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Agostic interactions in organometallic compounds. A Cambridge Structural Database study †

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Agostic interaction geometries, C–H ··· M (M = Li, Group 4 or 5 transition metal or other), have been investigated with data retrieved from the Cambridge Structural Database. Analysis of both neutron- and X-ray-derived structures shows that a strengthening of the H ··· M agostic bond is accompanied by a corresponding weakening of the C–H bond. A similarity in behaviour of Li to the heavier transition metals is observed in these agostic interactions. Di- and tri-bridged C–H ··· Li geometries involving alkyl groups occur in both intra- and inter-molecular cases.

Agostic interactions of C–H bonds with electron-deficient metals have been well studied using crystallographic and spectroscopic techniques.[2] The strengths of these interactions are estimated to be of the order of 30–60 kJ mol^{-1}, comparable to those of conventional hydrogen bonds (10–65 kJ mol^{-1}).[3] Agostic interactions are three-centre two-electron interactions (3c-2e). Recently, it has also been found that electron-rich or late transition metals can act as proton acceptors to form 3c-4e interactions, that is hydrogen-bond-like interactions with O–H, N–H and C–H groups.[4]

In agostic interactions lengthening of the C–H bond will occur if the back bonding from the metal atom (d_π) to the C–H group (σ^*) is strong. The acidity and electrophilicity of the C–H group will also increase due to this back bonding. To determine the kinetic pathway of these interactions, Crabtree and co-workers[5] studied a series of structures of complexes containing C–H ··· M interactions by the method of structure correlation and proposed that the C–H bond initially approaches the metal atom with a C–H ··· M angle of around 130°, resulting in a strong M–H interaction. The C–H bond then rotates, bringing the carbon atom close to the metal centre, preparing it for oxidative addition.[6]

Organolithium complexes are known to form short H ··· Li contacts with C–H bonds. These C–H ··· Li interactions play an important role in stabilising the crystal structures of some compounds like $LiBMe_4$, LiMe, LiEt, and cyclohexyllithium.[7] Theoretical studies on these interactions suggest that, although the primary reason for these short C–H ··· Li contacts is ionic, the overlap of the lithium orbitals with the carbon lone pair and those with the σ-C–H orbitals play a non-negligible role.[8,9] These studies also show that a C–H bond lengthening occurs when there are several C–H ··· Li contacts close to right angles.

Our attention was drawn to these bonding interactions during our ongoing study of hydrogen bonding in organometallic crystals[1,10] using the Cambridge Structural Database (CSD).[11] The importance of the CSD in exploring hydrogen-bonding interactions like O–H ··· O, N–H ··· O and C–H ··· O is well known in the field of structural organic chemistry.[5] Though the agostic interaction is different from a hydrogen bond, in that it is a 3c-2e rather than a 3c-4e interaction, it can be similarly approached with the CSD.

In this paper we report the results of CSD studies on agostic interactions in Group 4, 5 and lithium complexes. In particular, we discuss the lengthening of the C–H bond with H ··· M shortening and the similarity in behaviour of C–H ··· Li to C–H ··· M interactions.

Experimental

Data were retrieved from the 1995 update of Version 5.09 of the CSD (137 527 entries) for all ordered crystal structures with an exact match between chemical and crystallographic connectivity and containing at least one of the Group 4 or 5 metal atoms. Only entries where $R \leqslant 0.075$ and where atomic coordinates are given were considered. A *bona fide* agostic interaction was considered to be one where the H ··· M distance is between 1.80 and 2.50 Å. Structures in which the metal atoms have more than 16 electrons were removed manually.[2] Lithium-containing structures were retrieved separately with the all above constraints and with a C–H ··· Li contact assumed when the H ··· Li distance lies between 1.80 and 2.20 Å.

One of the main problems in the crystallographic study of hydrogen bonding is the lack of accuracy in the determination of the position of the most important atom in the bond, namely hydrogen. This is an even greater impediment in the study of agostic interactions, wherein the H atom is situated close to a heavy metal atom. Two approaches are commonly used in hydrogen-bonding studies to minimise this problem. With these approaches we attempt to obtain both accuracy and generality. The first is to consider only neutron structures and the second is to normalise the X-ray-derived H atom position along the X–H vector such that the X–H values corresponds to the neutron-derived values. Neither of these approaches, when taken alone, is fully satisfactory in the study of agostic interactions. The first approach is of very limited applicability because the number of pertinent neutron diffraction structures is small. Normalisation of H atom positions as obtained in an X-ray analysis is not really justified because these positions are subject to considerable variations by the very effect which is being studied, namely the agostic effect. So in the present study we first analysed all available neutron-diffraction structures (irrespective of the metal atom) and then considered X-ray diffraction structures (containing Group 4 and 5 metals) with $R \leqslant 0.075$ *without* normalising the H atom positions. Before an X-ray-diffraction structure was accepted for the analysis the method of location and refinement of the H atom positions and their estimated standard deviations (e.s.d.s) were scrutinised in the original papers. It was found that in almost all the structures of

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† Hydrogen bonding in organometallic crystals. Part 5.[1] *Supplementary data available* (No. SUP 57166, 14 pp): CSD quest and summary files, scattergrams. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Table 1 Mean geometrical parameters for C–H ··· M interactions in Group 4, 5 and lithium complexes

M	H ··· M/Å	C ··· M/Å	C–H ··· M/°	No. of hits	No. of compounds
Ti	2.36(2)	2.20(4)	68(3)	30	20
Zr	2.32(2)	2.53(5)	93(5)	26	21
Hf	2.28(5)	2.29(3)	79(3)	7	6
V	2.33(3)	2.37(8)	83(7)	23	16
Nb	2.35(4)	2.24(4)	72(5)	7	4
Ta	2.28(4)	2.10(3)	67(2)	23	16
Li (intramolecular)	2.07(1)	2.34(1)	94(1)	77	36
Li (intermolecular)	2.09(1)	2.35(3)	93(3)	26	10

Table 2 Geometrical parameters for C–H ··· M interactions in neutron-derived structures

Compound	T/K	C–H/Å	H ··· M/Å	C ··· M/Å	C–H ··· M/°	Ref.
$[Ni(\eta^3\text{-}C_3H_5)_2]$	100	1.094(2)	2.466	2.026	54.0	12
		1.090(2)	2.452	2.030	54.8	
$[TiMeCl_3(dmpe)]$ *	20	1.095(2)	2.448	2.123	60.0	13
$[Fe_4H(\eta^2\text{-}CH)(CO)_{12}]$	26	1.190(4)	1.754	1.927	79.2	14
		1.175(5)	1.747	1.921	79.6	
$[Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)]$	20	1.134(5)	2.041	1.946	68.9	15
$[Ta_2Cl_2(\mu\text{-}Cl)_2(CHCMe_3)_2(PMe_3)_2]$	110	1.131(3)	2.120	1.898	63.1	16
$[Fe\{P(OMe)_3\}_3(\eta^3\text{-}C_8H_{13})]^+[BF_4]^-$	30	1.165(3)	1.873	2.362	99.4	17

The values in the parentheses are the e.s.d.s of the C–H distances which were taken from the original structural papers. * dmpe = $Me_2PCH_2CH_2PMe_2$.

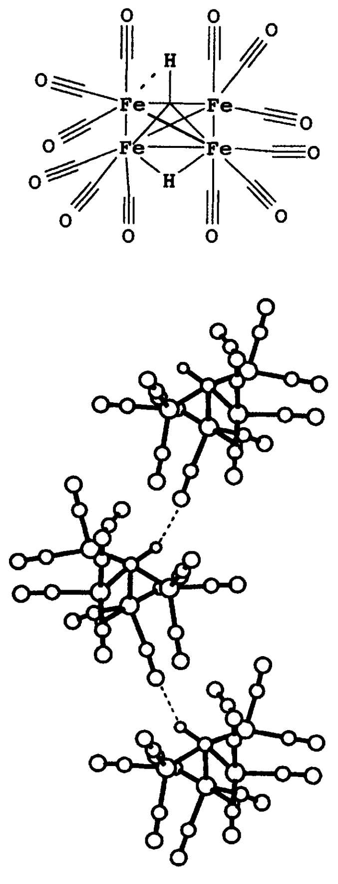


Fig. 1 The C–H ··· O hydrogen-bond network and C–H agostic bond in the neutron-derived crystal structure of $[Fe_4H(\eta^2\text{-}CH)(CO)_{12}]$

Ta and Zr the H atom positions had been located from Fourier-difference maps and refined isotropically. The e.s.d.s of these H atoms have been published in only a few cases but all were found to be satisfactory. Geometrical calculations were performed separately for each metal atom using QUEST3D-GSTAT, an automatic graphics non-bonded search program of the CSD. Geometrical questions constructed for the tantalum case are given in SUP 57166 as a representative example.

Results and Discussion

All average structural parameters from the CSD search for the Group 4, 5 metals and Li are given in Table 1. Plots of C–H ··· M angle *versus* H ··· M distance for M = Ti, Nb or Y and summary files for all the metals have been deposited (SUP 57166).

For neutron-diffraction structures there is a total of six compounds which contain eight agostic interactions C–H ··· M (M = Ti, Ni, Fe or Ta).[12–17] Of these eight agostic interactions, four each are formed by sp^2 and sp^3 C–H groups. The geometrical parameters are given in Table 2. Both α- and β-agostic interactions are found in this group. There are two agostic interactions in $[Fe_4H(\eta^2\text{-}CH)(CO)_{12}]$, corresponding to the two molecules in the asymmetric unit. Here, the C atom of the C–H group which forms the agostic interaction bridges the four Fe atoms in a μ_4 fashion. In addition to this agostic interaction, the C–H group is also involved in an intermolecular C–H ··· O hydrogen bond with one of the C≡O ligands (Fig. 1).

In principle, several geometrical parameters may be used to monitor the efficacy of the agostic interaction. The C, H and M atoms may be considered as forming a triangular array. The dimensions of any triangular array may be defined by three geometrical parameters (one or more distances and two or less angles). The choice of which parameters are to be used is based on their chemical usefulness. Here we have chosen the C–H and H ··· M distances and the C–H ··· M angle.

Fig. 2(*a*) is a plot of H ··· M distance *versus* C–H distance for the eight agostic interactions retrieved. The correlation between these parameters is excellent and shows that as the H ··· M separation decreases the C–H bond is weakened. In order better to compare these H ··· M distances which arise from different metals, the atomic radius of the particular metal (M = Ta, 1.47; Fe, 1.26; Pt, 1.39; Ti, 1.47; and Ni, 1.25 Å)[18] can be subtracted from the corresponding H ··· M distance. When these distance differences were plotted *versus* the C–H distances [Fig. 2(*b*)] a

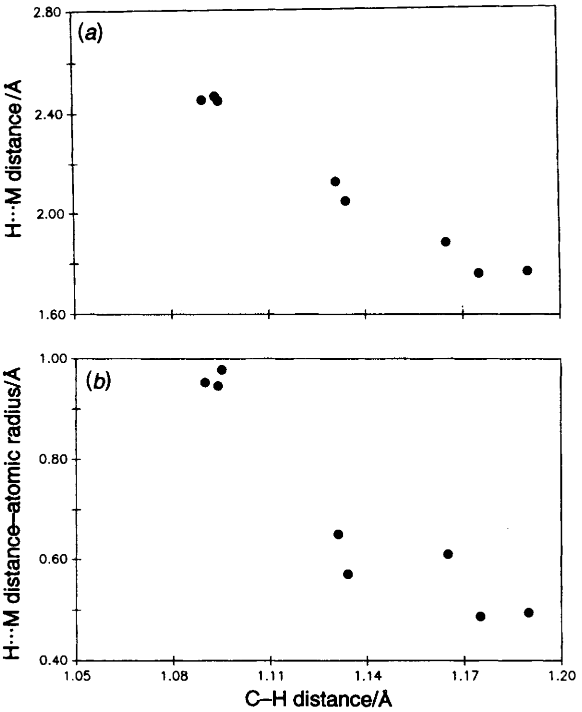


Fig. 2 (*a*) Plot of H···M distance *versus* C–H distance for eight neutron-derived C–H···M agostic geometries. (*b*) Plot of the difference values (H···M − atomic radius of M) *versus* C–H distance for eight neutron-derived C–H···M agostic geometries. A strengthening of the H···M interaction is accompanied by a weakening of the C–H bond

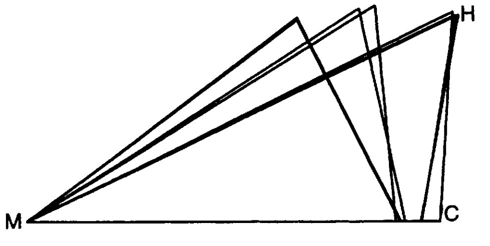


Fig. 3 Superposition plot of the seven C–H···M α-agostic bonds in Fig. 2. The metal atom is at the origin and the M–C vector along the *x* axis

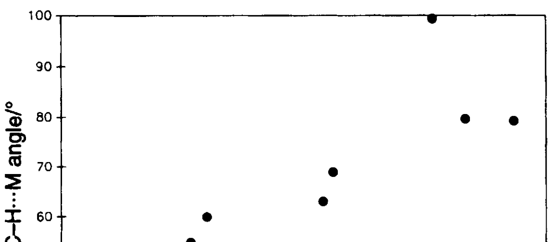
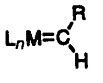


Fig. 4 Plot of C–H···M angle *versus* C–H distance for neutron-derived agostic geometries

behaviour similar to that seen in Fig. 2(*a*) was found. Fig. 2(*a*) and 2(*b*) therefore represent a structure correlation[5] of the breaking of the C–H bond by an adjacent electron-deficient metal atom and its general appearance is similar to structure-correlation diagrams of the O–H···O[19] and N–H···N[20] interactions wherein a shortening of one of the bonds formed by the H atom is accompanied by a concomitant lengthening of the other. Yet it must again be emphasised that the nature of the agostic interaction, C–H···M, which involves an electron-rich species (the C–H bond) and an electron-deficient species (the M atom) is quite different from that of a hydrogen bond, A–H···B, which may be viewed, in the broadest sense, as the positioning of an electron-deficient H atom between two electron-rich atoms, A and B.[1,10] Fig. 3 which is an overlap diagram of the C, H and M atom positions in these structures, shows that the C–H···M angle increases with a strengthening of the agostic H···M bond (and the weakening of the C–H bond). To summarise, Figs. 2(*a*), 2(*b*) and 3 are representations of the trajectory of the H atom as it moves between the C and M atoms.



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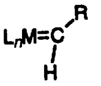

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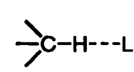
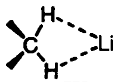


III



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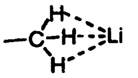


V

While the neutron results are adequate in themselves, it would be much more satisfying if the CSD-based approach could also be applied to the more numerous and variegated X-ray-derived structures available which contain agostic interactions. The main problem with such an extrapolation, from neutron- to X-ray-derived information, is the inaccuracy in the determination of H atom positions in X-ray studies. Therefore a direct correlation between C–H and H···M distances cannot be attempted. Even so, it may be observed from the neutron-derived data (Fig. 4) that the C–H distances and C–H···M angles are linearly correlated. The errors associated with the C–H···M angles are expected to be lower than those associated with the C–H distances because the C–H vector direction is determined more exactly than the C–H distance. The H···M distances were therefore plotted *versus* C–H···M angles in Fig. 5(*a*).

Fig. 5(*a*) is a plot of these X-ray-derived parameters for the 26 and 23 agostic interactions formed by Zr and Ta atoms respectively. It shows two populations for tantalum complexes. One of them contains seven data points from five compounds and lies roughly along the lower diagonal and shows a greater shortening of the H···Ta distance.[15,21–24] Interestingly, all these points represent agostic interactions formed by the neopentylidene moiety, =CHCMe$_3$. The geometrical parameters for these compounds are given in Table 3. It is known that in these complexes the expected carbene geometry **I** is distorted to **II** with remarkably small M–C–H angles as low as 78°, and correspondingly large M–C–C angles as high as 170°. Theoretical calculations on these systems show C–H bond activation and carbene pivoting with the bulky substituents on both the C atom of the carbene and that the metal atom is responsible for these distortions.[25] Fig. 5(*b*) is a neutron-derived crystal structure of the complex $[\mathrm{Ta}(\eta^5\text{-}\mathrm{C}_5\mathrm{Me}_5)(\mathrm{CHCMe}_3)(\eta^2\text{-}\mathrm{C}_2\mathrm{H}_4)(\mathrm{PMe}_3)]$ showing the C–H···Ta interaction and geometry of the neopentylidene moiety.

The upper diagonal corresponds to 'weaker' agostic interactions, and the points are not so tightly bunched. This region contains agostic C–H groups in a variety of chemical environments. For zirconium complexes all 26 points correspond to the 'weaker' population but even here the correlation between C–H···Zr and H···Zr is quite satisfactory. It may be noted that an analysis of X-ray-derived geometries in Fig. 5(*a*) is almost as reliable as the neutron analysis in Fig. 2.

Carbon–hydrogen–lithium interactions

We extend our analysis to intra- and inter-molecular C–H···Li interactions which have been recognised as the lithium-analogues of the C–H···M agostic bond.[9] The Li

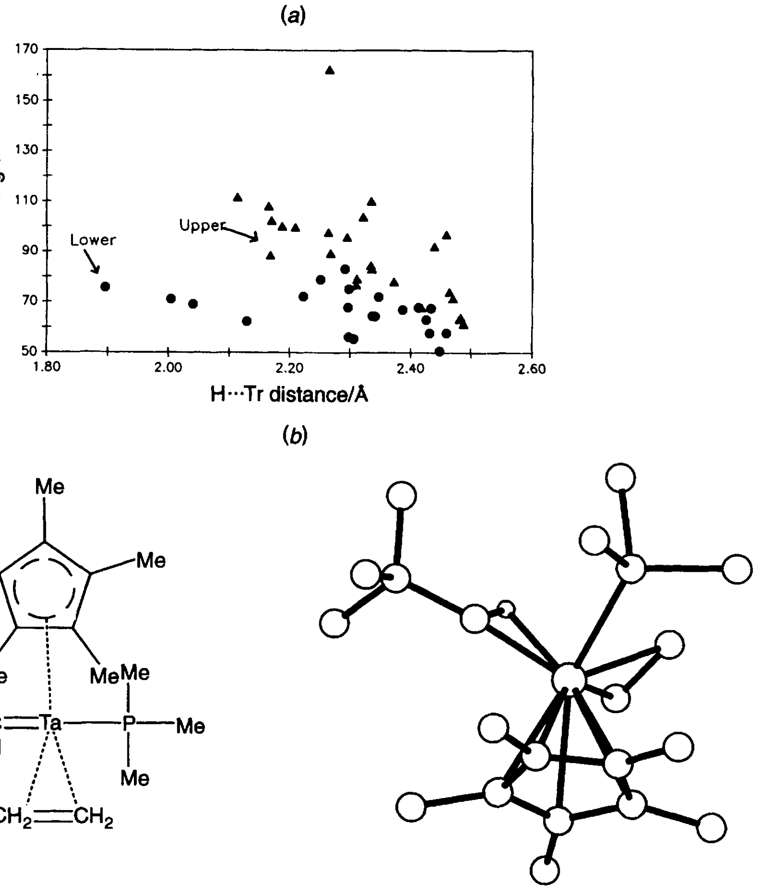
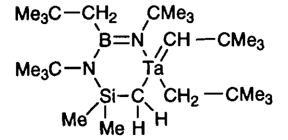


Fig. 5 (*a*) Plot of C–H ··· M angle *versus* H ··· M distance for 26 and 23 X-ray-derived agostic geometries of zirconium (▲) and tantalum (●) complexes. Note the two populations for the tantalum complexes. (*b*) Plot of the neutron-derived crystal structure of the complex [Ta(η^5-C_5Me_5)($CHCMe_3$)(η^2-C_2H_4)(PMe_3)]. Notice the distortion in the Ta–C–H and Ta–C–C angles. Only the hydrogen atom which is involved in the agostic interaction is shown. All the remaining hydrogen atoms are omitted for clarity

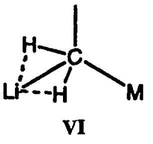
Table 3 Geometrical parameters for C–H ··· M interactions with the neopentylidene C–H group in tantalum complexes

Compound	H ··· M/Å	C ··· M/Å	C–H ··· M/°	Ref.
[Ta($CHCMe_3$)(CH_2CMe_3)(PMe_3)$_2$(μ-N_2)]	2.31	1.93	55.5	21
	2.30	1.94	56.2	
[Ta(η^5-C_5Me_5)(CH_2SiMe_3)$_2$($CHSiMe_3$)]	2.43	2.17	63.0	23
	2.00	1.92	71.1	
[$TaCl_2${$C_6H_3(CH_2NMe_2)_2$-2,6}($CHBu^t$)]	1.90	1.94	75.6	23
[Ta(η^5-C_5Me_5)($CHCMe_3$)(η^2-C_2H_4)(PMe_3)]	2.04	1.95	68.9	15
	2.13	1.89	62.2	24

atom can bind a C–H bond in the three types of structural configurations **III–V**, *i.e.* mono-, di- and tri-bridged. The last two geometries are not found in the Group 4 and 5 transition-metal complexes.

There are 77 intramolecular C–H ··· Li agostic geometries in 36 X-ray-derived crystal structures with the H ··· Li distance less than 2.20 Å. In these structures, 10 compounds form a dibridged configuration and none a tribridged C–H ··· Li geometry.[26–35] Relevant geometrical parameters for these 10 compounds are given in Table 4. In five the C–H ··· Li interactions are formed by a CH_2 group which acts as a bridge between Li and M (Er, Ga, Al, Cr, Si), **VI**. The bridging of the alkyl group between Li and M may be stablised by these C–H ··· Li interactions.

Fig. 6 is a plot of C–H ··· Li angles *versus* H ··· Li distances for the 77 intramolecular C–H ··· Li geometries. The correlation holds good at shorter distances (*i.e.* up to 2.10 Å) but



VI

it is less obvious at longer distances. It is evident from Figs. 5 and 6 that the geometries of C–H ··· M and C–H ··· Li are identical. The similarity in behaviour of Li to the heavier transition metals in these agostic bonds is noteworthy and in the extreme of the H atom trajectory it is known that alkyllithium compounds, RCH_2Li, thermally decompose to LiH and alkenyl derivatives.[8] The dibridged C–H ··· Li geometries are similar to that of monobridged geometries unlike the bifurcated hydrogen bonds in which the average geometry of the bifurcated hydrogen bond differs from that of non-bifurcated hydrogen bonds.[9]

Intermolecular C–H ··· Li contacts are less common than the intramolecular ones. There are 26 from 10 compounds for intermolecular interactions. Fig. 7 shows a plot of C–H ··· Li angles *versus* H ··· Li distances for these. The geometries of the intermolecular interactions are similar to those of the intramolecular C–H ··· Li interactions. Intermolecular dibridged geometries were found in three structures.[35–37] Relevant geometrical parameters are given in Table 5. The tribridged geometry is found in only one structure, $LiBMe_4$. This structure was confirmed in both X-ray and neutron diffraction studies. Fig. 8 is the neutron-derived structure of this compound. The BMe_4 units are linked together by one tri- and two di-bridged C–H ··· Li geometries to form a linear chain.

Conclusions

This work is a demonstration that a strengthening of the H ··· M (M = Li or transition metal) agostic bond is systematically accompanied by a weakening of the corresponding C–H bond. The dynamic profile of the C–H ··· M trajectory, conveyed by a simultaneous examination of geometries from several crystal structures, may be extrapolated

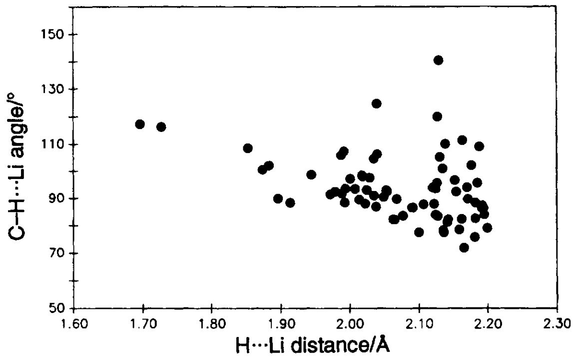


Fig. 6 Plot of intramolecular C–H ··· Li angle *versus* H ··· Li distance for 77 X-ray-derived agostic geometries. Notice the similarity between Figs. 5 and 6

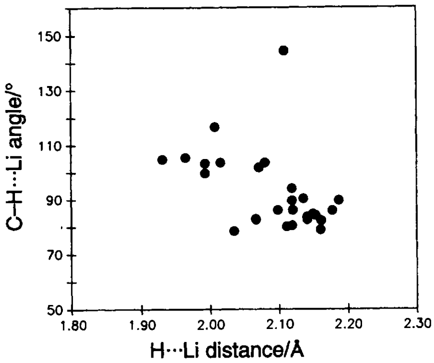
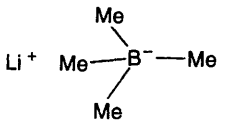


Fig. 7 Plot of intermolecular C–H ··· Li angle *versus* H ··· Li distance for 26 X-ray-derived agostic geometries. Notice the similarity between Figs. 6 and 7



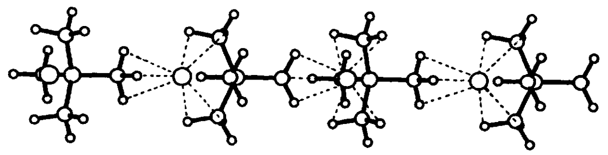
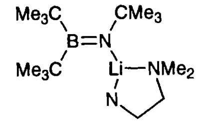
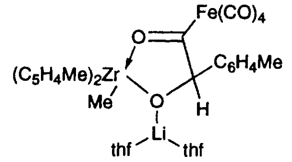
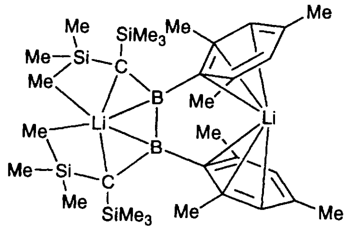


Fig. 8 Plot of the C–H ··· Li agostic bond network in the neutron-derived crystal structure of $LiBMe_4$. Notice the tri- and di-bridged C–H ··· Li geometries

Table 4 Geometrical parameters for dibridged C–H ··· Li intramolecular interactions in lithium complexes

Compound	Li ··· H¹/Å	Li ··· H²/Å	C ··· Li/Å	C–H¹ ··· Li/°	C–H² ··· Li/°	Ref.
$[(\eta^5\text{-}C_5H_5)_2Er(\mu\text{-}Me)_2Li(tmen)]$	2.02	2.20	2.26	88.0	79.1	26
	1.99	2.17	2.43	105.9	94.0	27
	1.98	1.99	2.24	92.5	91.8	28
$\{Li_2[MnOMe_3]\cdot 2Li_2[Meacac]\cdot tmen\}_2$[a]	2.12	2.12	2.39	93.9	93.6	29
	2.09	2.09	2.25	86.6	86.6	
	2.18	2.18	2.36	88.5	88.4	
$[\{Li[Ga(CH_2SiMe_3)_4]\cdot 1.5\,diox\}_2]$[b]	2.20	1.99	2.32	84.1	107.3	30
	2.17	2.07	2.30	89.8	89.7	
$Li_2[(Me_3SiCH_2)_3Al(CH_2)Al(CH_2SiMe_3)_3]$	2.13	1.89	2.19	77.6	89.9	31
$\{H_3CC[CH_2N(Li)CH(CH_3)_2]_3\}_2$	2.03	2.19	2.35	97.6	87.5	32
$[Li(tmen)_2][Cr(\kappa^2C,C'\text{-}CH_2SiMe_2CH_2)_2]$	2.14	2.18	2.16	78.5	75.9	33
	2.20	2.19	2.34	86.5	86.5	34
	2.19	2.19	2.34	86.5	86.5	
$Li_2[Hg(SiMe_3)_4]$	2.00	2.18	2.32	93.5	82.6	35

[a] Meacac = 4-methyl-2-penten-2,4-diolate, tmen = *N,N,N′,N′*-tetramethylethylenediamine. [b] diox = Dioxane.

Table 5 Geometrical parameters for dibridged C–H ··· Li intermolecular interactions in lithium complexes

Compound	Li ··· H^1/Å	Li ··· H^2/Å	C ··· Li/Å	C–H^1 ··· Li/°	C–H^2 ··· Li/°	Ref.
$LiAlEt_4$	2.15	2.15	2.30	84.5	84.5	36
$LiBMe_4$[a]	2.11	2.11	2.21	80.4	80.0	37
	2.18	2.18	2.36	85.9	85.9	
$LiBMe_4$[b]	2.16	2.07	2.19	78.9	82.8	
$Li_2[Hg(SiMe_3)_4]$	2.19	1.99	2.45	89.6	103.2	35

[a] From X-ray crystallography data. [b] From neutron diffraction data.

towards the ultimate scission of the C–H bond and is of relevance to studies of C–H bond activation. The similarity in geometries of C–H ··· Li interactions to the C–H ··· M interactions confirms that the former is the organolithium analogue of the agostic interactions of transition-metal complexes.

Acknowledgements

We thank the Ministero dell' Università e della Ricerca Scientifica e Technologica of Italy (D. B., F. G.) and the University Grants Commission (K. B.) and Department of Science and Technology (G. R. D.), Government of India for financial assistance.

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Received 19*th February* 1996; *Paper* 6/01185C