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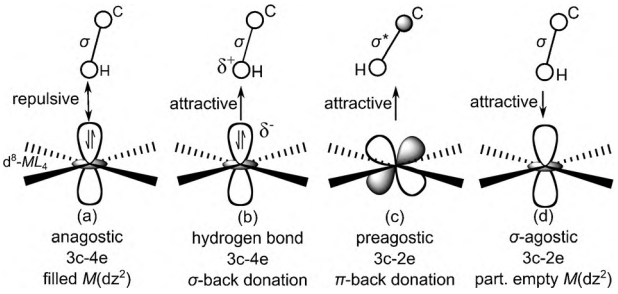
Anagostic Interactions under Pressure: Attractive or Repulsive?**

Wolfgang Scherer, Andrew C. Dunbar, José E. Barquera-Lozada, Dominik Schmitz, Georg Eickerling, Daniel Kratzert, Dietmar Stalke, Arianna Lanza, Piero Macchi,* Nicola P. M. Casati, Jihaan Ebad-Allah, and Christine Kuntscher*

Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

Abstract: *Square-planar d^8-ML_4 complexes might display subtle but noticeable local Lewis acidic sites in axial direction in the valence shell of the metal atom. These sites of local charge depletion provide the electronic prerequisites to establish weakly attractive 3c–2e M···H–C agostic interactions, in contrast to earlier assumptions. Furthermore, we show that the use of the sign of the ^{1}H NMR shifts as major criterion to classify M···H–C interactions as attractive (agostic) or repulsive (anagostic) can be dubious. We therefore suggest a new characterization method to probe the response of these M···H–C interactions under pressure by combined high pressure IR and diffraction studies.*

The term anagostic interactions was coined in 1990 by Lippard and co-workers to distinguish sterically enforced M···H–C contacts (M = Pd, Pt) in square-planar transition-metal d^8 complexes from attractive agostic interactions.[1a] This classification raised the fundamental question whether axial M···H–C interactions in planar d^8-ML_4 complexes are a) repulsive anagostic 3c–4e M···H–C interactions[1] (Scheme 1 a) or b) attractive 3c–4e M···H–C hydrogen bonds[2] in which the transition metal plays the role of a hydrogen-bond acceptor (Scheme 1 b). The latter bonding description is related to another bonding concept that describes these M···H–C contacts in terms of c) pregostic or preagostic interactions[3] (Scheme 1 c), which are considered as being on the way to becoming agostic, or agostic of the weak type.[4]



Scheme 1. Orbital interaction schemes for the various types of M···H–C interactions.

In contrast to the first two types of interactions, which require the presence of a fully occupied and axially oriented $M(d_{z^2})$ orbital, preagostic interactions are considered to lack any involvement of d_{z^2} orbitals in M···H–C interactions and rely mainly on $M(d_{xz,yz})\rightarrow\sigma^*$(C-H) π-back-donation.[3b]

The first observation of unusual axial M···H–C interaction in planar d^8-ML_4 complexes was made by S. Trofimenko, who pioneered the chemistry of transition-metal pyrazolylborato complexes.[5,6] Trofimenko also realized in 1968, on the basis of NMR studies, that the shift of the pseudo axial methylene protons in the agostic species $[Mo\{Et_2B(pz)_2\}(\eta^3\text{-allyl})(CO)_2]$ (**1**) (pz = pyrazolyl; allyl = H_2CCHCH_2) is comparable in magnitude but different in direction from that observed in $Ni[Et_2B(pz)_2]_2$ (**2**) (Scheme 2).[6,7]

Indeed, the protons of the methylene group that forms a close M···C contact of 2.954(2) Å[8] in **1** resonate at −2.41 ppm at RT,[9] while the corresponding signal of the methylene protons of **2** occurs at 3.64 ppm (*q*, CH_2, $^2J_{H-H}$ 8 Hz) and does not show any coalescence upon cooling to −90 °C, despite large differences in the calculated chemical shifts[10a] of both methylene protons (Scheme 2). In contrast, the ^{1}H NMR signal of the agostic methylene protons in **1** splits into two features (−0.83 and −4.3) below −53 °C,[9] in agreement with the computed NMR properties of our static DFT model (1.4 and −5.88 ppm) for the agostic $Mo\cdots H_{ago}$–C and non-coordinating methylene proton, respectively (Scheme 2). Trofimenko concluded that the agostic proton in **1** displays a hydridic character and that the agostic proton of **1** is intruding into a suitable empty metal orbital.[6a] He

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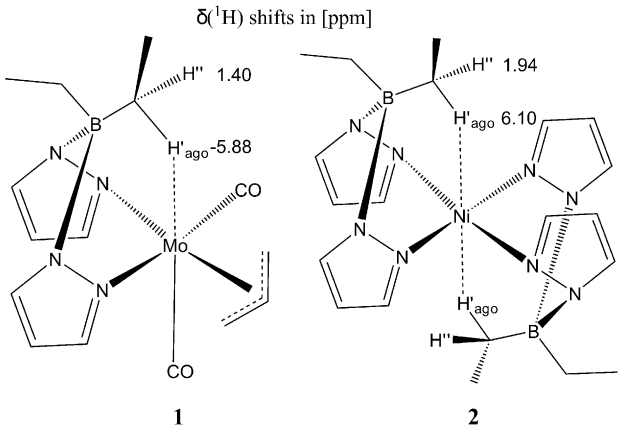

Scheme 2. Calculated ^{1}H chemical shifts of axial M···H–C interactions in the planar ML_4 complexes **1** and **2**.

therefore suggested that the M···H–C interactions in **1** is a bonding one causing an activation of the C–H bonds, as evident by the presence of CH stretch bands at remarkably low frequency of 2704 cm^{-1}.[6b] This concept was later developed and refined by Brookhart and Green, who coined the expression agostic for these kind of interactions.[11] According to the original criteria of Brookhart and Green, agostic interactions would be present in **1** but clearly absent in **2**, as the latter compound displays a pronounced δ(^{1}H) downfield shift in the case of the Ni···H–C coordinating methylene protons. This conclusion is also in accord with the structural study of **2** by Echols and Dennis in 1974, who concluded that steric restrictions dictate the conformation of the molecule, not an interaction of Ni with an apical H atom of one of the methylene groups of the pyrazolylborato ligand.[1b,12] A subsequent extended Hückel theory (EHT) study by Saillard and Hoffmann (SH)[1c] gave further evidence that the interaction between an axially approaching H–C ligand (for example, CH_4), and the d^8-ML_4 metal fragment might be actually even repulsive owing to the presence of a fully occupied and axially oriented M(d_{z^2}) orbital (Scheme 1 a).[1c] However, the nature of these d^8-M···H–C interactions and their description in terms of either a) anagostic interactions, b) hydrogen bonds, or c) pregostic interactions remains an ongoing matter of debate.[13] We will therefore outline in the following that all three bonding concepts (a–c; Scheme 1) basically rely upon an oversimplified description of the electronic situation in d^8-ML_4 complexes, which causes a misinterpretation of the fundamental C–H bond activation processes in these types of compounds.[13c]

We first reanalyze the potential energy surface (PES) of the σ model complex cation $[Co(CO)_4^+]\cdot[CH_4]$ (**3**) formed by methane and the positively charged d^8-$[ML_4]^+$ metal fragment. In line with the findings of Saillard and Hoffmann[3] (see above), the EHT-PES predicts a repulsive 3c–4e M···H–C interaction in the methane adduct **3**, which was selected by SH as benchmark model. In these model calculations one C–H moiety of the methane molecule was geometrically enforced to approach the square-planar d^8-$[ML_4]^+$ metal fragment in an axial coordination mode (Supporting Information, S2). However, considering electronic correlation effects by DFT methods reveals, in contrast to the EHT results, the actually attractive nature of the M···H–C interaction in this d^8-ML_4 benchmark system (Supporting Information, Figure S2a,b). The electronic situation of **3** is therefore characteristic for a H_3C–H···ML_4 σ complex, which at an early stage of the oxidative addition reaction coordinate exhibits a modest C–H activation owing to a covalent interaction between an occupied σ(C–H) orbital and a partially vacant metal orbital (Scheme 1 d).

Motivated by this result, we continue to reanalyze the electronic situation in **2** as a benchmark system of an uncharged d^8-ML_4 complex displaying an axial M···H–C interaction. Note that theoretical values will be specified in square brackets in the following. In the presence of a M-(d_{z^2})←σ(C–H) σ-type donation, as displayed by model complex **3** (Scheme 1 d), we would expect at least a subtle elongation of the bridging C–H bond. Indeed, **2** has a ν(C–H′$_{ago}$) stretching frequency at 2805 cm^{-1} [2878 cm^{-1}], which is clearly shifted to lower frequencies with respect to the ν(C–H″) stretching mode of 2864 cm^{-1} [2917 cm^{-1}] (Figure 2) of the non-coordinating methylene hydrogen atom of the same methylene group (Scheme 2). McKean's empirical correlation, which links r(C–H) bond lengths to isolated ν_{is}(C–H) stretching frequencies, predicts a slight activation of the C–H′$_{ago}$ bond (r(C–H′$_{ago}$) = 1.111 [1.108] Å) in comparison to its non-agostic reference moiety (r(C–H″) = 1.105 [1.104] Å).[14a,b] Thus, the bridging M···H–C moiety of **2** displays a minute, but noticeable C–H bond elongation which supports the presence of weak but attractive M-(d_z^2)←σ(C–H) interaction in **2**. Also in the case of our agostic benchmark system **1**, the observed (2704 cm^{-1}) and calculated (2709 cm^{-1}) ν(C–H) stretching modes of the Mo···H–C moieties are in agreement with a subtle C–H bond activation. Indeed, the theoretically predicted C–H′$_{ago}$ bond length of 1.128 Å is slightly longer than the non-coordinating C–H″ reference moiety (1.104 Å). Thus, the observed ν(C–H′$_{ago}$) stretching modes in the bridging M···H–C moieties of **1** and **2** fall into the typical range of complexes displaying weak agostic interactions; for example, in the β-agostic complexes $EtTiCl_3$(dmpe) (**4**, where dmpe = $Me_2PCH_2CH_2PMe_2$) (ν(C–H_{ago}) = 2585 cm^{-1}; r(C–H_{ago}) = 1.131 Å),[14c] and [CpTi-(iPr$_2$N)Cl$_2$] (**5**) (ν(C–H_{ago}) = 2716 cm^{-1}; r(C–H_{ago}) = 1.120 Å).[15]

To gain an even deeper insight into the nature of these subtle d^8-M···H–C interactions, we propose to analyze directly the chemical response of these d^8-M···H–C moieties upon shortening the respective M···H distances. Such a concept can be experimentally accomplished by combined X-ray diffraction (Figure 1) and IR spectroscopic (Figure 2) studies at various pressures. Figure 1 reveals that the M···C contacts between the metal and the coordinating methylene groups in **2** become significantly shortened with increasing pressure: r(M···C) = 3.18 [3.27] Å and 3.06 [3.14] Å at 0 and 5 GPa, respectively. Periodic DFT calculations[10b] also reveal that the respective M···H′$_{ago}$ distances are shortened upon increasing pressure (about 0.1 Å at 5 GPa: r(M···H) = 2.531 Å and 2.431 Å at 0 and 5 GPa, respectively). To study the pressure induced effect on the individual C–H bonds we also recorded IR spectra at approximately the same pressures as employed

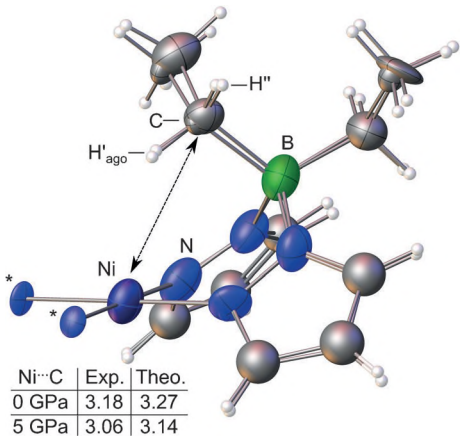

Figure 1. Overlay of structural fragments of **2** obtained by experimental X-ray diffraction studies at 0.0 and 5 GPa pressure using a diamond anvil cell (DAC); ellipsoids are set at 50% probability. For two of the nitrogen atoms (marked by ⋆) only the ellipsoids at 5 GPa were drawn to illustrate the significant reduction of thermal motion in **2** at elevated pressures. Values of the Ni···C distances are given in Å.

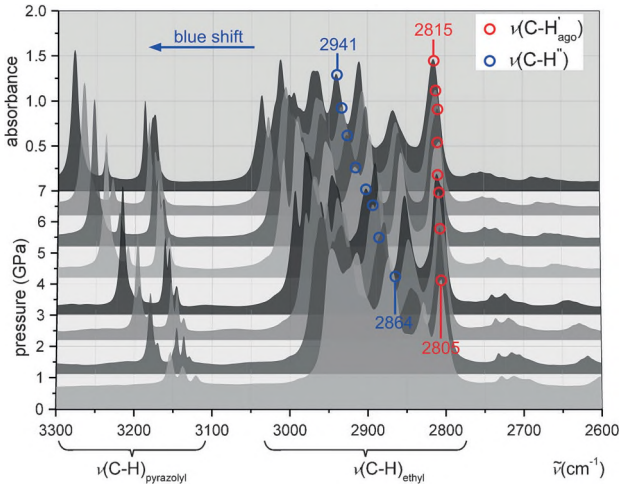

Figure 2. Pressure-dependency of the ν(C–H) stretching modes of the pyrazolyl and ethyl groups in **2**. All of these stretching modes display a blue-shift with increasing pressure but the agostic ν(C–H′$_{ago}$) mode of the metal-coordinated Ni···H′$_{ago}$–C moieties. This clearly signals the bonding character of these Ni···H′$_{ago}$–C interactions in **2**.

for the X-ray studies. Figure 2 clearly demonstrates that all ν(C–H) stretching modes of the pyrazolyl and ethyl groups in **2** are shifted to higher frequencies (blue-shifts), except for the ν(C–H′$_{ago}$) modes of the agostic Ni···H–C moieties, at increased pressure. This is in line with the theoretical predictions, which suggest that all C–H bonds of **2** display shorter lengths at elevated pressures, except for the agostic bonds: for example, *r*(C–H″) shrinks significantly by 0.09 Å, while the bond lengths of the agostic C–H′ moieties remain rather constant between 0.0 and 5.0 GPa. Accordingly, the corresponding ν(C–H′$_{ago}$) mode does not show any significant pressure dependency while the corresponding ν(C–H″) mode and all other ν(C–H) modes of **2** shift to higher frequencies (blue-shifted). The expected pressure-induced shortening of the C–H bonds in the agostic Ni···H–C moieties of **2** appears therefore to be equally balanced and compensated for by the increasing bond activation/elongation under pressure. Thus, shortening of the Ni···H bond distance in the agostic C–H groups activates the bridging C–H′$_{ago}$ in line with the attractive nature of these Ni···H–C bonds and their classification as M(d$_{z^2}$)←σ(C–H) σ-type agostic interactions. In the case where this type of interactions is more pronounced and/or further enhanced (for example by *M*(d$_{xz,yz}$)→σ*(C–H) back-donation), even a red-shift of the C–H′$_{ago}$ frequencies should be expected.

However, to characterize the nature of these agostic Ni···H′$_{ago}$–C interactions in **2** in terms of a M(d$_{z^2}$)←σ(C–H) σ-type donation process in our model system, we need to clarify whether the Ni(d$_{z^2}$) orbital can be considered as vacant or at least as a partially depleted acceptor orbital (Scheme 1 d). Indeed, analysis of the negative Laplacian of the experimental charge density distribution, $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$, in the valence shell of the metal atom of **2** clearly reveals the presence of a local charge depletion zone (denoted "CD" in Figure 3 c) in axial (*z*) direction (Figure 4 c). This $L(\mathbf{r})$ feature is in conformity with a partially vacant Ni(d$_{z^2}$) orbital, as the Laplacian is a well-established and experimentally accessible indicator to map regions of local charge concentration ($L(\mathbf{r}) > 0$).[16] The bond path between the σ-agostic hydrogen atoms and the metal center in **2** is thus an attractive donor interaction in the charge density picture (Figure 3). We note that an endocyclically curved M···H–C bond path topology

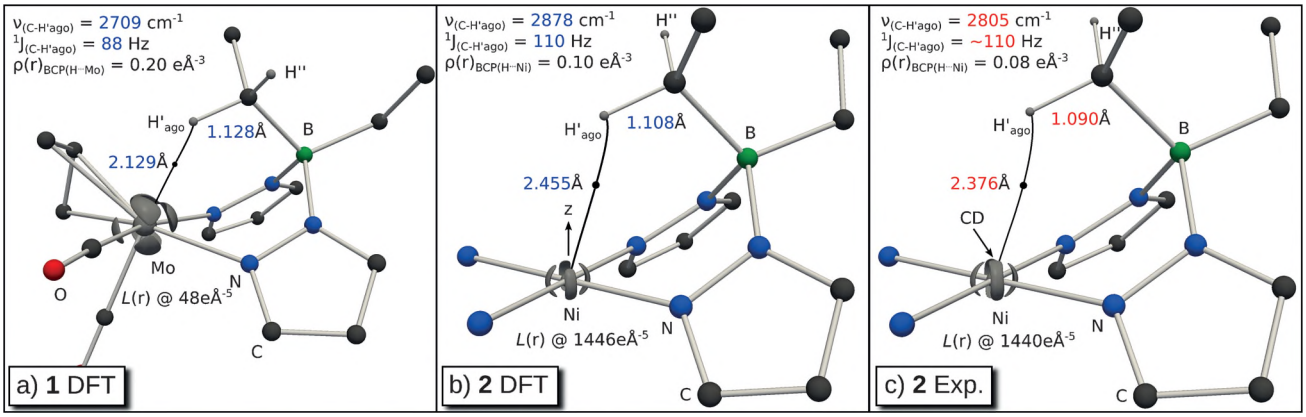

Figure 3. Theoretical and experimental $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ isocontour surface maps of complexes a) **1** and b,c) **2**. Only bond paths between the individual metal and agostic hydrogen (H′$_{ago}$) atoms are drawn.

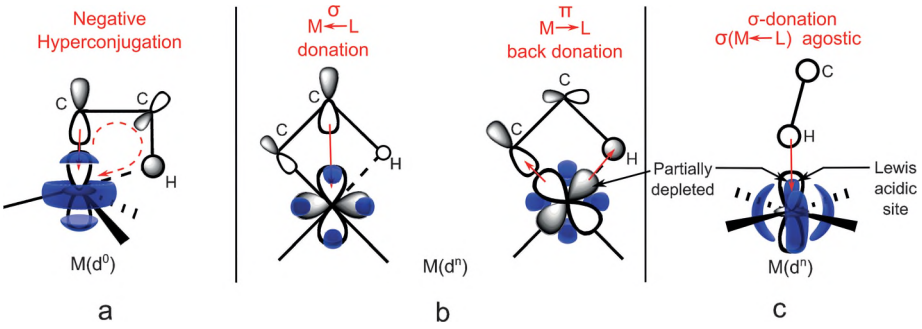

Figure 4. Three different types of agostic interactions in d^0 and d^n transition-metal complexes and their relevant molecular orbital contribution, which are directly linked with the $L(\mathbf{r})$ pattern (blue envelope maps) at the central transition-metal atoms (see also Ref. [17b]).

has been also experimentally observed in the case of β-agostic d^0 transition-metal alkyls (for example **4**; Figure 4a) and signals the electron-deficient nature of the respective M···H'_{ago}–C moieties in **2** and **4**.[17] Indeed, in both cases, the $M(d)\leftarrow\sigma(C\text{-}H)$ σ-type donation component is rather weak, as witnessed by the minute density accumulation in the M···H bonding domain (Figure 3). Accordingly, the electron density accumulation at the M···H'_{ago} bond critical point (BCP) in **2** is rather small ($\rho(\mathbf{r})_{exp} = 0.082(4)$; $\rho(\mathbf{r})_{calc} = [0.10]$ e Å^{-3}) and a BCP is even lacking in case of **4**.[18]

The weakness of the agostic interaction in **2** also becomes obvious by direct comparison with the d^8-Ni complex $[(DCpH)Ni(d^tbpe)]^+[BF_4]^-$ (**6**, DCpH = dicyclopentenyl),[19] which is our benchmark system for compounds displaying strong agostic interactions (Figure 4b): in that case the Ni···H BCP is well pronounced ($\rho(\mathbf{r}) = 0.553(4)$ e Å^{-3}), the Ni–H'_{ago} bond distance (1.671(9) Å) is significantly shorter than in **2** (2.376 Å), and the C–H activation is large (r(C–H) = 1.20(1) Å).[19] Apparently, complexes **2**, **4**, and **6** represent benchmark systems for three different scenarios of agostic interactions (Figure 4).

In the final step of our analysis, we will focus on the NMR properties of **1** and **2**, which display in ^{1}H NMR experiments rather different chemical shifts of the agostic protons (Scheme 2). The agostic protons in **1** are clearly shifted upfield ($\delta(^1H) = -5.88$ ppm) but downfield in **2** ($\delta(^1H) = +6.1$ ppm). However, the calculations show that the upfield/downfield shift of these agostic protons is not correlated with their "hydridic" character as originally proposed by Trofimenko[6a] and also postulated in the Brookhart and Green model[11] of agostic interactions. The agostic hydrogen atoms in **1** and **2** display both only small negative atomic charges and thus differ only marginally ($Q_{AIM,calc} = -0.14$ and -0.08 e, respectively). As outlined in greater detail recently,[13c] the chemical shifts of agostic protons in transition-metal alkyls rather depend on the polarization pattern of the valence shell density of the metal and/or the topology of the induced current density distributions in magnetic fields than on their hydridic character.[13c] In all of the agostic complexes studied so far by topological analyses of the charge and/or current density, pronounced upfield shifts are only observed when agostic C–H moieties are pointing toward a pronounced local Lewis acidic site in the valence shell of the metal atom.[17b]

Indeed, inspection of the Laplacian maps of **1** and **2** (Figure 3) reveals that only in case of **1** the agostic proton is intruding into a pronounced charge depletion zone, which represents a local Lewis acidic center in the charge density picture, or a vacant metal d-orbital in the MO model. A similar topological scenario is observed for the agostic protons in **2**; however, the axial Lewis acidic sites in the valence shell of the nickel atom are less pronounced relative to the d^4 complex **1**. Furthermore, the chemical shifts in planar d^8 complexes are also strongly influenced by the topology of the current density, which is dominant in the equatorial plane of square-planar d^8 complexes and thus causes a general deshielding of axially coordinating protons.[13c] Thus, the downfield chemical shift of the agostic proton in **2** does not rule out its agostic character. We therefore suggest that the sign of ^{1}H NMR shifts should not be used as major criterion to classify M···H–C interactions as attractive (agostic) or repulsive (anagostic). As outlined above, combined high-pressure IR and diffraction studies provide a more direct insight in the nature of these interactions, especially in combination with the analysis of the topology of the charge and current density.

In conclusion, we have unequivocally revealed that square-planar d^8-ML_4 complexes display subtle but noticeable local Lewis acidic sites in axial direction in the valence shell of the metal atom. These sites of local charge depletion provide the electronic prerequisites to establish weakly attractive 3c–2e M···H–C agostic interactions (Scheme 1d and Figure 4c), which are controlled by the extent of $M(d_{z^2})\leftarrow\sigma(C\text{–}H)$ donation. We therefore suggest that the expression "anagostic interactions", which describes M···H–C interactions in square-planar d^8-ML_4 in terms of repulsive 3c–4e interactions, should be used more carefully. Indeed, the latter bonding concept is based on a purely electrostatic description of M···H–C interactions in d^8-ML_4 complexes in terms of crystal field theory and ignores the consequences of strong covalent metal–ligand interactions that might induce local Lewis acidic sites in the valence shell of the metal in axial direction.

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Keywords: agostic interactions · bond activation · charge density · high pressure

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