

# Can C–H...C( $\pi$ ) Bonding Be Classified as Hydrogen Bonding? A Systematic Investigation of C–H...C( $\pi$ ) Bonding to Cyclopentadienyl Anions

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**Abstract:** The following ammonium and phosphonium cyclopentadienide complexes have been prepared, crystallized and investigated structurally: [Cp]<sup>−</sup>[Et<sub>4</sub>N]<sup>+</sup>, [Cp]<sup>−</sup>[Et<sub>4</sub>P]<sup>+</sup>, [Cp]<sup>−</sup>[Ph<sub>3</sub>PMe]<sup>+</sup>, [Cp]<sup>−</sup>[Ph<sub>2</sub>PMe<sub>2</sub>]<sup>+</sup>, [tBu(Me)Cp]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> and [Me<sub>4</sub>C<sub>2</sub>Cp<sub>2</sub>]<sup>2−</sup>[(Et<sub>4</sub>P)<sub>2</sub>]<sup>2+</sup>. The Cp anions in these complexes can not be considered as naked. Intermolecular bonding through characteristic (cation)C–H...C(Cp<sup>−</sup>) interactions results in the formation of polymeric networks. Generally, polymeric chains of alternating cations and

anions are formed that are reminiscent of the solid-state structures observed for cyclopentadienyl–alkalimetal compounds. Mutual comparison of all the known structures of ammonium and phosphonium cyclopentadienide complexes shows that intermolecular C–H...C(Cp<sup>−</sup>) bonding displays hydrogen-bond-like characteristics: i) directionality, ii) correlation between C–H

acidity and C–H...C bond lengths and iii) correlation between the strength of the hydrogen-bond acceptor and C–H...C bond lengths. These observations are also confirmed by ab initio calculations on coordination complexes of C–H donors (acetylene and methane) and the  $\pi$ -systems in benzene or the Cp<sup>−</sup> anion. Likewise, combinations of an alkali metallocene anion and a phosphonium cation show such C–H...C(Cp<sup>−</sup>) interactions in the crystalline state.

**Keywords:** crystal engineering • cyclopentadienes • hydrogen bonds

## Introduction

The concept of C–H...A (A = acceptor = O, N) hydrogen bonding dates back to the first part of this century<sup>[1]</sup> and presently attracts substantial attention.<sup>[2]</sup> Although C–H...A bonding is inferior to the well-established and generally accepted classical hydrogen bonding (such as O–H...O), the cooperative action of such weak bonding should not be underestimated. The importance of C–H...A hydrogen bonding lies in the frequent occurrence of C–H units in nearly all organic molecules. It is for this reason that this type of hydrogen bonding plays a major role in the rapidly growing field of crystal engineering,<sup>[3]</sup> that is, the study of intermolecular interactions in the solid state and their role in molecular conformation, crystal packing, molecular recognition and the prediction of crystal structures.

Nevertheless, the idea that a C–H unit can operate as a hydrogen-bond donor has been criticized in the past<sup>[4]</sup> as well as in the present.<sup>[5]</sup> This controversy arises not only from the weakness and therefore difficult experimental verification of C–H...A bonding, but also from the lack of a conclusive definition of hydrogen bonding.<sup>[3c]</sup> The recognition that “the value of the hydrogen-bond concept lies in the wilderness of

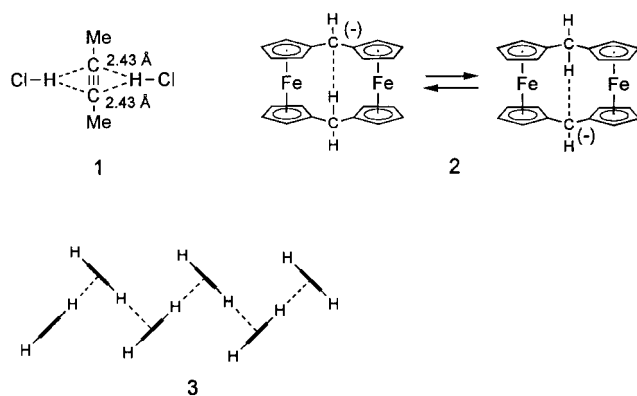
idea, and not within the wall of words”<sup>[3c]</sup> is not generally accepted: “It is clear that the field [the field of C–H...A hydrogen bonding] is getting muddier and muddier as the definition of a hydrogen bond is relaxed.”<sup>[5]</sup> Problems also arise from the absence of a definite cut-off value for the C–H...A distance and the C–H...A angle. Occasionally, the sum of the van der Waals radii of the interacting atoms is taken as the limit. However, as has been stated before, this value cannot be accepted as a cut-off value in hydrogen bonding.<sup>[2b, 2g]</sup> Hydrogen bonding is a predominantly electrostatic interaction<sup>[2b, g–h, 3c]</sup> and slowly falls off with a 1/*r* dependence, that is, much slower than covalent bonding or van der Waals interactions. This means that C <sup>$\delta$ −</sup>–H <sup>$\delta$ +</sup>...A <sup>$\delta$ −</sup> interactions, which are longer than the sum of the van der Waals radii for carbon and hydrogen ( $\approx 2.90$  Å), can still be of significant value (provided the C–H...C angle is not too small).

Notwithstanding all criticism, statistical crystal structure analyses clearly show, that C–H...A hydrogen bonds feature the same characteristics as the classical hydrogen bond.

- 1) C–H...A hydrogen bonds are directional and aim for linearity.<sup>[2a]</sup>
- 2) C–H...A bond lengths correlate well with the acidity of the C–H unit: the more acidic C–H units form shorter, stronger bonds.<sup>[2c]</sup>
- 3) C–H...A bond lengths correlate with the strength of the hydrogen-bond acceptor: stronger Lewis bases are more efficient hydrogen-bond acceptors.<sup>[2d]</sup>

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Apart from the recognition of C–H units as donors in hydrogen bonds, unusual bonds with carbon as the acceptor (D–H···C; D = donor) have also been observed.<sup>[6]</sup> Such interactions are generally described as D–H··· $\pi$  or D–H···anion bonds, since only unsaturated carbon atoms or carbanions can accept hydrogen bonds. This kind of bonding can be of considerable strength when good hydrogen donors are available, as shown by the extremely short Cl–H···C distances in the coordination complex [2-butyne·(HCl)<sub>2</sub>] (**1**).<sup>[6b]</sup>



At the lower end of hydrogen-bond interactions stands the combination of a weak hydrogen-bond donor with a weak acceptor: the C–H···C bond.<sup>[7]</sup> Although a strong interaction can be expected in the case of C–H···C(anion) bonding (such as in **2**<sup>[7a]</sup>), C–H···C( $\pi$ ) bonding as in the classical example of the benzene herringbone structure (**3**)<sup>[8]</sup> is one of the weakest C–H···C interactions encountered. This C–H···C( $\pi$ ) bond has been well-studied and controls a range of self-assembly phenomena such as:

- Stacking of benzene molecules in the gas phase and in solution.<sup>[8, 9]</sup>
- Crystal packing and hence material properties of aromatic molecules in the solid state.<sup>[10]</sup>
- Three-dimensional folding of proteins.<sup>[11]</sup>
- Molecular recognition of drugs by biological receptors.<sup>[12]</sup>

Nevertheless, there is some reluctance to identify C–H···C( $\pi$ ) interactions as hydrogen bonds. Statistical database studies on such weak interactions are hampered by the presence of other intermolecular forces that influence the three-dimensional crystal structure. Recently, evidence for the characterization of the C–H···C( $\pi$ ) bond as a weak hydrogen bond has been presented.<sup>[7]</sup> The structures of two isomorphous solvent-inclusion compounds (one with toluene and one with chlorobenzene) show a significantly shorter C–H···C( $\pi$ ) bond to the toluene molecule. This observation indicates a relationship between the length of the C–H···C bond and the strength of the hydrogen-bond acceptor (the electron density in the  $\pi$ -system)—a feature also observed in classical hydrogen bonding.

In order to learn more about C–H···C( $\pi$ ) bonding in general, and in order to establish whether the hydrogen-bonding characteristics mentioned above (1–3) also apply to C–H···C( $\pi$ ) interactions, a systematic investigation into intermolecular interactions in a series of [Cp]<sup>–</sup>[X]<sup>+</sup> complexes has been initiated. Although the C–H···C( $\pi$ ) interaction in

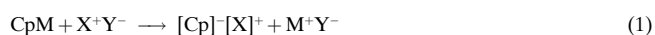
these complexes involves both a C–H···C( $\pi$ ) as well as a C–H···C(anion) interaction, the nature of its bonding is comparable with that of the C–H···arene system. Such a study of the intermolecular interactions in [Cp]<sup>–</sup>[X]<sup>+</sup> complexes has several advantages. First of all, charge-assisted C–H···Cp<sup>–</sup> bonding is stronger and much more distinct than C–H···arene bonding.<sup>[38]</sup> Secondly, in contrast to the laborious and poorly controllable syntheses of inclusion compounds with differently substituted arenes,<sup>[7]</sup> [Cp]<sup>–</sup>[X]<sup>+</sup> complexes with a variety of cations (X<sup>+</sup>) and substituents on the Cp ring are readily available. This means that the hydrogen-bond acceptor and donor abilities can be varied easily. In addition to this investigation of crystal structures, a comparison of ab initio calculations for C–H···C(benzene) and C–H···C(Cp<sup>–</sup>) interactions is presented here.

## Results

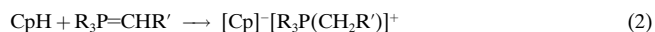
### Syntheses and crystal structures of [Cp]<sup>–</sup>[X]<sup>+</sup> complexes:

Although several crystal structures of organometallic complexes with free Cp<sup>–</sup> anions are known,<sup>[13]</sup> the systematic investigation described here is limited to ammonium and phosphonium cyclopentadienide salts, of which three structures have already been published: [Cp]<sup>–</sup>[Ph<sub>4</sub>P]<sup>+</sup>, [Cp]<sup>–</sup>[Bu<sub>4</sub>N]<sup>+</sup> and [(CF<sub>3</sub>)<sub>5</sub>Cp]<sup>–</sup>[Bu<sub>4</sub>N]<sup>+</sup>.<sup>[14, 7h, 15]</sup>

The general method used in the preparation of such salts is the reaction of a cyclopentadienyl–alkalimetal complex with an ammonium or phosphonium halide [Eq. (1)]. Equation (2)



(M = alkalimetal; X<sup>+</sup> = ammonium or phosphonium cation; Y<sup>–</sup> = halide anion)



depicts the reaction of a Wittig reagent with cyclopentadiene, which also results in the formation of a phosphonium cyclopentadienide complex. The latter method is favoured because of the absence of any side-products.

The new geometrical data presented here originate from good-quality, low-temperature structure determinations in which all the hydrogens could be located and isotropically refined. Nevertheless, calculated hydrogen positions (assuming C–H distances of 1.08 Å) are used in the geometrical comparison of the C–H···Cp<sup>–</sup> bonds observed in these structures. Observed and refined hydrogen positions show relatively large errors: the C–H distances generally vary from 0.90 to 1.10 Å. The fact that C–H distances are hardly influenced by such weak C–H···C( $\pi$ ) interactions (neutron diffraction studies show elongations of up to 0.01 Å)<sup>[16]</sup> justifies the use of calculated hydrogen positions. In this respect, Cotton's remarks<sup>[17]</sup> on the position of a hydrogen atom are relevant: "Neutron diffraction sees the location of the hydrogen's nucleus, the *proton*. X-ray diffraction sees the hydrogen's *electron cloud*. Which of these is the hydrogen atom? Both, the nucleus and the electron density of an atom are essential parts, and it is therefore impossible to assert

rationaly that the position of either the one or the other is *the* position of the atom.” In C–H⋯Cp<sup>−</sup> bonding, it is the hydrogen’s nucleus that is attracted by the electron rich  $\pi$ -system. This justifies the use of calculated (neutron-diffraction like) hydrogen positions.<sup>[18]</sup>

The networks of hydrogen bonding in all ammonium and phosphonium cyclopentadienide complexes are shown in Figures 1–9. Detailed information on the short C–H⋯Cp<sup>−</sup> contacts is summarized in Table 1.

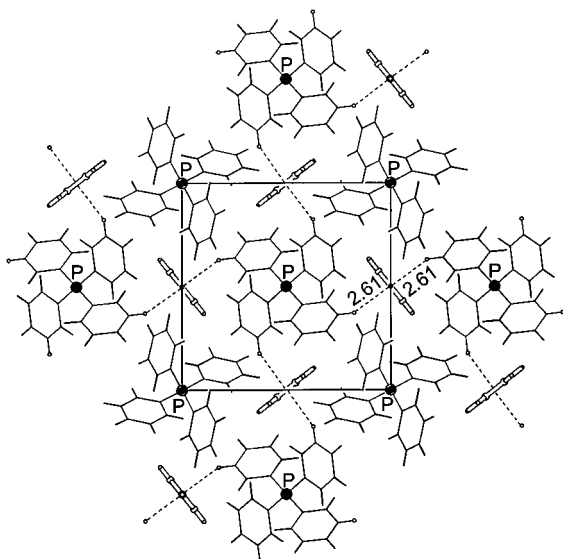


Figure 1. The crystal structure of [Cp]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> (space group  $P\bar{4}$ ) shown along the fourfold symmetry axes. The shortest intermolecular C–H⋯C contacts are depicted as dashed lines. The shortest C–H⋯(Cp<sup>−</sup>) contact to the other crystallographically independent phosphonium cation is much longer (> 2.90 Å).<sup>[14]</sup>

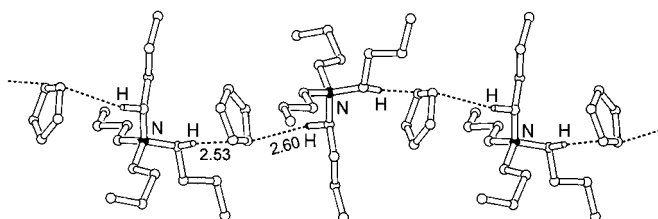


Figure 2. The crystal structure of [Cp]<sup>−</sup>[Bu<sub>4</sub>N]<sup>+</sup> displays a linear chain of alternating cations and anions connected by short C–H⋯C(Cp<sup>−</sup>) contacts (only the hydrogen atoms involved in the shortest intermolecular contacts are shown).<sup>[7b]</sup>

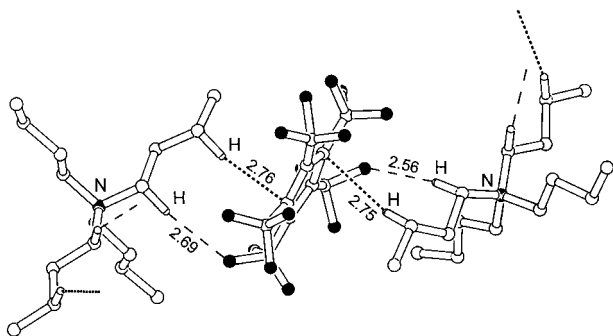


Figure 3. The crystal structure of [(CF<sub>3</sub>)<sub>3</sub>Cp]<sup>−</sup>[Bu<sub>4</sub>N]<sup>+</sup> (hydrogen atoms only partly shown).<sup>[15]</sup> Short intermolecular C–H⋯C and C–H⋯F bonds are shown as dashed lines.

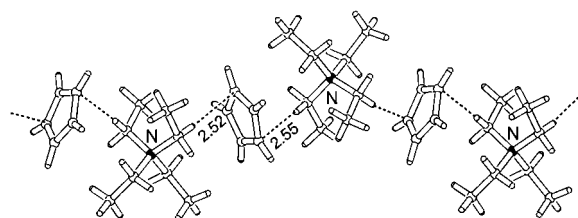


Figure 4. The crystal structure of [Cp]<sup>−</sup>[Et<sub>4</sub>N]<sup>+</sup> shows a chain of alternating [Cp]<sup>−</sup> anions and [Et<sub>4</sub>N]<sup>+</sup> cations. The shortest NCH<sub>2</sub>⋯C(Cp<sup>−</sup>) contacts are indicated by dashed lines.

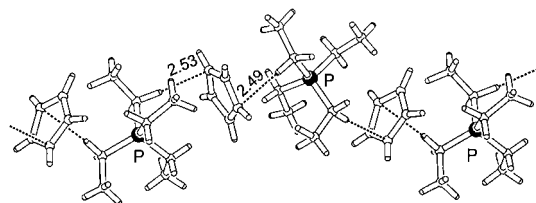


Figure 5. The intermolecular hydrogen-bond network in the crystal structure of [Cp]<sup>−</sup>[Et<sub>4</sub>P]<sup>+</sup>. Although the crystal structures and cell parameters of [Cp]<sup>−</sup>[Et<sub>4</sub>N]<sup>+</sup> and [Cp]<sup>−</sup>[Et<sub>4</sub>P]<sup>+</sup> are closely related, they are not isomorphous: the phosphonium salt crystallizes in an orthorhombic crystal system, whereas the ammonium salt is monoclinic.

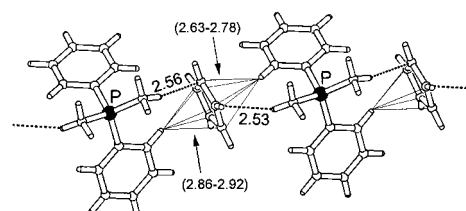


Figure 6. The shortest C–H⋯C(Cp<sup>−</sup>) interactions in the crystal structure of [Cp]<sup>−</sup>[Ph<sub>2</sub>PMe<sub>2</sub>]<sup>+</sup> are shown by dashed lines. An *ortho*-phenyl C–H unit is situated directly over the Cp ring (short C–H⋯C contacts indicated by thin solid lines).

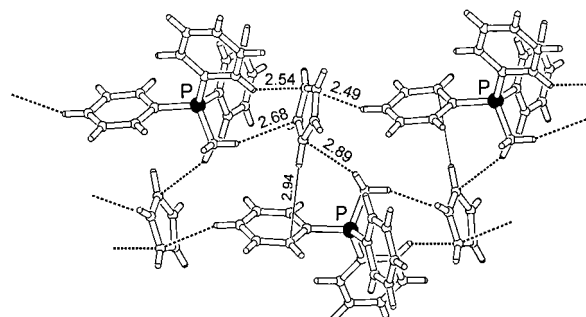


Figure 7. The crystal structure of [Cp]<sup>−</sup>[Ph<sub>3</sub>PMe]<sup>+</sup> displays parallel chains of alternating cations and anions. Short C–H⋯C(Cp<sup>−</sup>) contacts between the chains are also shown. Interestingly, the shortest C–H⋯C(Cp<sup>−</sup>) interaction (2.49 Å) does not involve the most acidic P–Me group but an aryl C–H moiety. An additional (Cp)C–H⋯phenyl contact is indicated by a thin solid line.

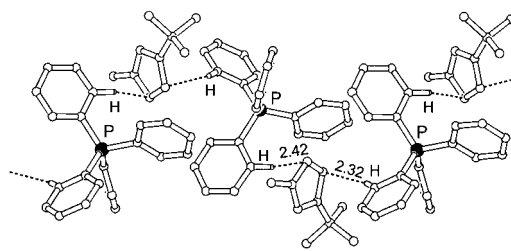


Figure 8. The crystal structure of [tBu(Me)Cp]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> shows a zigzag chain of alternating cations and anions (only the hydrogens involved in the shortest intermolecular C–H⋯C(Cp<sup>−</sup>) interactions are shown).

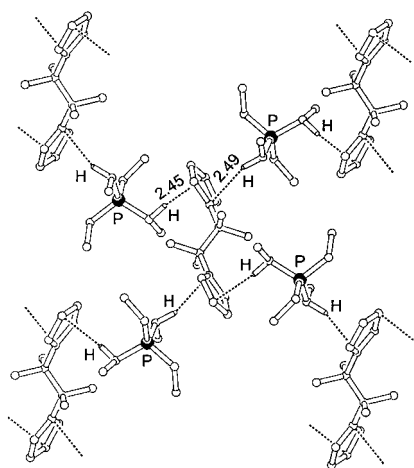


Figure 9. The crystal structure of  $[\text{Me}_4\text{C}_2\text{Cp}]^{2-}[(\text{Et}_4\text{P})_2]^{2+}$  displays a two-dimensional hydrogen-bond network (hydrogen atoms only partly shown).

**Ab initio study:** A theoretical study on the relatively weak interaction of a C–H bond with a  $\pi$ -system should be performed with high-level ab initio calculations. Only optimizations with correction for electron correlation (MP2) can yield reliable geometries for such weakly bound complexes. The additional use of an extended split-valence basis set with extra diffuse and polarization functions (6-311++G\*\*) gives reliable complexation energies with relatively small BSSEs.<sup>[19, 20]</sup> A schematic overview of the computational results obtained for the interaction of methane and acetylene with the  $\pi$ -system in benzene and the cyclopentadienyl anion is shown in Figure 10. The C–H  $\cdots \pi$  interaction between methane and the  $\pi$ -system of ben-

zene is very weak. Increasing the acidity of the hydrogen donor (for example, by exchange of methane for acetylene) results in a higher complexation energy and a shorter C–H  $\cdots$  benzene distance. Considerably stronger complexation and consequently shorter C–H  $\cdots$  C distances are observed in the C–H  $\cdots$  Cp<sup>−</sup> complexes. The minimal energy structures of such coordination complexes show the location of the hydrogen donor to be exactly over the aromatic ring centre (this was confirmed by frequency analyses). However, the energy surface is very shallow and distortions from the energy minimum can be easily accomplished. This is demonstrated by a haptotropic search<sup>[21]</sup> on the HC≡CH  $\cdots$  Cp<sup>−</sup> complex (Figure 11). The hydrogen donor is shifted over the Cp ring, while the rest of the geometry is optimized. Moving the acetylene molecule to the  $\eta^1$ -position results in an energy loss of only 3.1 kcal mol<sup>−1</sup> and in an elongation of the C–H  $\cdots$  plane

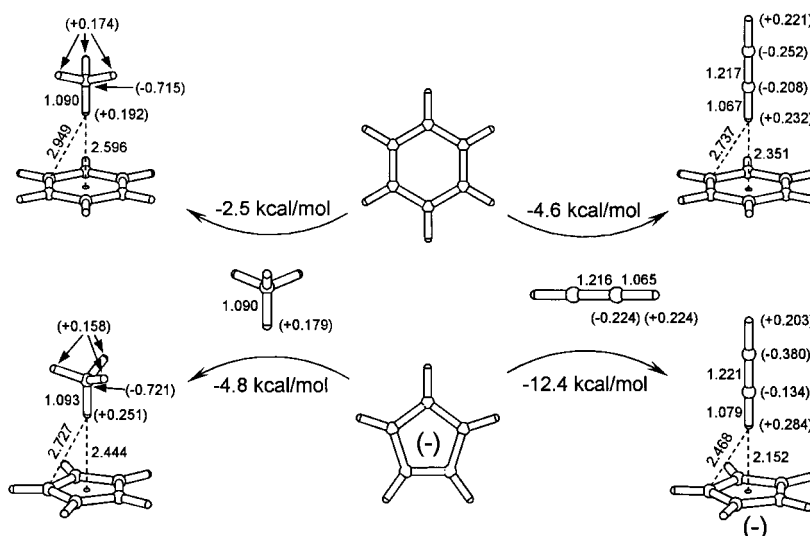


Figure 10. Overview of ab initio (MP2/6-311++G\*\*) calculations on intermolecular bonding between C–H donors (methane and acetylene) and the  $\pi$ -systems in benzene and the Cp<sup>−</sup> anion (distances, Å; NPA-charges shown in parentheses).

Table 1. A list of the shortest C–H  $\cdots$  C contacts (including angles) to each C atom and the centre of the Cp ring in cyclopentadienide ammonium and phosphonium complexes (the shortest C–H  $\cdots$  C contact between cation and anion is underscored).<sup>[a]</sup> The average values and the quantity  $(-\cos(\Psi))/\langle d \rangle$  are also given.

	CH $\cdots$ C [Å]					CH $\cdots$ Cp <sub>c</sub>	$\langle d \rangle$	$(-\cos(\Psi))/\langle d \rangle$
	C–H $\cdots$ C [°]					C–H $\cdots$ Cp <sub>c</sub>	$\langle \Psi \rangle$	[ $\times 1000$ ]
[Cp] <sup>−</sup> [Ph <sub>4</sub> P] <sup>[14]</sup>	<u>2.61</u>	2.77	2.77	2.98	2.98	2.63	2.790	249
	150°	125°	125°	131°	131°	143°	134.2°	
[Cp] <sup>−</sup> [Et <sub>4</sub> N] <sup>+</sup>	<u>2.52</u>	2.55	2.57	2.62	2.83	2.51	2.600	325
	139°	169°	171°	141°	122°	145°	147.8°	
[Cp] <sup>−</sup> [Bu <sub>4</sub> N] <sup>[7b]</sup>	<u>2.53</u>	2.60	2.61	2.64	2.87	2.52	2.628	335
	148°	145°	175°	149°	135°	158°	151.7°	
[Cp] <sup>−</sup> [Ph <sub>2</sub> PMe <sub>2</sub> ] <sup>+</sup>	<u>2.53</u>	2.56	2.64	2.75	2.78	2.43	2.615	344
	178°	144°	174°	129°	146°	153°	154.0°	
[Cp] <sup>−</sup> [Et <sub>4</sub> P] <sup>+</sup>	<u>2.49</u>	2.53	2.61	2.61	2.70	2.53	2.578	351
	160°	179°	141°	148°	146°	154°	154.7°	
[Cp] <sup>−</sup> [Ph <sub>3</sub> PMe] <sup>+</sup>	<u>2.49</u>	2.54	2.62	2.68	2.76	2.41	2.583	354
	147°	134°	171°	176°	150°	160°	156.3°	
[tBu(Me)Cp] <sup>−</sup> [Ph <sub>4</sub> P] <sup>+</sup>	<u>2.32</u>	2.42	2.64	2.68	2.70	2.30	2.510	319
	149°	150°	127°	143°	141°	149°	143.2°	
[(CF <sub>3</sub> ) <sub>5</sub> Cp] <sup>−</sup> [Bu <sub>4</sub> N] <sup>[15]</sup>	<u>2.75</u>	2.76	2.85	2.89	2.96	2.75	2.828	323
	157°	152°	171°	171°	135°	149°	155.8°	
[Me <sub>4</sub> C <sub>2</sub> Cp <sub>2</sub> ] <sup>2−</sup> [(Et <sub>4</sub> P) <sub>2</sub> ] <sup>2+</sup>	<u>2.45</u>	2.49	2.57	2.57	2.60	2.35	2.505	373
	154°	159°	161°	166°	147°	169°	159.3°	

[a] For sake of comparison the hydrogen atoms have been placed at idealized positions with a C–H distance of 1.08 Å.

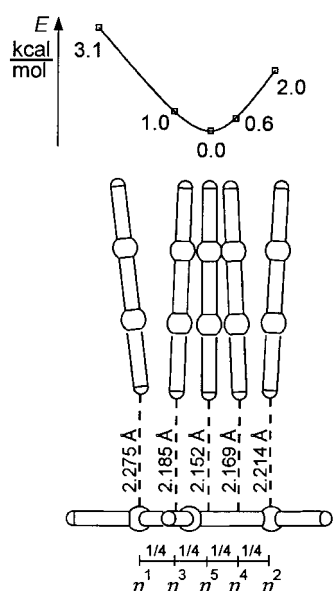


Figure 11. Geometries and energy profile for shifting the HC≡CH molecule over the ring of the Cp<sup>-</sup> anion (MP2/6-311++G\*\* calculations).

distance by only 0.123 Å (for comparison, a similar  $\eta^5 \rightarrow \eta^1$  shift of the Li<sup>+</sup> cation in CpLi gives an energy loss of 20.8 kcal mol<sup>-1</sup>).<sup>[21]</sup> Similarly, elongation of the C–H...Cp<sub>c</sub> distance by 0.5 Å costs only 2.1 kcal mol<sup>-1</sup> (this corresponds to C–H...Cp<sub>c</sub> and C–H...C distances of 2.652 and 2.912 Å, respectively; Cp<sub>c</sub> = geometrical centre of the Cp ring).

The calculated NPA-charges (shown in parentheses in Figure 10) show that the interaction of the  $\pi$ -system with the C <sup>$\delta^-$</sup> –H <sup>$\delta^+$</sup>  dipole is of electrostatic origin with negligible charge transfer between the interacting species. Analyses of atomic charges in the hydrogen-bond complexes also show considerable polarization of the C–H bond involved in the hydrogen bonding. In HC≡CH... $\pi$  complexes, additional polarization of the C≡C bond is observed. Complexes involving the stronger hydrogen bond acceptor Cp<sup>-</sup> show larger charge polarization in the hydrogen-bond donor.

The interaction of the C <sup>$\delta^-$</sup> –H <sup>$\delta^+$</sup>  dipole with a  $\pi$ -system only affects slightly its C–H bond length. A maximum elongation of 0.014 Å is observed in HC≡CH...Cp<sup>-</sup>, the complex with the most acidic C–H donor and the strongest hydrogen-bond acceptor. This is in line with the experimental observation mentioned earlier.<sup>[16]</sup>

## Discussion

The ammonium and phosphonium cyclopentadienide crystal structures listed here allow a preliminary analysis of C–H...Cp<sup>-</sup> bonding. Although one should be careful if the number of crystal structures sampled is small, there seems to be at least a rough correlation between the shortest C–H...C(Cp<sup>-</sup>) contact (underscored in Table 1) and the C–H acidity of the cation. Alarming, however, seems the fact that the shortest C–H...C contact between the cation and Cp<sup>-</sup> anion does not always involve the most acidic C–H unit of the cation, for example, the most acidic group in [Cp]<sup>-</sup>[Ph<sub>3</sub>PMe]<sup>+</sup>, the PMe

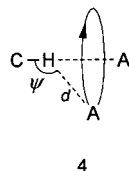
group, is involved in the longer C–H...C(Cp<sup>-</sup>) contacts. Although steric shielding of the methyl group by three phenyl groups will certainly occur, such anomalies can also be explained by the existence of many more weaker C–H...Cp<sup>-</sup> bonds. Crystal packing optimizes the cooperative effects of *all* intermolecular interactions (Figure 6). For example, packing in the crystal structure of [Ph<sub>3</sub>PMe]<sup>+</sup>[Cp]<sup>-</sup> is such that short C–H...C interactions exist not only within a linear chain of alternating anions and cations, but also between such chains (Figure 7). Also noteworthy is the contact between a cyclopentadienyl C–H unit and a phenyl-ring carbon (shown in Figure 7 by a continuous thin line). To evaluate the overall strength of X<sup>+</sup>...Cp<sup>-</sup> hydrogen bonding, not only the contribution of the shortest C–H...C(Cp<sup>-</sup>) contact, but also the cooperative effect of other short C–H...C(Cp<sup>-</sup>) interactions should be considered. Table 1 lists the shortest C–H...C(Cp<sup>-</sup>) contacts (including C–H...C angles) for every carbon atom in the Cp ring. The shortest C–H...Cp<sub>c</sub> distance is also shown. For comparison of X<sup>+</sup>...Cp<sup>-</sup> hydrogen-bond strength, the average values of these 6 distances ( $\langle d \rangle$ ) are given. These values show that the X<sup>+</sup>...Cp<sup>-</sup> bond strengthens along the series for X<sup>+</sup> = Ph<sub>4</sub>P<sup>+</sup> < alkylammonium cation < alkylphosphonium cation in line with increasing cation acidity.

A similar relation exists between C–H...C(Cp<sup>-</sup>) distances and anion basicity. Substituents on the Cp ring can have a considerable effect on the X<sup>+</sup>...Cp<sup>-</sup> bond strength. This is demonstrated by a comparison of the average C–H...C distances for the pairs [Cp]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup>/[*t*Bu(Me)Cp]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> and [Cp]<sup>-</sup>[Et<sub>4</sub>P]<sup>+</sup>/[Me<sub>4</sub>C<sub>2</sub>Cp]<sup>2-</sup>[(Et<sub>4</sub>P)<sub>2</sub>]<sup>2+</sup>. Alkylation of the Cp anion results in higher electron density in the  $\pi$ -system with concomitant stronger C–H...C( $\pi$ ) bonding towards the cation. On the other hand, fivefold CF<sub>3</sub> substitution on the Cp ring sharply decreases the charge in the Cp  $\pi$ -system and thus weakens the C–H...C(Cp<sup>-</sup>) bond. Comparison of the crystal structure of [Cp]<sup>-</sup>[Bu<sub>4</sub>N]<sup>+</sup> with that of [(CF<sub>3</sub>)Cp]<sup>-</sup>[Bu<sub>4</sub>N]<sup>+</sup> does indeed show longer C–H...C contacts in the latter compound.

Not only the D–H...A distance, but also the D–H...A angle, determines the strength of classical hydrogen bonds. Therefore, the bonding angles of C–H...C(Cp<sup>-</sup>) interactions should also be taken into account. However, C–H...C(Cp<sup>-</sup>) interactions differ markedly from classical hydrogen bonds, as the hydrogen-bond acceptor is not a localized electron density but a diffuse  $\pi$ -cloud. It is therefore not straightforward to define hydrogen-bond angles in C–H...Cp<sup>-</sup> bonding. Should the angle be defined with respect to the ring centre or the nearest C atom? Ab initio calculations show an energy minimum for hydrogen bonding to the ring centre. There is, however, very poor agreement between this calculated, most stable geometry for C–H...Cp<sup>-</sup> bonding (in which the C–H unit binds perpendicular to the centre of the Cp ring, Figure 10) and the experimentally observed C–H...Cp<sup>-</sup> bonding geometries. Such deviation from ideal bonding geometry is caused not only by the extremely shallow energy surface for the C–H...Cp<sup>-</sup> interaction (Figure 11), but also by a statistical factor. This situation is comparable with the rarely observed linearity of classical hydrogen bonds: linear O–H...O hydrogen bonds are the most stable. However, statistical

database analyses show a maximum around  $165^\circ$ . Two factors are responsible for this effect.

- 1) The hydrogen-bond energy decreases with  $\cos \Psi$  ( $\Psi$  is the hydrogen-bond angle), such that small deviations from linearity have extremely small effects on the energy.
- 2) Statistics: the number of possible structures for a bent D–H...A geometry is larger than for a linear arrangement (4).<sup>[22]</sup>



Similar statistical arguments also hold for the experimentally observed geometries of C–H...Cp<sup>−</sup> interactions, as the number of possible structures is larger for off-centre bonding. Figure 11 shows that an off-centre C–H donor slightly directs itself to the edge of the Cp ring, which suggests that the C–H...C angles should also be considered. The angles for each C–H...C and C–H...Cp<sub>c</sub> contact, together with their average value ( $\Psi$ ), are given in Table 1. All the C–H...C and C–H...Cp<sub>c</sub> angles are larger than  $120^\circ$  with an overall average value of  $150.8^\circ$ . However, there does not seem to be a very distinct correlation between bond angles and bond lengths. This is mainly because of the very shallow energy surface for the directionality of the C–H...Cp<sup>−</sup> interaction and the arbitrary definition of the C–H...C angle as the hydrogen-bond angle. Nevertheless, in order to facilitate a comparison of X<sup>+</sup>...Cp<sup>−</sup> bond strength (including angle information) the expression  $(-\cos \Psi)/d$  is used ( $d$  = the average C–H...C distance,  $\Psi$  = the average C–H...C angle). Its value represents a crude estimate of the strength of C–H...Cp<sup>−</sup> hydrogen bonding that is largely electrostatic in nature and follows Coulomb's law. Strong hydrogen bonding is indicated by a large value of  $(-\cos \Psi)/d$ . The average  $d$  and  $\Psi$  values combined in  $(-\cos \Psi)/d$  show that the X<sup>+</sup>...Cp<sup>−</sup> bond strengthens along the series, X<sup>+</sup> = Ph<sub>4</sub>P<sup>+</sup> < Et<sub>4</sub>N<sup>+</sup> ≈ Bu<sub>4</sub>N<sup>+</sup> < Ph<sub>2</sub>PMe<sub>2</sub><sup>+</sup> ≈ Et<sub>4</sub>P<sup>+</sup> ≈ Ph<sub>3</sub>PMe<sup>+</sup>, in line with increasing cation acidity. The  $(-\cos \Psi)/d$  values likewise illustrate the more pronounced C–H...Cp<sup>−</sup> interactions with alkylated Cp anions. It should be noted, however, that C–H...C angles for the strong interactions between Ph<sub>4</sub>P<sup>+</sup> and *t*Bu(Me)Cp<sup>−</sup> deviate considerably from linearity. This is mainly because of steric repulsion: the shortest cation–anion contacts involve the least-substituted side of the Cp ring. The large angles for the weak C–H...C bonds in [(CF<sub>3</sub>)Cp]<sup>−</sup>[Bu<sub>4</sub>N]<sup>+</sup> are likewise remarkable. It should be mentioned, however, that the most acidic groups (the N–CH<sub>2</sub> groups) do not interact with the Cp π-system but with the electron-rich F atoms. It is therefore likely that C–H...C(Cp<sup>−</sup>) bonding in [(CF<sub>3</sub>)Cp]<sup>−</sup>[Bu<sub>4</sub>N]<sup>+</sup> is of secondary importance and is dominated by C–H...F interactions. These interactions keep the Bu-arm in close proximity of the Cp ring, and thus determine the C–H...C(Cp<sup>−</sup>) bond geometry.

An interesting aspect of the tetraphenylphosphonium cyclopentadienide salts is their unexpected reddish colour.

For example, [Cp]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> is a dark-red substance in the solid state as well as in solution. This colour is not typical for Cp<sup>−</sup> anions in general; the complexes [Cp]<sup>−</sup>[Et<sub>4</sub>P]<sup>+</sup> and [Cp]<sup>−</sup>[Et<sub>4</sub>N]<sup>+</sup> are colourless. Also, the Ph<sub>4</sub>P<sup>+</sup> cation itself is not a coloured species. Only the combination [Cp]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> is red. Therefore, it is presumed that this intense colour originates from a charge-transfer process between the anion and cation. Such a process also explains the black appearance of crystals of [*t*Bu(Me)Cp]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> (the extremely dark-red colour of the substance can only be seen in small micro-crystals). We observed that crystals of [Cp\*]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> are also black (extremely dark red). Alkylation of the Cp anion facilitates its oxidation<sup>[23]</sup> and intensifies the charge-transfer process. The species [Cp]<sup>−</sup>[Ph<sub>3</sub>PMe]<sup>+</sup> and [Cp]<sup>−</sup>[Ph<sub>2</sub>PMe<sub>2</sub>]<sup>+</sup> are also reddish. However, the intensity and colour depend on the number of Ph substituents on the phosphorus atom: [Cp]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> (dark red) > [Cp]<sup>−</sup>[Ph<sub>3</sub>PMe]<sup>+</sup> (red) > [Cp]<sup>−</sup>[Ph<sub>2</sub>PMe<sub>2</sub>]<sup>+</sup> (orange).

### C–H...Cp<sup>−</sup> bonding in alkali metallocene phosphonium complexes:

Over the last few years, we have published a series of crystal structures of anionic alkali metallocene sandwich complexes with Ph<sub>4</sub>P<sup>+</sup> as the counterion: [Cp<sub>2</sub>Li]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup>, [Cp<sub>2</sub>Na]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> and [Cp<sub>3</sub>Cs<sub>2</sub>]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup>.<sup>[24, 14, 25]</sup> Anionic alkali metallocenes can also function as donors in C–H...Cp<sup>−</sup> hydrogen bonding. Detailed analyses of their crystal structures show that networks of intermolecular bonding do indeed exist (Figure 12). In all cases, the shortest contact between cation and anion is a (cation)C–H...Cp<sup>−</sup> interaction (Table 2).

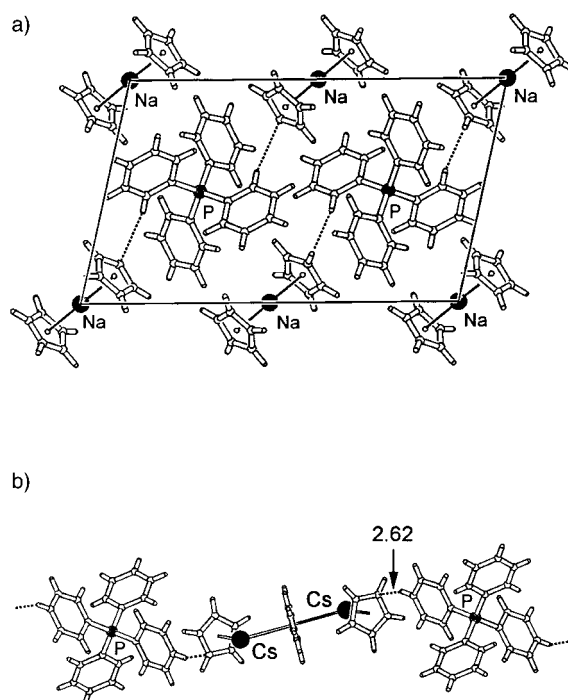


Figure 12. a) The shortest intermolecular C–H...C(Cp<sup>−</sup>) distances in the isomorphous crystal structures of [Cp<sub>2</sub>Li]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> and [Cp<sub>2</sub>Na]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup> are 2.75 and 2.71 Å, respectively. b) The shortest intermolecular C–H...C(Cp<sup>−</sup>) distance in the crystal structure of [Cp<sub>3</sub>Cs<sub>2</sub>]<sup>−</sup>[Ph<sub>4</sub>P]<sup>+</sup>.

Table 2. A list of the shortest C–H...C contacts (including angles) to each C atom and the centre of the Cp ring in a series of alkali metalocene phosphonium complexes (the shortest C–H...C contact between cation and anion is underscored).<sup>[a]</sup> The average values and the quantity  $(-\cos(\Psi))/\langle d \rangle$  are also given.

	CH...C [Å] C–H...C [°]					CH...C <sub>p</sub> C–H...C <sub>p</sub>	$\langle d \rangle$ $\langle \Psi \rangle$	$(-\cos(\Psi))/\langle d \rangle$ [× 1000]
[Cp <sub>2</sub> Li] <sup>-</sup> [Ph <sub>4</sub> P] <sup>+</sup> [24]	<u>2.75</u>	2.88	2.90	3.05	3.12	3.16	2.977	232
	143°	130°	121°	138°	136°	134°	133.7°	
[Cp <sub>2</sub> Na] <sup>-</sup> [Ph <sub>4</sub> P] <sup>+</sup> [14]	<u>2.71</u>	2.74	2.94	3.03	3.07	3.11	2.933	230
	138°	136°	124°	128°	138°	131°	132.5°	
[Cp <sub>3</sub> Cs <sub>2</sub> ] <sup>-</sup> [Ph <sub>4</sub> P] <sup>+</sup> [25]	<u>2.62</u>	2.70	2.98	2.99	3.03	3.04	2.893	259
	147°	138°	127°	125°	157°	137°	138.5°	
[ <i>t</i> BuCp <sub>2</sub> Li] <sup>-</sup> [Ph <sub>2</sub> PMe <sub>2</sub> ] <sup>+</sup> [26]	<u>2.66</u>	2.70	2.77	2.87	3.04	2.76	2.800	312
	143°	149°	160°	149°	141°	164°	151.0	
	<u>2.53</u>	2.82	2.90	3.12	3.18	3.02	2.928	
	158°	144°	158°	149°	157°	179°	157.5°	

[a] For sake of comparison the hydrogen atoms have been placed at idealized positions with a C–H distance of 1.08 Å.

The crystal structures of [Cp<sub>2</sub>Li]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> and [Cp<sub>2</sub>Na]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> are isomorphous. The data in Table 2 show only a slightly shorter C–H...Cp<sup>-</sup> contact between [Ph<sub>4</sub>P]<sup>+</sup> and [Cp<sub>2</sub>Na]<sup>-</sup>. Both structures, however, show very weak overall hydrogen bonding between the anion and cation. Stronger hydrogen bonding is observed in [Cp<sub>3</sub>Cs<sub>2</sub>]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (Figure 12b). The stronger hydrogen-bond acceptor character of the caesocene anion, [Cp<sub>3</sub>Cs<sub>2</sub>]<sup>-</sup>, is in line with high ionicity and the long bond length in the Cp–Cs unit.

Tetraphenylphosphonium complexes not only of cyclopentadienide anions, but also of alkali metalocene anions are coloured substances. The colour intensifies and shifts towards red along the sequence: [Cp<sub>2</sub>Li]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (yellow) → [Cp<sub>2</sub>Na]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (orange) → [Cp<sub>3</sub>Cs<sub>2</sub>]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (red) → [Cp]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (dark red). This is the row along which the Cp–M distance increases, that is, the row along which the Cp anion gradually becomes “free” and its oxidation potential decreases. The hydrogen-bond acceptor abilities increase along the same row.

Although not recognized by the authors, strong C–H...C bonding is observed in the recently published crystal structure of [(*t*BuCp)<sub>2</sub>Li]<sup>-</sup>[Ph<sub>2</sub>PMe<sub>2</sub>]<sup>+</sup>.<sup>[26]</sup> Anions and cations are arranged alternately in a linear chain and are connected by short interactions between the most acidic P–Me groups and the *t*BuCp anions (Figure 13). The considerable strength of hydrogen bonding in this complex arises on the one hand from the availability of an acidic C–H donor (the P–Me unit) and on the other hand from the presence of a strong hydrogen acceptor (an alkylated Cp ring).

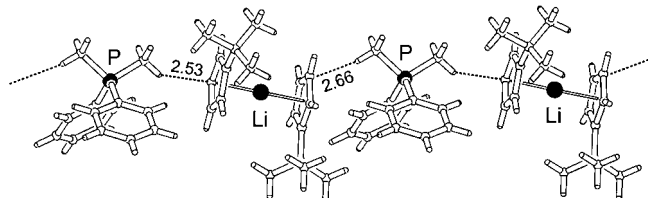


Figure 13. The crystal structure of [(*t*BuCp)<sub>2</sub>Li]<sup>-</sup>[Ph<sub>2</sub>PMe<sub>2</sub>]<sup>+</sup> consists of a linear array of alternating anions and cations, which show strong intermolecular C–H...C hydrogen-bonding interactions.

## Conclusion

The Cp anions in the crystal structures of ammonium and phosphonium cyclopentadienide complexes can not be con-

sidered as naked. Likewise, the ammonium and phosphonium cations in such complexes can not be thought of as non-coordinating cations. Intermolecular bonding through characteristic C–H...C(Cp<sup>-</sup>) interactions results in the formation of polymeric networks. One of the networks observed most often is a chain structure of alternating cations and anions (reminiscent of polymer chains of cyclopentadienyl–alkali metal compounds). Higher, linked polymers with additional intermolecular interaction between the chains are also formed.

Experimental and theoretical observations show that intermolecular C–H...C(Cp<sup>-</sup>) bonding displays similar characteristics to the hydrogen bond.

- 1) Directionality (albeit weak).
- 2) Correlation between C–H acidity and C–H...C bond lengths.
- 3) Correlation between the strength of the hydrogen-bond acceptor and C–H...C bond lengths.

Thus, the C–H...C(Cp<sup>-</sup>) contact can be truly regarded as a hydrogen-bond interaction.

Likewise, combinations of an alkali metalocene anion with a phosphonium cation show such C–H...C(Cp<sup>-</sup>) hydrogen bonds in the crystalline state. Although these intermolecular interactions are less important than those in the crystal structures of ammonium and phosphonium cyclopentadienide complexes, their contribution to the crystal packing can still be significant (especially when acidic cations and alkylated Cp anions are involved).

The reddish colour of [Cp]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> and [Cp<sub>2</sub>M]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> complexes is presumably due to a charge-transfer process between the anion and cation. The colour intensifies along the series [Cp<sub>2</sub>Li]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (yellow) → [Cp<sub>2</sub>Na]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (orange) → [Cp<sub>3</sub>Cs<sub>2</sub>]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (red) → [Cp]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (dark red) → [*t*Bu(Me)Cp]<sup>-</sup>[Ph<sub>4</sub>P]<sup>+</sup> (black), as the Cp anion gradually becomes free, and its oxidation potential decreases. The hydrogen-bond acceptor ability of the anion increases along the same series.

## Experimental Section

All experiments were carried out under an inert argon atmosphere with Schlenk techniques and syringes. Solvents were freshly distilled from calcium hydride or sodium/benzophenone before use. NMR spectra were

recorded on Bruker AC250 (250 MHz) and WM250 (250 MHz) machines.  $^1\text{H}$  NMR frequencies were referenced internally to the solvent: acetonitrile, 1.93; methanol, 3.30; and pyridine, 8.71. The Wittig reagents described here were prepared by reacting the corresponding phosphonium bromide (or iodide) with  $\text{KN}(\text{TMS})_2$  (1.0 equiv) (or  $\text{NaNH}_2$  in the case of  $\text{Et}_3\text{P}=\text{CHMe}$ ) in THF. A clear solution was then isolated and the solvent and amine subsequently removed in vacuo. NMR analyses of crystalline ammonium and phosphonium cyclopentadienide samples showed that the  $\text{C}_5\text{H}_5^-:\text{R}_4\text{N}^+$  (or  $\text{R}_4\text{P}^+$ ) ratio was generally 5–20% too low. This is because of partial decomposition of the highly reactive, free cyclopentadienide anion (probably by hydrolysis and partial H/D exchange with the deuterated solvent).

**X-Ray crystallography:** Crystal structure measurements were performed on an Enraf–Nonius CAD4 diffractometer with  $\text{MoK}\alpha$  X-ray radiation (0.71073 Å). All crystals were mounted on glass fibre under a thin layer of paraffin oil. The structures were solved with SHELXS-86<sup>[27]</sup> and refined with the SHELXL-93<sup>[28]</sup> programs. No absorption corrections were applied. The EUCLID package was used for all plots and geometry calculations.<sup>[29]</sup> In all the structure determinations, hydrogen atoms were located in the difference Fourier map and refined freely with isotropic displacement factors. However, calculated hydrogen-atom positions (C–H = 1.08 Å) were used for a comparison of C–H $\cdots$ C(Cp $^-$ ) bonding. In most cases the hydrogen positions are fixed unambiguously by the heavy-atom positions. Only with Me groups as the hydrogen-bond donors ([Cp] $^-$ [Ph $_3$ PMe] $^+$ , [Cp] $^-$ [Ph $_2$ PMe $_2$ ] $^+$  and [tBu(Me)Cp] $^-$ [Ph $_3$ PMe] $^+$ ) might there be strong deviation between calculated and observed positions. However, all observed hydrogen geometries show, within error, staggered Me–PR $_3$  structures as used in the calculation model. The crystal structure data have been summarized in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101843 and 101848. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Ab initio calculations:** Ab initio calculations were performed with gradient optimization techniques, tight convergence criteria (opt = tight) and the standard basis set, 6-311++G\*\* incorporated in the GAUSSIAN-94 program system.<sup>[30]</sup> All optimizations were performed at the MP2(fc) level.

The need to include this electron-correlation approximation in geometry optimizations of the weakly bound systems studied here is shown by a comparison with RHF-optimized geometries. The RHF-optimized complexes showed similar geometry minima, but with much longer C–H $\cdots$ C distances and smaller binding energies. However, RHF/6-31+G\*-optimized structures were used in the frequency analyses (optimized complexes showed only positive frequencies) and in an approximation of zero-point energies (all energies in the text have been corrected for zero-point vibration). Charges have been calculated by use of the natural population analysis (NPA). Mulliken population analyses failed to give a useful and reliable characterization of the charge distribution in many cases, especially when highly ionic compounds were involved. Charges calculated according to NPA did not show these deficiencies and were relatively independent of the basis set.<sup>[31]</sup>

**Synthesis of [Cp] $^-$ [Et $_4$ N] $^+$ :** CpNa (1.50 g, 17.0 mmol) and Et $_4$ NCl (2.82 g, 17.0 mmol) were mixed in pyridine (30 mL). The resulting, slightly turbid solution was centrifuged, and the clear solution was slowly cooled over 15 hours to  $-35^\circ\text{C}$ . Colourless, needlelike crystals were precipitated from the yellow solution. The crystals were isolated by quick filtration and washed twice with THF (5 mL). Yield = 1.95 g, 59%;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  = 1.52 (t,  $J$  = 7.0 Hz, 12H; Me), 3.08 (q,  $J$  = 7.0 Hz, 8H; CH $_2$ ), 5.43 (s, Cp).

**Synthesis of [Cp] $^-$ [Et $_4$ P] $^+$ :** Cyclopentadiene (0.40 g, 6.05 mmol) was added to a solution of Et $_3\text{P}=\text{CHCH}_3$  (0.33 g, 2.26 mmol) in THF (10 mL). A white suspension formed immediately and was then centrifuged. The remaining white solid was washed twice with hexane (15 mL) and then dried in vacuo. The resulting white powder was dissolved in pyridine (8 mL) and then carefully layered with hexane (10 mL). The product crystallized as long, colourless needles (yield = 0.36 g, 75%).  $^1\text{H}$  NMR ( $[\text{D}_5]$ pyridine,  $25^\circ\text{C}$ ):  $\delta$  = 0.97, 1.04 (dt,  $^3J(\text{H,H})$  = 7.7 Hz,  $^3J(\text{P,H})$  = 17.7 Hz, 12H; Me), 1.88, 1.93 (dq,  $^3J(\text{H,H})$  = 7.7 Hz,  $^3J(\text{P,H})$  = 13.2 Hz, 8H; CH $_2$ ), 6.43 (s, Cp).

**Synthesis of [Cp] $^-$ [Ph $_3$ PMe] $^+$ :** Cyclopentadiene (1.0 g, 15.1 mmol) was added to a yellow solution of Ph $_3\text{P}=\text{CH}_2$  (0.38 g, 1.38 mmol) in Et $_2\text{O}$  (10 mL). The solution turned red and a bright-red precipitate was formed, which slowly turned into an oil. The oily product was recrystallized from hot THF and yielded red, needlelike crystals (0.26 g, 55%).  $^1\text{H}$  NMR ( $[\text{D}_5]$ pyridine,  $25^\circ\text{C}$ ):  $\delta$  = 2.90 (d,  $^3J(\text{P,H})$  = 13.5 Hz, 3H; Me); 6.57 (s, Cp), 7.20–7.69 (m, 15H; Ph).

Table 3. Summary of crystal structure determination data.

	[Cp] $^-$ [Et $_4$ N] $^+$	[Cp] $^-$ [Et $_4$ P] $^+$	[Cp] $^-$ [Ph $_3$ PMe] $^+$	[Cp] $^-$ [Ph $_2$ PMe $_2$ ] $^+$	[tBu(Me)Cp] $^-$ [Ph $_4$ P] $^+$	[Me $_4$ C $_2$ Cp $_2$ ] $^{2-}$ [(Et $_4$ P) $_2$ ] $^{2+}$
crystal dimensions [mm $^3$ ]	0.2 $\times$ 0.2 $\times$ 0.6	0.3 $\times$ 0.4 $\times$ 0.6	0.2 $\times$ 0.2 $\times$ 0.5	0.3 $\times$ 0.3 $\times$ 0.5	0.3 $\times$ 0.5 $\times$ 0.5	0.3 $\times$ 0.3 $\times$ 0.3
colour	colourless	colourless	orange	red	black <sup>[a]</sup>	colourless
crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$Pbca$
$a$ [Å]	10.207(2)	7.888(9)	10.287(2)	9.5134(7)	10.440(2)	14.354(2)
$b$ [Å]	7.7601(5)	10.195(1)	12.304(1)	9.6661(9)	14.737(3)	15.069(1)
$c$ [Å]	16.122(3)	16.930(2)	14.997(3)	9.7347(9)	17.805(1)	14.989(1)
$\alpha$ [°]	90.0	90.0	90.0	94.018(7)	90.0	90.0
$\beta$ [°]	92.398(8)	90.0	99.030(8)	115.014(7)	104.22(1)	90.0
$\gamma$ [°]	90.0	90.0	90.0	99.179(7)	90.0	90.0
$V$ [Å $^3$ ]	1275.8(2)	1361(2)	1874.7(5)	791.3(1)	2655.4(8)	3242.0(5)
formula	C $_{15}$ H $_{25}$ N	C $_{13}$ H $_{25}$ P	C $_{25}$ H $_{23}$ P	C $_{19}$ H $_{21}$ P	C $_{34}$ H $_{35}$ P	C $_{32}$ H $_{60}$ P $_2$
$Z$	4	4	4	2	4	4
$\rho_{\text{calcd}}$ [g cm $^{-3}$ ]	1.017	1.036	1.256	1.177	1.187	1.038
$2\theta_{\text{max}}$ [°]	54.9	52.9	53.0	51.9	49.9	51.0
$\lambda$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
scan mode	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
$T$ [°C]	$-120(2)$	$-105(2)$	$-120(2)$	$-75(2)$	$-120(2)$	$-105(2)$
refl $_{\text{meas}}$	3074	3167	8181	3295	4927	2992
refl $_{\text{indep}}$ ( $R_{\text{int}}$ )	2914(0.016)	2812(0.023)	3870(0.069)	3097(0.022)	4655(0.020)	2992(0.0)
refl $_{\text{obs}}$ [ $I > 2\sigma(I)$ ]	2275	2346	2308	2171	3204	1713
refined parameters	227	227	318	265	456	274
$R1$ [ $I > 2\sigma(I)$ ]	0.042	0.037	0.050	0.039	0.044	0.047
$wR2$ [ $I > 2\sigma(I)$ ]	0.108	0.080	0.099	0.082	0.115	0.094
$R1$ (all data)	0.063	0.060	0.108	0.089	0.092	0.131
$wR2$ (all data)	0.120	0.087	0.121	0.096	0.144	0.119
largest diff. peak/hole [e Å $^{-3}$ ]	0.153/ $-0.231$	0.176/ $-0.218$	0.247/ $-0.298$	0.297/ $-0.306$	0.260/ $-0.248$	0.336/ $-0.205$

[a] Small fragments of the crystal show an extremely dark-red colour.



**Synthesis of  $[\text{Cp}]^-[ \text{Ph}_2\text{PMe}_2 ]^+$ :**  $\text{Ph}_2(\text{Me})\text{P}=\text{CH}_2$  (0.45 g, 2.10 mmol) was carefully layered with THF (10 mL), such that a solution with a concentration gradient was formed. This solution was layered with cyclopentadiene (0.40 g, 6.05 mmol). Orange crystals were formed overnight (0.15 g, 25%). All crystals show holes or open spaces inside, but can be easily cut into fragments suitable for X-ray diffraction.  $^1\text{H}$  NMR ( $[\text{D}_3]\text{pyridine}$ ,  $25^\circ\text{C}$ ):  $\delta$  = 2.45 (d,  $^2J(\text{P,H})$  = 14.8 Hz, 6H; Me), 6.57 (s, Cp), 7.20–7.80 (m, 10H; Ph).

**Synthesis of  $[\text{tBu}(\text{Me})\text{Cp}]^-[ \text{Ph}_4\text{P} ]^+$ :** Addition of caesium 3-methyl-3-pentanoate (1.70 g, 7.27 mmol) to  $\text{Me}(\text{tBu})\text{CpLi}$  (1.0 g, 7.03 mmol) dissolved in THF yielded a yellow solution. The solvent was removed and the remaining white powder was dried (0.01 Torr,  $80^\circ\text{C}$ ; 30 min) and subsequently washed with dry hexane ( $3 \times 15$  mL). The product,  $\text{tBu}(\text{Me})\text{CpCs}$ , was then dried (0.01 Torr,  $60^\circ\text{C}$ , 30 min). A solution of  $\text{tBu}(\text{Me})\text{CpCs}$  (0.40 g, 1.49 mmol) in THF (8 mL) was added to a suspension of  $\text{Ph}_4\text{PCl}$  (0.28 g, 0.75 mmol) also in THF (2 mL). This gave a slightly turbid, red solution which was centrifuged. The clear, dark-red solution was carefully layered with hexane. After several days, large cubelike black (or very dark red) crystals were formed (yield = 0.25 g, 70% based on  $\text{Ph}_4\text{PCl}$ ). Quenching of the crystals in  $\text{CD}_3\text{OD}$  and subsequent NMR analysis of the resulting solution showed the composition to be  $[\text{tBu}(\text{Me})\text{Cp}]^-[ \text{Ph}_4\text{P} ]^+$ .

**Synthesis of  $[\text{Me}_4\text{C}_2\text{Cp}]^2-[ (\text{Et}_4\text{P})_2 ]^{2+}$ :**  $\text{Me}_4\text{C}_2(\text{CpH})_2^{[32]}$  (0.20 g, 0.93 mmol) was added to a solution of  $\text{Et}_3\text{P}=\text{CHMe}$  (0.28 g, 1.93 mmol) in THF (12 mL). The resulting solution was slowly cooled to  $-20^\circ\text{C}$  to give colourless crystals (yield = 0.20 g, 42%). Quenching of the crystals in  $\text{CD}_3\text{OD}$  and subsequent NMR analysis of the resulting solution showed the composition  $[\text{Me}_4\text{C}_2\text{Cp}]^2-[ (\text{Et}_4\text{P})_2 ]^{2+}$ .

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