

Characterisation of agostic interactions by a topological analysis of experimental and theoretical charge densities in [EtTiCl₃(dmpe)] [dmpe = 1,2-bis(dimethylphosphino)ethane]

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Topological analysis of the experimental and theoretical electron densities in [EtTiCl₃(dmpe)] (dmpe = Me₂PCH₂CH₂PMe₂) suggests the presence of a (3, -1) bond critical point (CP) between titanium and the β-agostic hydrogen atom; the characteristic curvature in the Ti–C_α bond is proposed as a more general criterion for identifying a β-agostic interaction.

Agostic interactions are of particular interest in organotransition-metal chemistry in view of their potential relevance to important processes like C–H activation. Reliable ways of pinning down these interactions are still at a premium, notwithstanding the numerous examples reported on the basis of structural or spectroscopic measurements or of theoretical studies. Theoretical considerations have led Popelier and Logothetis (PL) recently to suggest topological analysis of the charge density as a means of identifying agostic interactions.¹ We have tested this hypothesis on a real agostic system by analysing experimental and theoretical electron densities. The ethyltitanium trichloride complex [EtTiCl₃(dmpe)] **1** (dmpe = Me₂PCH₂CH₂PMe₂) was chosen since its β-agostic interaction has been delineated by a variety of independent techniques.²

Long X-ray exposure times hitherto needed for accurate charge density studies have prevented the study of labile organometallic compounds like **1**; with conventional serial data collection techniques using a single scintillation counter, data accumulation may take months. However, Luger and others have demonstrated very recently that charge density studies can be accomplished with exposure times in the order of days using a CCD detector.³ In our study we have been able to contrive short X-ray exposure times by combining two experiments using a CCD and an imaging plate detector system, both being connected to a rotating anode assembly providing highly intense

Mo-Kα radiation. Charge densities were derived from the experimental X-ray data† using the XD program suite⁴ based on a standard multipole model as formulated by Hansen and Coppens.⁵ Theoretical charge densities were determined by B3LYP DFT calculations⁶ using standard basis sets of triple-ζ quality plus polarisation.⁷ All such calculations were performed with the Gaussian94 package.⁸ The topological analysis of charge densities, based on Bader's 'Atoms In Molecules' (AIM) theory,⁹ was effected with the AIMPAC and XD suite.^{4,10}

While the geometrical parameters clearly indicate the presence of a β-agostic interaction in **1**: Ti–C 2.1522(9) [2.159], C–C 1.5117(12) [1.518], C_β–H_β 1.13 [1.13], Ti···H_β 2.10 [2.12] Å and Ti–C–C 84.5(1) [85.1]° (calculated values in square brackets), no significant charge accumulation between Ti and the C_βH_β unit is evident from the total electron density. More information can be gained from the *gradient vector field* ∇ρ(*r*) of the calculated and experimental electron density. Hence all bond critical points (CPs)‡ along the bond paths connecting the atoms in **1** can be located [Fig. 1(a,b) and Table 1].

At the bond CP of the C–C bond we determine an electron density (ρ_{b,calc} = 1.616 e Å⁻³), slightly higher than the corresponding value (1.606 e Å⁻³) for the C–C bond in ethane or EtTiCl₃, **2** (1.576 e Å⁻³), and significantly lower than that (2.326 e Å⁻³) for the C=C bond in ethene (Table 1). Since the magnitude of the charge density at the bond CP provides a sensitive measure of the bond strength, one might conclude that the C–C bond order in **1** is only slightly enhanced vs. **2**. However, the bond ellipticity parameter (ε)§ of the C–C bond in **1** clearly deviates from zero indicating some double bond character. This accords with the experimental observation of shorter C–C bond lengths in **1** vs. **2**,² and with the topology of the experimental electron densities (Table 1). Like the C–C bond, the agostic C–H_β bond in **1** combines the high electron

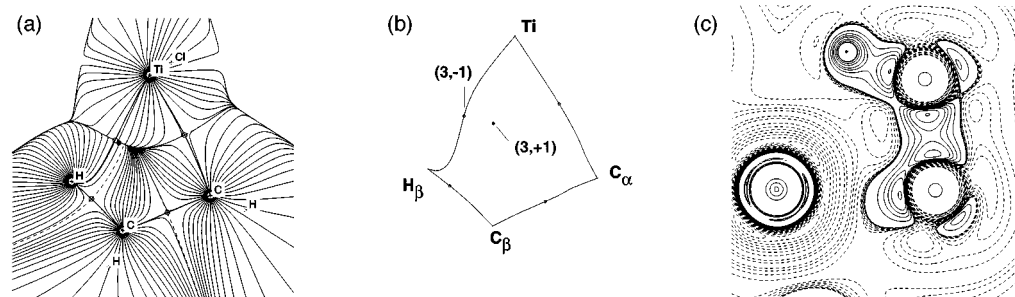


Fig. 1 (a) Calculated gradient vector field ∇ρ(*r*). Bond CPs are denoted by open circles and the ring CP by a filled circle; nuclei on the molecular plane are denoted by + while the projections of the out-of-plane nuclei are denoted by ∓. Inside the TiC_αC_βH_β four-membered ring all gradient paths originate at the (3, +1) ring CP and terminate either at the nuclei or at a (3, -1) bond CP (dashed lines). The gradient vectors linking the (3, -1) bond CP with the atoms constitute the bond paths (thick lines). (b) Bond paths in the TiC_αC_βH_β fragment based on experimental charge densities. (c) Experimental -∇²ρ(*r*) function in the TiC_αC_βH_β plane (negative values are marked by broken lines).¶

Table 1 Analysis of bond CPs (ρ in $e \text{ \AA}^{-3}$; ∇^2 in $e \text{ \AA}^{-5}$; distances in \AA , and angles in degrees) in EtTiCl_3 and $[\text{EtTiCl}_3(\text{dmpe})]$

Unit	Parameter	EtTiCl_3 DFT ^a	$\text{EtTiCl}_3(\text{dmpe})$ DFT	$\text{EtTiCl}_3(\text{dmpe})$ X-Ray
Ti–C $_{\alpha}$	Distance	2.042	2.159	2.1522(9)
	ρ_b	0.84	0.63	0.55(3)
	∇^2_b	0.28	1.5	3.09(5)
	ϵ	0.02	0.06	0.16
C–C	Distance	1.529	1.518	1.5117(12)
	ρ_b	1.58	1.62 ^b	1.90(4) ^c
	∇^2_b	–12.1	–12.4 ^b	–18.7(1) ^c
	ϵ	0.04	0.1 ^b	0.02 ^c
C–H $_{\beta}$ ^d	Distance	1.096	1.132	1.132
	ρ_b	1.83	1.67	1.52(5)
	∇^2_b	–21.5	–17.6	–12.6(2)
	ϵ	0.01	0.0	0.12
Ti \cdots H $_{\beta}$ ^d	Distance		2.118	2.096
	ρ_b		0.212	0.17(1)
	∇^2_b		3.3	1.67(1)
	ϵ		11.28	0.70
ring CP	ρ_r		0.213	0.16(2)
	∇^2_r		3.5	3.00(2)
Ti–C–C	Angle	116.68	85.1	84.5(1)

^a Geometry optimisations in C_s symmetry. ^b Standard (ρ_b , ∇^2_b , ϵ) values for ethane and ethene at the same level of theory: 1.606, –13.3, 0.0 and 2.326, –24.906 and 0.34, respectively. ^c Corresponding values of the C–C bond in the dmpe backbone: 1.76(2), –15.42(6), 0.06. ^d β -hydrogen atom in the $\text{TiC}_{\alpha}\text{C}_{\beta}$ plane.

density at the bond critical point ($\rho_{b,\text{calc}} = 1.67 e \text{ \AA}^{-3}$) and the large *negative* value of the Laplacian ∇^2 ($\nabla^2\rho_{b,\text{calc}} = -17.6 e \text{ \AA}^{-5}$) characteristic of covalent bonds [Fig. 1(c)]. The topologies of the Ti–C $_{\alpha}$ and Ti \cdots H $_{\beta}$ interactions are, however, different; in each case the electron density at the bond CP ($\rho_{b,\text{calc}} = 0.63$ and $0.21 e \text{ \AA}^{-3}$) is rather low, and the Laplacian ($\nabla^2\rho_{b,\text{calc}} = 1.5$ and $3.3 e \text{ \AA}^{-5}$) is *positive*.

Similar topologies were found for the corresponding bonds in the agostic model compound EtTiCl_2^+ **3** studied by PL, who invoked an ionic, closed shell Ti \cdots H $_{\beta}$ interaction.¹ It would seem better to make the distinction between covalent and ionic bonds on the basis of the wavefunction.¹¹ Compared with **3**, the β -agostic interaction in **1** is significantly weaker,² and closer inspection of the gradient vector field indicates that the Ti \cdots H $_{\beta}$ bond CP and the ring CP in **1** are proximal and not very pronounced. The electron densities calculated for the Ti \cdots H $_{\beta}$ bond CP and the ring CP inside the $\text{TiC}_{\alpha}\text{C}_{\beta}\text{H}_{\beta}$ fragment are nearly identical, differing not significantly by $<0.001 e \text{ \AA}^{-3}$. Simultaneously the negative curvature (λ_2) at the bond CP associated with the axis directed at the ring CP almost vanishes. Thus, the bond and ring CPs almost merge into a singularity in ρ , a phenomenon characteristic of bond fission. This conclusion accords with our experimental findings, showing the gradient path between the ring and the Ti \cdots H $_{\beta}$ bond CPs to be extremely flat. We expect therefore that Ti \cdots H bond CPs may not always be found in molecules where the agostic interaction is weaker than in **1**.

However, a further characteristic of the agostic interaction manifests itself in the gradient vector map $\nabla\rho(\mathbf{r})$ as significant curvature in the Ti–C $_{\alpha}$ bond path (Fig. 1a,b). This follows the ridge of maximum charge density between a pair of bonded nuclei, the bond CP of the Ti–C bond is displaced outwards by 0.06 \AA from the $\text{TiC}_{\alpha}\text{C}_{\beta}\text{H}_{\beta}$ ring. Such behaviour complies with the conclusions of a previous theoretical study,² namely that the M–C $_{\alpha}$ bonding electrons in **1** are delocalised over the entire ethyl group, reduction of the TiCC valence angle permitting Ti to establish a significant covalent interaction with C $_{\beta}$, and perhaps to a lesser extent with H $_{\beta}$. The consequence is a bent Ti–C $_{\alpha}$ bond path. Inspection of the Ti–C $_{\alpha}$ bond path of **1** and all the model agostic systems suggested by PL¹ reveals in every case curvature of the Ti–C $_{\alpha}$ bond. Moreover, the agostic C $_{\beta}$ –H $_{\beta}$ bonds are bent away from the metal centre. Thus, the bond CP of the C $_{\beta}$ –H $_{\beta}$ bond is displaced inside the formal $\text{TiC}_{\alpha}\text{C}_{\beta}\text{H}_{\beta}$ ring, a result in keeping with the calculated C $_{\alpha}$ –C $_{\beta}$ –H $_{\beta}$ angle

which is always several degrees larger than the normal value (*ca.* 109°).

In conclusion, we have shown that experimental electron densities can be obtained for a labile transition-metal complex using now-standard laboratory technology and near-normal data acquisition times. Some agostic interactions may be identified solely on the basis of charge densities, but the non-linearity of the Ti–C $_{\alpha}$ bond probably offers a more robust criterion of β -agostic interaction.

Notes and references

† *Crystal data* for $[\text{EtTiCl}_3(\text{dmpe})]$: $\text{C}_8\text{H}_{21}\text{P}_2\text{Cl}_3\text{Ti}$, $M = 333.4$, red rhombic crystals; monoclinic, space group $P2_1/n$, $a = 782.95(2)$, $b = 1611.04(2)$, $c = 1182.16(3) \text{ pm}$, $\beta = 91.613(1)^\circ$, $V = 1490.54(6) \times 10^6 \text{ pm}^3$; $T = 105(1) \text{ K}$; $Z = 4$, $F(000) = 688$, $D_c = 1.495 \text{ g cm}^{-3}$, $\mu = 13.0 \text{ cm}^{-1}$, 35928 (16334) Bragg reflections with $\sin\theta/\lambda_{\text{max}} = 1.097 (0.66) \text{ \AA}^{-1}$ were collected on a kappa-CCD system from Nonius [image plate system from Stoe (IPDS)] with a rotating anode generator (Nonius FR591; Mo–K α , $\lambda = 0.71073 \text{ \AA}$) within 48 (32) h. 13425 (CCD data set) and 3205 (IPDS data set) independent reflections; $R_{\text{int}} = 0.029$ (CCD)/0.025 (IPDS). The deformation density was described by a multipole model in terms of spherical harmonics multiplied by Slater-type radial functions with energy-optimised exponents.¹² The multipole expansion was terminated at the hexadecapolar and dipolar level for the heavy and hydrogen atoms, respectively. The C–H bond distances were constrained to the calculated values. The refinement of 434 parameters against 13241 observed reflections [$F > 3\sigma(F)$] converged to $R = 0.027$, $R_w = 0.037$, and a featureless residual $\rho(r)$. CCDC 182/1048.

‡ (3, –1)/(3, +1) CPs: two curvatures are negative/positive and ρ is a maximum/minimum at the CP in the plane defined by the axes corresponding to the negative/positive curvatures. ρ is a minimum/maximum at the CP along the third axis which is perpendicular to this plane.

§ The ellipticity ϵ ($\epsilon = \lambda_2/\lambda_1 - 1$) of a bond is a measure of the asymmetry between the two principal curvatures (λ_1, λ_2) of ρ at the bond CP perpendicular to the bond.

¶ Values of $\nabla^2\rho(\mathbf{r}) < 0$ indicate that charge is locally concentrated at \mathbf{r} , while positive $\nabla^2\rho(\mathbf{r})$ values are characteristic of regions suffering local charge depletion.

- 1 P. L. A. Popelier and G. Logothetis, *J. Organomet. Chem.*, 1998, **555**, 101.
- 2 W. Scherer, T. Priemer, A. Haaland, H. V. Volden, G. S. McGrady, A. J. Downs, R. Boese and D. Bläser, *Organometallics*, 1998, **17**, 4406 and references quoted therein.
- 3 See for example: T. Koritsanszky, R. Flaig, D. Zobel, H.-G. Krane, W. Morgenroth and P. Luger, *Science*, 1998, **279**, 356; P. Macchi, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1998, **120**, 1447.
- 4 T. Koritsanszky, S. Howard, P. R. Mallinson, Z. Su, T. Richter and N. K. Hansen, XD—a Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data, Free University of Berlin, 1997.
- 5 N. K. Hansen and P. Coppens, *Acta Crystallogr., Sect. A*, 1978, **34**, 909.
- 6 The ED of **1** was discussed on the basis of the B3LYP//BPW91 level of theory.
- 7 A. J. H. Wachters, *J. Chem. Phys.*, 1970, **52**, 1033; A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639; R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650; A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111.
- 8 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian 94, Revision C.2 and E.2, Gaussian, Inc., Pittsburgh PA, 1995.
- 9 See, for example: R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990.
- 10 R. F. W. Bader, *Acc. Chem. Res.*, 1985, **18**, 9.
- 11 J. Cioslowski and S. T. Mixon, *Inorg. Chem.*, 1993, **32**, 3209.
- 12 E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, 1974, **14**, 177.