom and the molecular environment.

Introduction

Knowledge of individual bond strengths is crucial for the design of transition-metal-based catalysts. While for strong covalent bonds the frequently used bond dissociation enthalpies (BDE) and other indirect methods can be far from describing an intrinsic strength of a particular bond,[1,2] the unique experimental determination of agostic bond strengths is often not possible at all and only approximate values are proposed.[3] These difficulties lead to uncertain estimations of those interaction strengths between 1 and 20 kcal mol^{-1}.[4] To separate real differences from artifacts of different indirect proxy methods, alternative ways to directly determine agostic bond strengths—without reference to arbitrary or ill-defined states with no agostic interaction—is therefore needed. Further, since theoretical studies on the nature of agostic interactions are often based on those noisy energetic data, the need for reliable information on the intrinsic interaction strength is evident. The calculation of compliance constants[5] (diagonal elements of the inverted Hessian matrix) offers such an alternative. Compliance constants describe what came into focus of experiment and theory: the mechanical strength of a bond, which, in principle, is measurable by atomic force microscopy (AFM) of single molecules.[6] These physical measurements provide upper bounds to the mechanical strength of chemical bonds described by force constants or compliance constants. A force constant gives the force required to stretch a particular bond *without reorganizing* the rest of the molecule. While the numerical values of force constants depend on the coordinate system, this is not the case for compliance constants. A compliance constant is the displacement of a bond due to the application of a unit force on that bond *including reorganization*. This means that a higher numerical value is connected with a weaker bond. Introduced to vibrational theory by Decius[7] and others,[8] experimental compliance fields obtained by Jones and Swanson from vibrational data clarified the bonding forces in metal cyanides and carbonyls,[9] while Williams used compliance matrices for the description of chemical reactivity.[10] Calculations of full compliance fields have been used to investigate Ga−Ga[11] and Si−C[12] multiple bonds, the metal−metal bond character in homoleptic transition-metal carbonyls,[13] hydrogen bonds in Watson−Crick base pairs,[14] and polyphosphorus compounds.[15] Recently, Andreoni and coworkers used compliance constants plus Car−Parinello molecular dynamic simulations in order to analyze a proposed Si−Si

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[†] This paper is dedicated to Professor Henning Hopf on the occasion of his 65th birthday.

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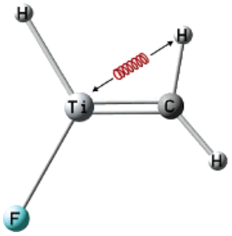
Table 1. Evaluation of Several Quantum-Chemical Methods with Respect to Their Ability To Describe an α-Agostic Interaction Using Compliance Constants C_{ij}



	HF I	MP2 I	SVWN I	BPW91 I	BLYP I	B3LYP I	CCSD(T) I	CCSD(T) II (ecp)[b]	B3LYP II (ecp)[b]
r(Ti···H) (Å)	2.572	1.961	2.001	2.109	2.202	2.163	2.140	2.086	2.182
C_{ij}(Ti···H) (Å mdyn^{-1})	***10.47***	***2.067***	***2.405***	***4.702***	***7.877***	***6.330***	***7.356***	***4.980***	***6.936***
r(Ti=C) (Å)	1.855	1.797	1.783	1.817	1.836	1.814	1.855	1.825	1.810
C_{ij}(Ti=C) (Å mdyn^{-1})	0.367	0.172	0.224	0.265	0.310	0.276	0.377	0.322	0.281
Ti−C−H (deg)	119.7	80.6	83.3	88.2	93.0	92.0	88.4	86.4	92.3
out of plane (cm^{-1})	170.4	128.0	−146.0	−21.2	−57.9	57.0	145.5	109.2	−113

[a] The optimized distance r(Ti···H)(agostic), the angle Ti−C−H(agostic), and the frequency of the out-of-plane vibration are also given. [b] LanL2DZ (Ti).

triple bond.[16] These studies showed the usefulness of compliance constants as unique bond strength descriptors, due to their independence of the coordinate system, while their transferability allows a comparison of any atom−atom interaction, bonded or not, in different molecular surroundings.

Here, we report on the performance of several wave function or density based methods in describing α-agostic interactions by using generalized compliance matrices (inverse of the redundant Hessian matrix) from first-principle ab initio and density functional theory. Evaluation of the different compliance force fields was done for CH_2=TiHF as a model system, because it is small enough for a treatment with highly correlated wave functions in combination with large, all-electron basis sets. Further, due to the pioneering work of Andrews and co-workers, experimental and theoretical data are now available for many simple methylidene complexes.[17] In a second step, the effect of both the molecular environment and the nature of the metal on the agostic interaction strength was studied for [W(≡$CCMe_3$)(=$CHCMe_3$)(CH_2CMe_3)(dmpe)] (**1**; dmpe = (dimethylphosphino)ethane).

Computational Details

In the present work, all optimizations and frequency calculations were performed using the Gaussian 03 program set.[18] We did simple Hartree−Fock (HF), second-order Møller−Plesset perturbation (MP2),[19] local density (SVWN),[20] generalized gradient (BLYP[21] and BPW91[22]), hybrid density functional theory (B3LYP),[23] and coupled cluster theory calculations with single and double substitutions and noniterative triple excitations (CCSD(T)).[24] All optimizations were done in C_s symmetry. The all-electron basis set was of triple-ζ quality augmented with one set of diffuse functions and two sets of polarization functions on all atoms (6-311++G(2d,2p); basis set I). The necessity to use polarization functions on carbon to characterize agostic distortions has been emphasized by Andrews.[17] Additional DFT and CCSD(T) calculations were done using a smaller triple-ζ basis set without diffuse functions (6-311G(d,p)) in combination with the Los Alamos LanL2DZ[25] effective core potential for titanium, basis set II. Energy minimizations were followed by a characterization of the stationary point using frequency calculations. After the energy second derivatives (Cartesian Hessian matrix) were transformed into a redundant internal coordinate system containing all possible atom−atom distances—including the agostic metal···H distance—the generalized compliance matrix (generalized inverse of the Hessian matrix[26]) was calculated using a modified Moore−Penrose formalism.[27] Both the transformation and the inversion was performed using our *compliance* routine.[28] The Moore−Penrose algorithm circumvents the necessity of defining a nonredundant coordinate system, making the production of the compliance force fields, even for large systems with complicated topologies, a straightforward task.

Results

CH_2=TiHF. The results are shown in Table 1. The coupled cluster Ti···H compliance constant of 7.356 Å mdyn^{-1} points to an α-agostic (methylidene) interaction strength in CH_2=TiHF which is comparable—though different in nature—to that of a weak hydrogen bond.[14] Using CCSD(T) as a reference method, Hartree−Fock theory severely underestimates the agostic interaction (no Ti−C−H angle distortion; Ti···H compliance constant 10.472 Å mdyn^{-1}), while MP2, SVWN, and—less pronounced—BPW91 overestimates the agostic bond strength (Ti···H compliance constants 2.067, 2.405, and 4.702 Å mdyn^{-1}, respectively). Both the hybrid functional B3LYP (Ti···H compliance constant 6.330 Å mdyn^{-1}) and the pure DFT method BLYP (Ti···H compliance constant 7.877 Å mdyn^{-1}) reproduce

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Table 2. Selected Experimental and Theoretical Bond Lengths (DFT/II LanL2DZ(W)) and Their Theoretical Bond Dissociation Energies in Complex 1 as Well as Important Compliance Constants C_{ij} in Complexes 1 and 2

	M≡C	M═C	M−C	M···H
		M = W		
R_{exptl} (Å)[13]	1.785(8)	1.942(9)	2.258(8)	2.370
R_{theory} (Å)	1.792	1.942	2.256	2.377
C_{ij} in **1** (Å mdyn^{-1})	***0.151***	***0.275***	***0.722***	***2.657***
C_{ij} in **2** (Å mdyn^{-1})	***0.148***	***0.282***	***0.639***	***3.184***
BDE (kcal mol^{-1})	150.761	93.713	59.151	
		M = Mo		
R_{theory} (Å)	1.770	1.937	2.269	2.369
C_{ij} (Å mdyn^{-1})	***0.163***	***0.304***	***0.818***	***2.442***
		M = Cr		
R_{theory} (Å)	1.640	1.781	2.156	2.127
C_{ij} (Å mdyn^{-1})	***0.166***	***0.304***	***0.952***	***2.942***

the coupled cluster result and should therefore give reliable results for larger systems, which are out of reach for sophisticated post-Hartree−Fock methods. Since, at least in combination with basis set I, the B3LYP method additionally reproduces the correct sign of the out-of-plane mode, we decided to use the hybrid functional for all other calculations. An effective core approximation[25] for the metal in combination with the small triple-ζ basis set (6-311G(d,p), basis II) for all other atoms produces a Ti···H compliance constant (B3LYP: 6.936 Å mdyn^{-1}), which is still close to the coupled cluster result (basis I), while the coupled cluster theory itself shows a much more pronounced dependence on the basis set: the compliance constant drops from 7.356 (basis I) to 4.980 Å mdyn^{-1} (basis II).

[W(≡CCMe$_3$)(═CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)]. In a second step, we therefore performed B3LYP calculations of the ground-state geometry and the full compliance field of the tungsten complex [W(≡CCMe$_3$)(═CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)][29a] (**1**; dmpe = (dimethylphosphino)ethane), which—although it has been known for 25 years—remains to date the only complex confirmed by single-crystal structure analysis,[29b,c] featuring an agostic W···H−C interaction and a formal tungsten−carbon single, double, and triple bond. This offers the unique opportunity of an internal calibration[29d] by studying an agostic W···H interaction and several covalent W−C bonds of different orders in a single molecule.[30] The ground-state geometry was obtained from full optimization using the B3LYP functional in combination with the basis set 6-311G(d,p)/Los Alamos LanL2DZ ECP at W (DFT/II LanL2DZ(W)). In agreement with the X-ray structure of complex **1** a pentacoordinate tungsten in the center of a slightly distorted square pyramid is surrounded by an apical neopentylidyne ligand, basal neopentyl and neopentylidene ligands, and a basal (dimethylphosphino)ethane unit. A comparison of experimental and calculated W−C, W═C, and W≡C bond lengths is given in Table 2. We also included the theoretical bond dissociation energies (BDEs) computed with respect to the following equations.

(i) W−C single bond: **1** → [W(≡CCMe$_3$)(═CHCMe$_3$)(dmpe)] (^{2}A state) + CH$_2$CRMe$_3$ (^{2}A state)

(ii) W═C double bond: **1** → [W(≡CCMe$_3$)(CH$_2$CMe$_3$)(dmpe)] (^{1}A state) + CHCMe$_3$ (^{3}A state)

(iii) WC triple bond: **1** → [W(═CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)] (^{4}A state) + CCMe$_3$ (^{1}A state)

Since we are not interested in absolute dissociation energies but in the trend for individual W−C bonds in **1**, we did not correct the individual BDEs for basis set superposition errors (BSSE). Though BDEs and compliance constants describe not only different regions of the energy surface but also measure different physical properties, both quantities should show the same tendency. At least in the case of complex **1**, on comparing BDEs and the compliance constants (see Table 2), a relationship can be found (though it is not linear). A stronger W−C bond (lower compliance constant) is connected with a higher bond dissociation energy (see Table 2). While the W−C single bond is described by a compliance constant of 0.722 Å mdyn^{-1} and a BDE of 59.15 kcal mol^{-1}, the W═C double bond and the W≡C triple bond show compliance values of 0.275 Å mdyn^{-1} (BDE = 93.71 kcal mol^{-1}) and 0.151 Å mdyn^{-1} (BDE = 150.76 kcal mol^{-1}), respectively. One should keep in mind that, in contrast to BDEs, which also include relaxation of the dissociated fragments, compliance constants reflect the intrinsic bond strength exactly at the equilibrium geometry without making any reference to the fragment stability. That means, for agostic interactions—or any case, where it is hard to uniquely define a reference system of dissociated fragments—compliance constants allow a direct and unambiguous characterization of the interaction strength.

Using Scherer's definition of an agostic interaction,[4b] we find in our B3LYP optimized structure a geometrical distortion of the neopentylidene ligand, which has already been noted by Churchill et al.:[29b] the W−C2−C4 angle of 152° deviates from the ideal 120°. Calculating the vibrational frequencies, the stationary point was then further characterized as a minimum. To determine the W···H interaction strength, we again included the agostic W···H distance in the set of internal coordinates. Because of the transferability, the resulting generalized W···H compliance constant can directly be compared with the agostic bond in our benchmark system CH$_2$═TiHF or any other type of atom−atom interaction. The resulting generalized compliance constant in **1** (C_{W}···H, 2.657 Å mdyn^{-1}; W···H distance, 2.377 Å; Table 2) points to a much stronger agostic interaction in comparison with CH$_2$═TiHF. The agostic interaction strength is now comparable with that of a strong, linear NH···N hydrogen bond[14] but is still well below 10 kcal/mol.

Effect of Steric Constraint and the Metal Atom: Compliance Coupling Constants. To further evaluate (a) the steric influence[31] of the large substituents in **1** and (b) the effect of the central metal atom, we also did compliance constant calculations on a model system with significantly reduced steric strain [W(≡CMe)(═C(H)Me)(Et)(dmpe)] (**2**) (Figure 1, Table 2) as well as on **1** where tungsten is substituted by chromium and molybdenum. The transferability of the compliance constants again allows a direct comparison of the interaction strengths and should further clarify the nature of the agostic bond. The larger $C_{\mathrm{W\cdots H}}$ compliance constant (weaker interaction) of 3.184 Å mdyn^{-1} in **2**, where the steric strain is significantly lowered by the ethylidene ligand, points to an assisting effect of the substituents operative in complex **1**: the agostic hydrogen in **1** is beeing "pushed" close to the metal center by the large neopentylidene substituent. Concerning the nature of the metal atom in [M(≡CCMe$_3$)(═CHCMe$_3$)(CH$_2$CMe$_3$) (dmpe)] in the triad M = Cr, Mo, W, the strongest agostic bond is found for

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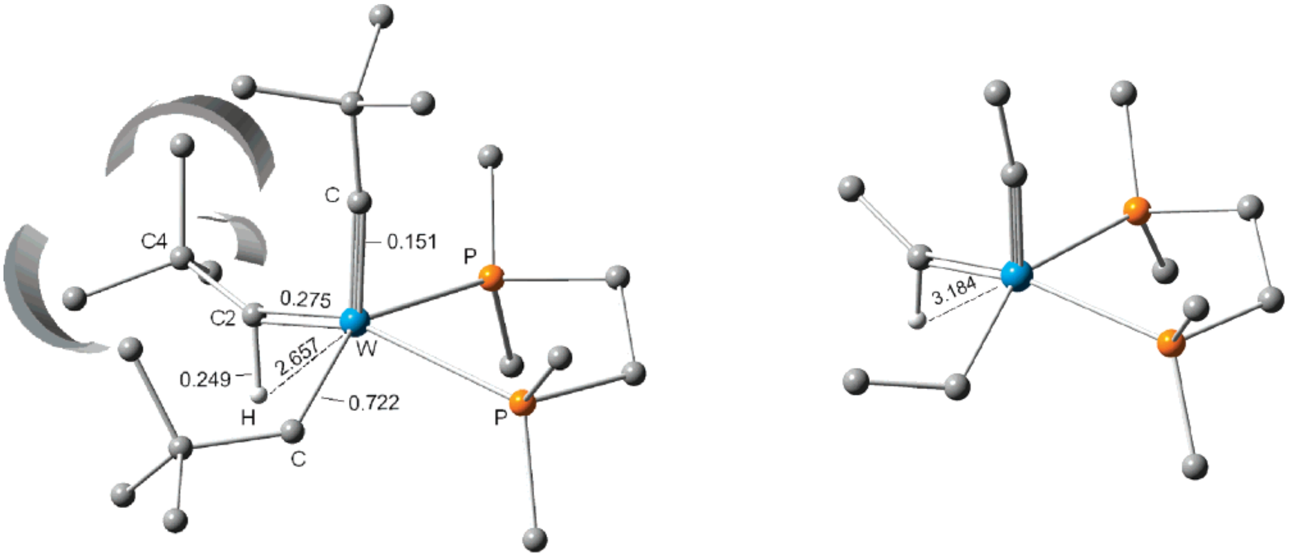

1 **2**

Figure 1. Effect of steric strain on the agostic interaction. DFT/II LanL2DZ(W) optimized structure and selected compliance constants in Å $mdyn^{-1}$ for the W−C, W═C, W≡C, and the C−H⋯W bond in $[W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)]$ (**1**) and model system **2** with reduced strain. A higher compliance constant is connected with a weaker bond.

Table 3. Part of the Symmetric 204 × 204 DFT/II LanL2DZ(W) Compliance Matrix for 1[a]

	W≡C	W═C	W−C	agostic W⋯H	H−C
W≡C	**0.151**				
W═C	−0.010	**0.275**			
W−C	−0.005	−0.011	**0.722**		
agostic W⋯H	−0.026	**0.405**	−0.076	**2.657**	
H−C	0.003	−0.025	0.006	−0.017	**0.249**

[a] The values are given in units of Å $mdyn^{-1}$. Note the large C(agostic W−H)−(W═C) coupling constant. A higher numerical value of a diagonal element (a compliance constant) describes a weaker bond. Coupling constants (off-diagonal elements) are directly proportional to the amount of interaction of the coupling coordinates.

molybdenum with a compliance constant of 2.442 Å $mdyn^{-1}$, followed by tungsten (2.657 Å $mdyn^{-1}$) and chromium (2.942 Å $mdyn^{-1}$).

While the diagonal elements of the compliance matrix correspond with the internal coordinates (bond lengths, angles, or dihedrals) the interactions of internal coordinates are being described by the off-diagonal elements (interaction compliance constants). Column *k* of the full compliance matrix can be interpreted as the vector of coordinate displacement from the minimum configuration upon applying a force of unit amount on coordinate *k* while the remainder of the molecule relaxes to a new minimum with coordinate *k* displaced.[12b] Table 3 shows the interaction compliance constants—that is, the change in the electronic configuration upon displacement of a specific bond *j*—for the tungsten complex describing further details of the bonding forces in **1**. A participation of the neopentylidene C−H bond in the agostic bond formation should result in a significant C(agostic W−H)−(H−C) compliance coupling constant. Instead, while most of the interaction compliance constants are moderate, we found a large C(agostic W−H)−(W═C) coupling constant of 0.405 Å $mdyn^{-1}$. At least for the formation of the agostic W⋯H bond in the alkylidene complex $[W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)]$ (**1**), this points to a strong contribution of the W═C bond to the total energy lowering.

Systematic calculations to quantify the individual contributions on a variety of complexes containing agostic interactions as well as the influence of the metal and the molecular environment are underway.

Conclusions

(a) The generalized compliance matrix (generalized inverse of the Hessian matrix) allows a direct and unique quantitative determination of agostic bond strengths, without reference to arbitrary or even ill-defined reference points. This feature makes the comparison of agostic interaction strengths in different molecular surroundings a straightforward task.

(b) Using the small methylidene complex $CH_2{=}TiHF$ as a benchmark system, MP2, LSDA and—less pronounced—BPW91 theory overestimates the α-agostic interaction strength, while simple Hartree−Fock theory severely underestimates it. Both the hybrid functional B3LYP and the pure DFT method BLYP seem to offer a more balanced description of covalent and electrostatic contributions as well as short-range dispersion.

(c) For both systems, $CH_2{=}TiHF$ and $[W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)]$, the strength of the α-agostic bond is in the range—though different in nature—of a typical hydrogen bond (≤10 kcal/mol).

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