The effect of the counter ion on M—H···H—X (X = O, N) interactions in crystalline transition metal hydrides†

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Received (in Montpellier, France) 3rd July 1998; Revised m/s received 16th November 1998, Accepted 19th November 1998

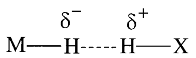
The relationship between molecular and crystal structures of organometallic complexes showing intramolecular interactions of the M—H···H—X type (M = transition metal, X = O, N, and S) has been investigated by a combined use of molecular orbital calculations and crystal packing analysis. Molecular and crystal structures determined by neutron and/or X-ray diffraction data of coordination complexes and clusters showing intramolecular (M—H···H—X) interactions within the range 1.5–2.5 Å have been retrieved from the Cambridge Structural Database. DFT calculations were performed for the majority of compounds in order to determine the nature of the H···H interaction. The optimized geometries obtained by DFT are usually in good agreement with the experimentally determined ones, short H···H distances being also found. Most of the systems analysed, such as *cis*-$[IrH(OH)(PMe_3)_4][PF_6]$, involve cationic complexes. It has been found that the counter ion exerts a strong influence in bringing together the two hydrogens. When it is included in the calculations, the agreement between the observed and the calculated structures is much better.

Since systematic studies of intermolecular interactions have begun to encompass the organometallic chemistry area, hydrogen bonding has become a source of new discoveries.[1] Hydrogen bonding is not only of great relevance in supramolecular chemistry[2] but also the masterkey interaction in crystal engineering,[3] materials chemistry[4] and biochemistry.[5]

Indeed, the great structural diversity of organometallic systems is reflected in the types and patterns of hydrogen bonding and other intermolecular interactions that are present in organometallic crystals.[1] The capacity to form hydrogen bonds is not confined to the "traditional" acceptor and donor groups of organic molecules. Although rather scattered in the scientific literature, several spectroscopic[6] and structural studies[7] have concurred to show that metal atoms can act as donors or acceptors in hydrogen bond formation. Hydrogen bonds formed by strong donor/acceptor groups such as —COOH and —OH systems,[8a] as well as by primary $—CONH_2$ and secondary amido —CONHR groups belonging to metal-coordinated ligands have been investigated and compared with those formed by the corresponding organic molecules in their crystals.[8b] Hydrogen bonds of the C—H···O type have also been studied, showing that these interactions are pervasive in crystalline organometallic transition metal complexes and clusters where C—H groups (mainly in sp^2 and sp hybridized systems) and the CO base are abundant.[8c]

The Cambridge Structural Database (CSD) has been used to investigate the occurrence of M—H···O intermolecular interactions in which metal bound "hydride" ligands are donated to a suitable base.[9] The metal atoms in coordination complexes have also been shown to be able to accept hydrogen bond donation from O—H, N—H and C—H groups.[10] As pointed out by Pearson and Shriver on separate occasions,[11] the M—H bond appears to be chemically very similar to the C—H bond since in both bonds the hydrogen reacts as H^+, $H^{\cdot}$, or H^-, depending on the relative stability of the resulting species. These studies lead to a picture of M—H as an extremely soft and polarizable bonding system.

In this paper, we tackle the intramolecular interaction between two hydrogen atoms, one of which is bound to a metal atom ("metal hydride") and the second is bound to an electronegative main group atom (C, N, O, S), as shown in Chart 1.



$$\mathrm{M{-\!-}\overset{\delta^-}{H}{-}{-}{-}{-}{-}\overset{\delta^+}{H}{-\!-}X}$$

Chart 1

The intramolecular Ir—H···H—N interaction in the ionic complex $[Ir\{H(\eta^1\text{-}SC_5H_4NH)(PCy_3)_2\}]^+$ was analysed, using the extended Hückel method,[12a] by Liu and Hoffmann who showed that the interaction is weakly attractive, in agreement with the NMR experimental findings of Lough *et al.*[12b] The structure was not fully established, as neither hydrides nor other hydrogen atoms were located. Related intermolecular interactions in other systems have been analysed.[12c,d] Such a M—H···H—X interaction has been considered as a new type of hydrogen bonding, which is specific to organometallic systems, having no parallel in the neighbouring organic chemistry field. Similar systems have been independently discovered

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† *Supplementary material available*: (the Quest file used in the CSD search)
For direct electronic access see http://www.rsc.org/suppdata/nj/1999/219, otherwise available from BLDSC (No. SUP 57480, 2 pp.) or the RSC Library. See Intructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).
Non-SI unit employed: 1 kcal ≈ 4.18 kJ.

and studied by Crabtree and co-workers.[13] Evidence of intermolecular ReH_2···H—N attractive interactions has also been obtained from the structural investigation of the crystalline complex $[ReH_5(PPh_3)]_3]\cdot$indole$\cdot C_6H_6$ and confirmed by theoretical calculations.[14a] This type of interaction has been used in a more systematic way to prepare new materials containing an organometallic hydride complex acting as an acceptor and a convenient donor.[14b] NMR studies have also provided information about intramolecular Os—H···H—N[15a] interactions and the conversion of the two hydrogen atoms involved in a Ru—H···H—OR interaction into a coordinated H_2 molecule.[15] There is increasing evidence that even the C—H fragment may take part in intramolecular M—H···H—C interactions, as shown by structural studies[16a–c] and a CSD survey.[16d] A recent review addresses some structural aspects of these new interaction types.[16e]

In order to put these findings into a broader context we have systematically examined the crystalline complexes in which short *intra*molecular M—H···H—X contacts are present. This has been done by searching the CSD[17] for all those complexes of the type M—H···H—X that present H···H distances below 2.5 Å (see below). The nature of the H···H interactions in some structures retrieved from the CSD has been investigated by means of density functional theory (DFT)[18] calculations. The results of an investigation of *inter*molecular M—H···H—X interactions in crystalline organometallic complexes and coordination compounds have been reported elsewhere.[19]

Results and discussion

The structures

The CSD search yielded 17 structures of hydride complexes, determined by neutron and X-ray diffraction, which satisfy the criterion (M)—H···H—(X) < 2.5 Å (M = transition metal, X = O, N, and S). These structures were manually screened to remove those where the hydride position was not well-defined, leaving us with 12 compounds. These complexes are listed in Table 1 together with the relevant structural parameters and the references to the original structural papers. Formulae and CSD REFCODES will be used to refer to the compounds in Table 1. Unless otherwise stated, all structural parameters are calculated on the basis of observed H(hydride) positions present in the CSD files, whereas bond lengths of hydrogen atoms bound to main group elements have been normalized to the neutron-derived bond distance values (see Experimental).

The two complexes *cis*-$[IrH(OH)(PMe_3)_4][PF_6]$[20a,b] and *cis*-$[IrH(SH)(PMe_3)_4][PF_6]$[20b] offer an intriguing entry point into the subject. Importantly, for the first compound, hydrogen atoms were located by X-ray and neutron diffraction. In terms of molecular structures the two complexes differ essentially in the orientation of the X—H group (X = O, S) relative to the hydride and in the H—Ir—X angle, which is much smaller in the S derivative (76.0°) than in the O-derivative (91.0°). The structures of the two cations are shown in Fig. 1, together with relevant labels.

Table 1 Compound formulae, REFCODES and relevant geometrical parameters for M—H···H intramolecular interactions for transition metal "hydrides" with intramolecular H···H distances <2.5 Å

Compound, REFCODE[a]	*T*/K	M—H/Å	M—H···H[c]/Å	X—H···Y(intra)[c]/Å	X—H···Y(inter)[c]/Å	Ref.
$[IrH(OH)(PMe_3)_4][PF_6]$, DUPSEM01[b]	20	1.617(9)	H(1)···H(2) 2.334	C(2)—H(7)···O(1) 2.323	C(2)—H(8)···F(2) 2.480 C(5—H(14)···F(1) 2.438 C(5)—H(16)···F(4) 2.480	20*a*
$[IrH(SH)(PMe_3)_4][PF_6]$, DUPSOW	173	1.64(5)	···	C(23)—H(231)···S(1) 2.758 C(32)—H(32A)···S(1) 2.773	S(1)—H(10)···F(3) 2.368 C(22)—H(22)···F(1) 2.410 C(31)—H(31)···F(2) 2.376 C(41)—H(41)···F(2) 2.364 C(22)—H(221)···F(1) 2.470 C(41)—H(411)···S(1) 2.869	20*b*
$[Rh_2H_2(\mu\text{-}SH)_2\{MeC(CH_2PPh_2)_3\}]$- $[BPh_4]_2[HCON(Me)_2]$, FATXON	298	1.70(1)	H(1)···H(2) 1.891	C(64)—H(64)···S(1) 2.449 C(66)—H(66)···S(1) 2.611	C(33)—H(33)···O(21) 2.562 C(43)—H(43)···O(21) 2.571 C(57)—H(57)···O(21) 2.555 C(62)—H(62)···O(1) 2.302	21*a*
$[(\mu\text{-}H)_2Ir_2(\mu\text{-}NH_2)_2(PEt_3)_4$ $(NH_3)_2][(CH_3)_2CO]$, FEJCOM	173	1.61(5)	H(1)···H(4) 2.260 H(2)···H(4) 2.189		C(29)—H(38)···O(1) 2.340 C(35)—H(52)···O(1) 2.321	21*b*
$[IrH_2(CO)(PPh_3)_2(pzH—N)][BF_4]$- $[C_6H_5Me]$,[d] FEZFUL	298	1.662[f] 1.654[f]	H(2)···H(33) 2.007 H(1)···H(28) 2.187 H(2)···H(13) 2.356		N(2)—H(33)···F(4) 1.863 C(16)—H(10)···F(2) 2.327 C(39)—H(29)···O(1) 2.577 C(41)—H(31)···F(3) 2.345	22
$[IrH(Cl)(L)][PF_6]$,[e] GAVBAG	298	1.57(13)	H(1)···H(4) 2.335 H(1)···H(20) 2.484	C(5)—H(9)···Cl(1) 2.732 C(7)—H(15)···Cl(1) 2.747	N(1)—H(4)···Cl(1) 2.323 C(5)—H(10)···Cl(1) 2.747	23
$[IrH(Cl)(PEt_3)_2(NHPhC_7H_{10})]$, GINWEF	203	1.705(75)	H(1)···H(3) 2.242 H(1)···H(11) 2.206 H(1)···H(31) 2.154 H(1)···H(46) 2.284	C(9)—H(13)···Cl(1) 2.464 C(15)—H(21)···Cl(1) 2.780 C(21)—H(37)···Cl(1) 2.697	C(13)—H(17)···Cl(1) 2.590	24
$[(\mu\text{-}H)Ru_3(CO)_9(\mu\text{-}H_3N_2\text{-}4,5\text{-}Me_2\text{-}1,2\text{-}$ phenylene)], JEBPIP	298	1.904[f] 1.840[f]	H(1)···H(3) 2.383	N(1)—H(2)···O(8) 2.327	N(2)—H(3)···O(7) 2.578 N(2)—H(4)···O(6) 2.284 C(16)—H(8)···O(3) 2.565	25
$[Ru_6(\mu\text{-}H)_6(\mu^3\text{-}\eta^2\text{-}ampy)(CO)_{14}]$,[g] LEHXAX10	200	2.0(1)	H(2)···H(4) 2.064	C(19)—H(17)···N(1) 2.611	C(10)—H(9)···O(4) 2.392 C(10)—H(9)···O(3) 2.539 C(22)—H(19)···O(5) 2.508 C(34)—H(33)···O(1) 2.411	26
$[IrH(\eta^1\text{-}SC_5H_4NH)_2(\eta^2\text{-}$ $SC_5H_4N)(PCy_3)][BF_4]\cdot 0.72CH_2Cl_2$, POLFEB	173	1.60(5)	H···H 1.9 ± 0.2			12*d*
$[Cp_2Zr(NHAr)(\mu\text{-}H)(\mu\text{-}N\text{-}Bu^t)IrCp^*]$- $[C_6H_5Me]$, PESXUG	167	1.58(6) 2.03(6)	H(1)···H(2) 1.717	—	—	27
$[IrH(PCy_3)(2\text{-thiazialidinethione})_4]$ $[BF_4]_2$, ZUQYUF	173	1.44(6)	H···H 2.10(10) H···H 2.27(9)			12*c*

[a] References of original structural reports as provided in the CSD. [b] Neutron study. [c] Based on normalized C—H, N—H and O—H distances. [d] pzH—N = 3,5-dimethylpyrazolato-*N*. [e] L = 7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene-*N*, *N*′, *N*″, *N*‴. [f] e.s.d.s not available in the original papers. [g] Hampy = 2-amino-6-methylpyridine.

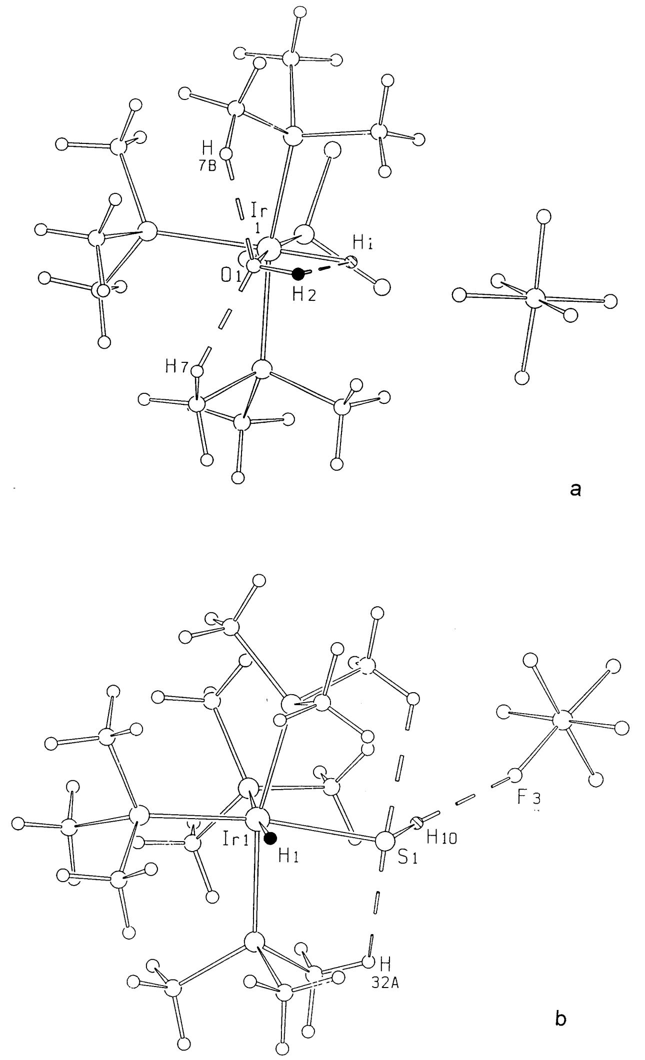

Fig. 1 Comparison of the ion arrangement and intramolecular interactions in crystalline (*a*) *cis*-$[IrH(OH)(PMe_3)_4][PF_6]$ and (*b*) *cis*-$[IrH(SH)(PMe_3)_4][PF_6]$.

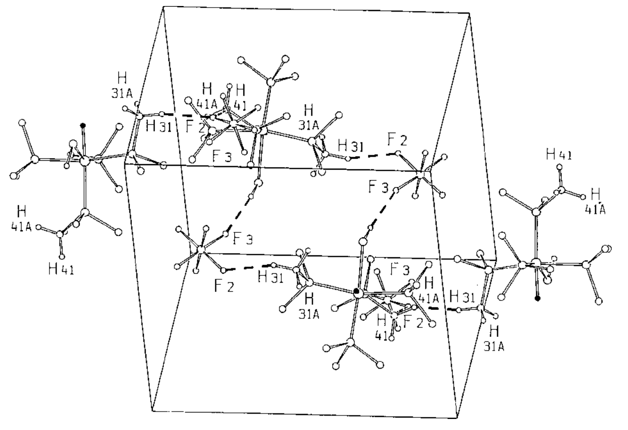

Fig. 2 Interion hydrogen bonding patterns in crystalline *cis*-$[IrH(SH)(PMe_3)_4][PF_6]$. Note the large ring formed by two anions and two cations *via* S—H···F and C—H···F interactions.

As was well-described in the original paper, the hydrogen atom bound to the metal-coordinated oxygen in the first complex exhibits a close contact with the hydride ligand [H(1)···H(2) 2.334 Å]. In the isoelectronic SH derivative, the orientation of the SH group is such that the sulfur bound hydrogen atom points outwards, far away from the hydride ligand. In both systems the F atoms of the PF_6^- anions participate in an intricate network of interion interactions involving the phosphine methyl hydrogens (see Table 1). Such interactions are chiefly of the C—H···F type and comparable in length in the two crystals, the shortest distances ranging from 2.368 to 2.480 Å. The *S*-bound hydrogen atom in *cis*-$[IrH(SH)(PMe_3)_4]^+$ also participates in an intermolecular link with one PF_6^- anion. Each anion bridges two cations *via* S—H···F and C—H···F interactions (2.368 Å *vs.* 2.376 Å), as shown in Fig. 2.

The next compounds in Table 1 are $[Rh_2H_2(\mu\text{-}SH)_2\{MeC(CH_2PPh_2)_3\}_2]$ $[BPh_4]_2[HCON(Me)_2]$[21a] and $[(\mu\text{-}H)_2\text{-}Ir_2(\mu\text{-}NH_2)_2(PEt_3)_4(NH_3)_2][(CH_3)_2CO]$.[21b] Both complexes show the presence of short intramolecular H···H contacts involving the hydride ligands and the hydrogen atoms attached to the bridging SH and NH_2 groups, respectively. These contacts are shown in Fig. 3. The Rh—H···H—S distance is particularly short in the first complex (1.891 Å). Both complexes also show several other short intramolecular contacts (see Table 1). A relevant feature of the structure of the iridium complex is the intermolecular link *via* C—H···O bonds [H(38)···O(1) 2.340 Å and H(52)···O(1) 2.321 Å] between a solvent molecule and the complex, as shown in Fig. 3(*b*).

These two complexes present many similarities but also a significant difference: the Rh one exhibits a strong distortion of the octahedral coordination sphere of phosphines and hydrides around the metal atoms (Fig. 4). Such a distortion is not observed in the iridium complex.

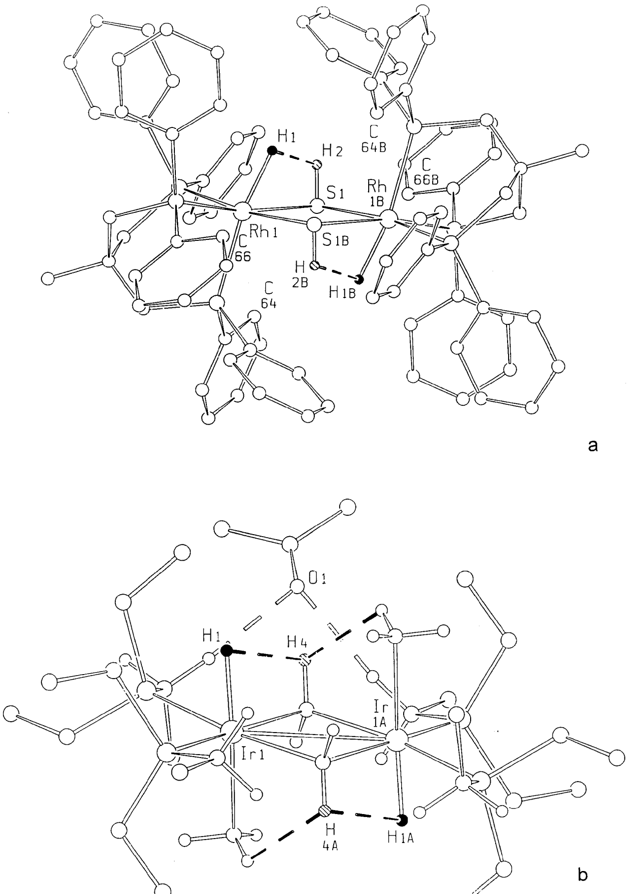

Fig. 3 The intramolecular H···H interactions involving the hydride ligands and the hydrogen atoms attached to the bridging SH and NH_2 groups, respectively, in (*a*) in $[Rh_2H_2(\mu\text{-}SH_2)_2\{MeC\text{-}(CH_2\text{-}PPh_2)_3\}][BPh_4]_2[HCON(Me)_2]$ and (*b*) $[(\mu\text{-}H)_2Ir_2(\mu\text{-}NH_2)_2(PEt_3)_4(NH_3)_2][(CH_3)_2CO]$. Note the intermolecular link between a solvent molecule and the complex. H atoms of the other phenyl group are omitted for clarity.

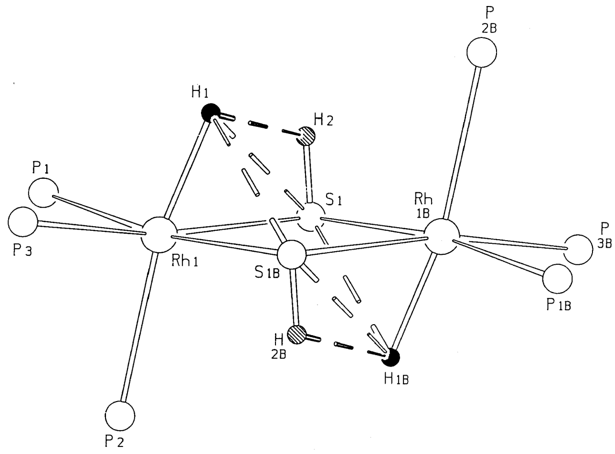

Fig. 4 The inner framework of $[Rh_2H_2(\mu\text{-}SH)_2\{MeC(CH_2PPh_2)_3\}]$-$[BPh_4]_2[HCON(Me)_2]$ emphasizing the distortion of the rhodium coordination sphere.

$[IrH_2(CO)(PPh_3)_2(pzH{-}N)][BF_4][C_6H_5Me]$[22] carries two *cis*-hydride ligands [see Fig. 5(*a*)]. One hydride ligand is close to a pyrazole hydrogen [H(2)···H(33) 2.007 Å] and a phenyl hydrogen of a phosphine ligand [H(2)···H(13) 2.356 Å], while the second interacts only with the phenyl group of the phosphine ligand [H(1)···H(28) 2.187 Å]. A diffuse network of intermolecular bonds involving the BF_4^- anion as well the CO ligand is present in the crystal [see Fig. 5(*b*)]. The pyrazole hydrogen participates in one such link [H(33)···F(4) 1.863 Å].

In the structure of $[IrH(Cl)(L)][PF_6]$ (for L see footnote to Table 1)[23] the H···H separations between the hydride ligand and the neighbouring hydrogen atoms are relatively long [H(1)···H(4) 2.335 Å; H(1)···H(20) 2.484 Å], probably because of the presence of a rigid macrocycle framework [see Fig. 6(*a*)]. However, the intermolecular interactions established by the chlorine atom are more interesting. As shown in Fig. 6(*b*), four molecules are connected by two Cl ligands [Cl(1)···H(4) 2.323 Å] by linking an amino group hydrogen and by joining a second molecule in a bifurcated interaction *via* a C—H···Cl bond [Cl(1)···H(10) 2.747 Å].

In the complex $[IrH(Cl)(PEt_3)_2(NHPhC_7H_{10})]$,[24] the terminal hydride ligand in the structure is embedded in a crowded ligand shell [see Fig. 7(*a*)], leading to a number of short intramolecular contacts involving it. The Cl atom participates in intermolecular interactions with C—H donors [Fig. 7(*b*)], as well as in some intramolecular C—H···Cl interactions (see Table 1).

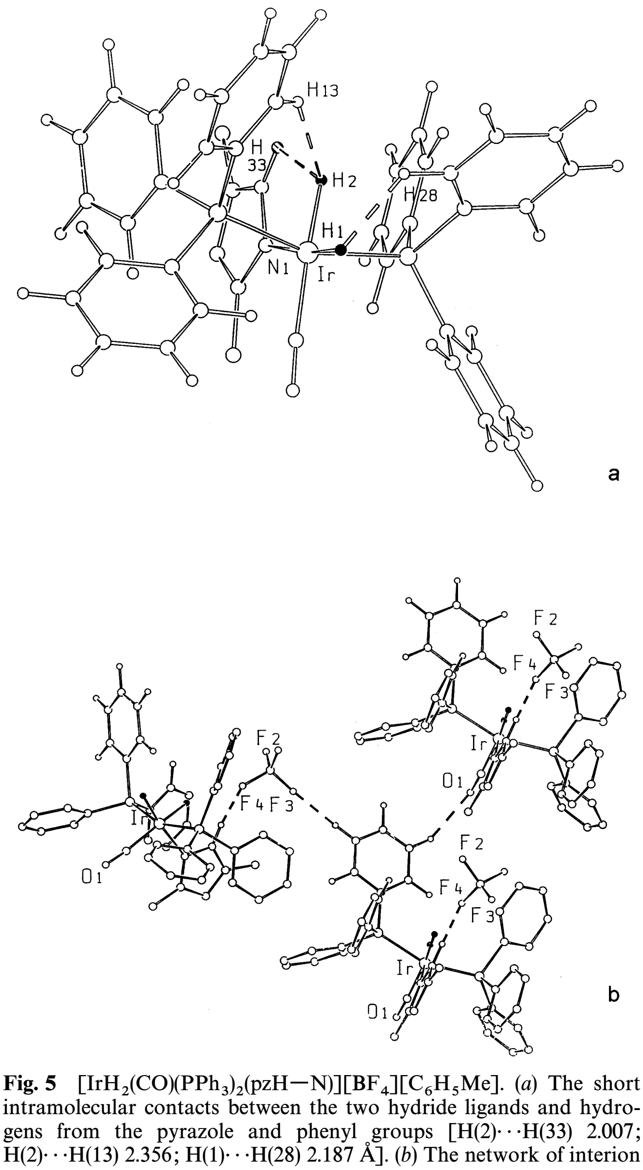

Fig. 5 $[IrH_2(CO)(PPh_3)_2(pzH{-}N)][BF_4][C_6H_5Me]$. (*a*) The short intramolecular contacts between the two hydride ligands and hydrogens from the pyrazole and phenyl groups [H(2)···H(33) 2.007; H(2)···H(13) 2.356; H(1)···H(28) 2.187 Å]. (*b*) The network of interion hydrogen bonds involving the BF_4^- anion and the CO ligand of the complex [N(2)—H(33)···F(4) 1.863; C(16)—H(10)···F(3) 2.327 Å].

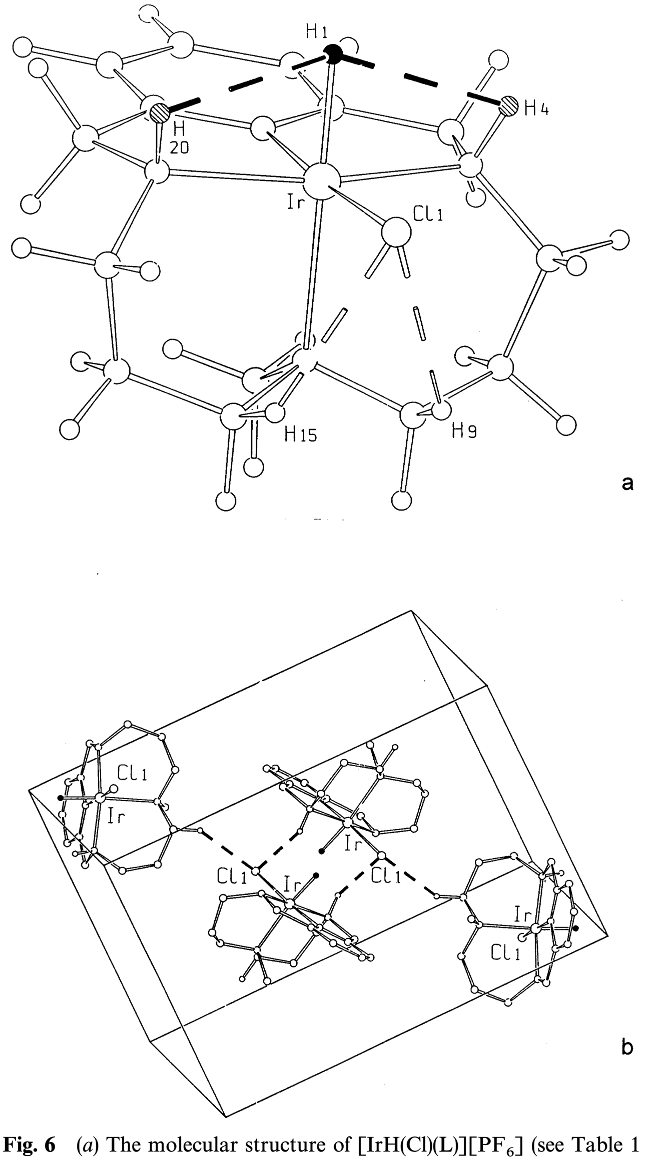

Fig. 6 (*a*) The molecular structure of $[IrH(Cl)(L)][PF_6]$ (see Table 1 footnote for definition of L). (*b*) The chloride ligand connects four molecules by forming a cyclic dimer [Cl(1)···H(4) 2.323 Å] *via* a N—H···Cl hydrogen bond and by joining a second molecule in a bifurcated interaction *via* a C—H···Cl bond [Cl(1)···H(10) 2.747 Å].

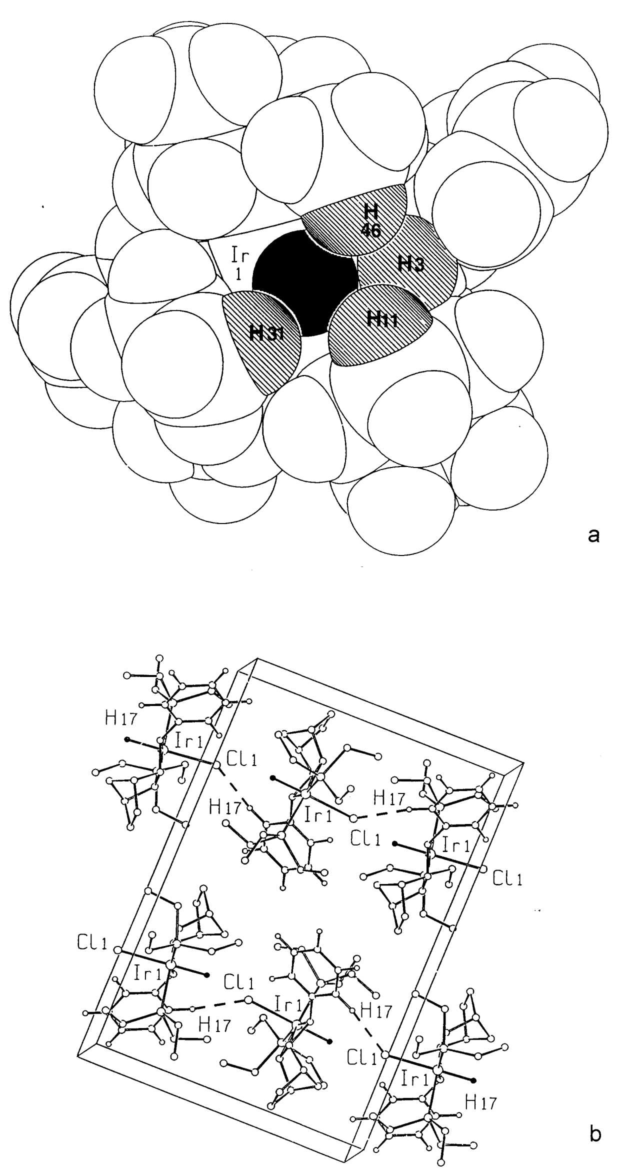

Fig. 7 (*a*) The structure of [IrH(Cl)(PEt$_3$)$_2$(NHPhC$_7$H$_{10}$)] showing the crowded environment around the hydride ligand. (*b*) Intermolecular C—H···Cl interactions in the crystal. H atoms of the other phenyl group are omitted for clarity.

The cluster [(μ-H)Ru$_3$(CO)$_9$(μ-H$_3$N$_2$-4,5-Me$_2$-1,2-phenylene)]^{25} carries a bridging hydride ligand [Fig. 8(*a*)]. The shortest *intra*molecular H···H separation [H(1)···H(3) 2.383 Å] is between this hydride and a hydrogen atom of the amino group of the chelating ligand. At the intermolecular level, the same amino hydrogens participate in hydrogen bonding interactions with the carbonyl oxygens, as shown in Fig. 8(*b*).

In the cluster [Ru$_6$(μ-H)$_6$(μ^3-η^2-ampy)(CO)$_{14}$]^{26}, two triangular Ru$_3$ units are in contact through two relatively long Ru—Ru bonds [3.292(3) Å, compared to 2.724(2), 2.799(2) and 2.991(2) in the triangle]. The system possesses a bridging hydride that approaches a H(N) from the chelate ligand at a distance of 2.064 Å (after normalization of the N—H distance), as seen in Fig. 9.

The shortest approach between H atoms (1.717 Å) found in this search is present in the third binuclear complex, [Cp$_2$Zr(NHAr)(μ-H)(μ-N-Bu^t)IrCp*],^{27} and involves a bridging hydride (see Fig. 10).

The other two compounds in Table 1, [IrH(η^1-SC$_5$H$_4$NH)$_2$(η^2-SC$_5$H$_4$N)(PCy$_3$)][BF$_4$]·0.72CH$_2$Cl$_2$ and [IrH(PCy$_3$)(2-thiazialidinethione)$_4$][BF$_4$]$_2$, were described in detail in ref. 12*d* and *c*, respectively. They exhibit short hydride···H(N) distances. The following general observations can be made with regard to the compounds described above (Table 1):

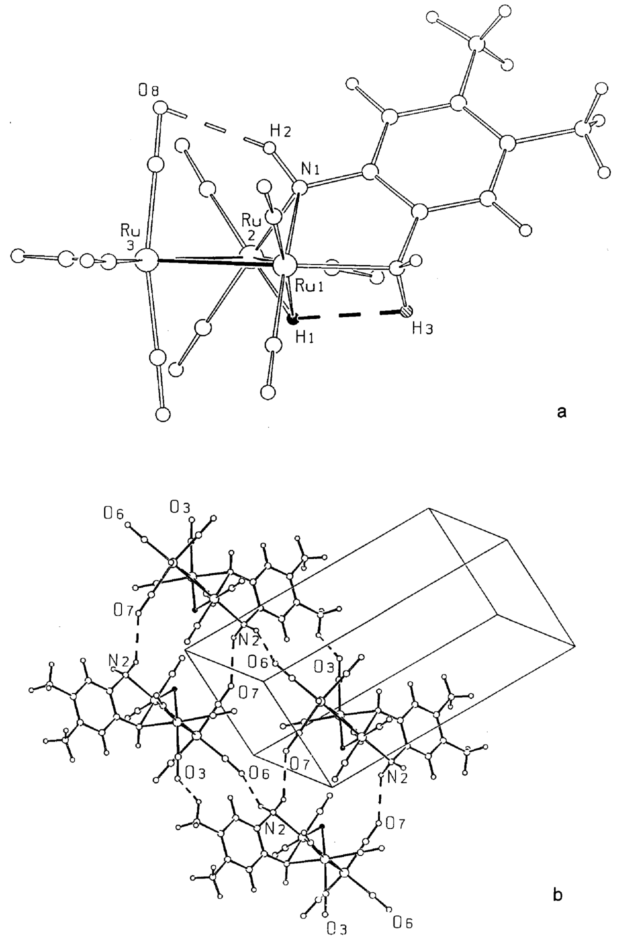

Fig. 8 (*a*) Solid state molecular structure of [(μ-H)Ru$_3$(CO)$_9$(μ-H$_3$N$_2$-4,5-Me$_2$-1,2-phenylene)]. (*b*) Intermolecular hydrogen bonding interactions involving the amino hydrogens and carbonyl oxygens.

(*i*) H···H separations span a fairly large range, from 1.891 Å in FATXON and 1.717 Å in PESXUG, to 2.484 Å in GAVBAG.

(*ii*) Some complexes are cations, the counter ions being BF$_4^-$ (FEZFUL, ZUQYUF) and PF$_6^-$ (DUPSEM01, DUPSOW, GAVBAG). Both DUPSEM01 and DUPSOW show several C—H···F interactions. Among the ionic species only FATXON is crystallised with BPh$_4^-$.

(*iii*) There are a number of both *inter*- and *intra*molecular hydrogen bonds involving C—H donors: the acceptor can be sulfur (as in DUPSOW and FATXON), chlorine (as in GAVBAG and GINWEF), nitrogen (GINWEF and FEJCOM) and oxygen (JEBPIP and DUPSEM01). In some cases, more than one type of M—H···H—X short distance is

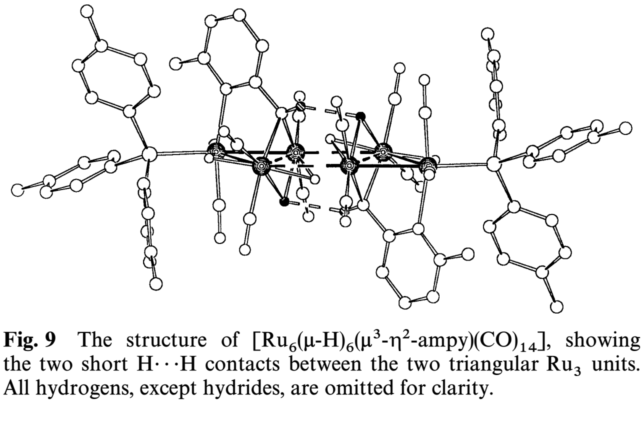

Fig. 9 The structure of [Ru$_6$(μ-H)$_6$(μ^3-η^2-ampy)(CO)$_{14}$], showing the two short H···H contacts between the two triangular Ru$_3$ units. All hydrogens, except hydrides, are omitted for clarity.

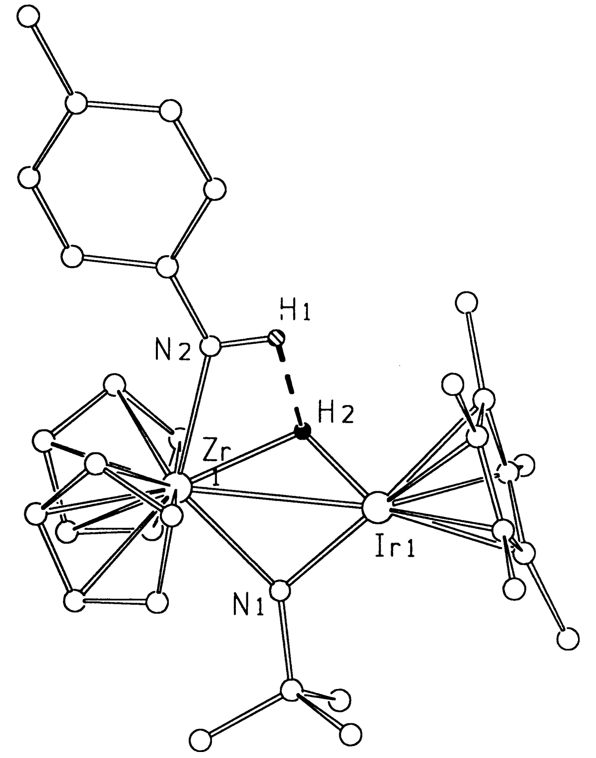

Fig. 10 The structure of [Cp$_2$Zr(NHAr)(μ-H)(μ-N-Bu^t)IrCp*] showing the short intramolecular H···H separation. H atoms of the other phenyl group are omitted for clarity.

present and some of the M—H···H—C distances can be even shorter than those involving conventional hydrogen bonds.

(*iv*) When intermolecular C—H···X interactions are established, the accepting sites are usually carbonyl oxygens; C—H···O distances can be as short as 2.321 Å (FEJCOM) and are in general comparable with C—H···O distances observed in other crystalline organometallic complexes.[8c] A short C—H···N distance is seen in LEHXAX10.

Theoretical evaluation

DFT calculations[18] were performed on almost all the compounds described above, giving a general picture of a charge distribution compatible with a negatively charged hydride interacting with a positively charged proton attached to an electronegative atom. Only the results concerning the compounds *cis*-[IrH(OH)(PMe$_3$)$_4$][PF$_6$][20a,b], *cis*-[IrH(SH)(PMe$_3$)$_4$][PF$_6$][20b] and [IrH$_2$(CO)(PPh$_3$)$_2$(pzH—N)][BF$_4$]-[C$_6$H$_5$Me][22] will be discussed in detail, in order to illustrate the role of the counter ion in determining the structures, which has not been shown previously.

An optimization of the geometry of the *cis*-[IrH(OH)(PH$_3$)$_4$]$^+$ cation was carried out, using the ADF programme[28] (see Experimental for details), under C_s symmetry, with the Ir—O—H group in the mirror plane and the two axial P—Ir bonds perpendicular to that plane. In the optimized geometry, the distances were Ir—H 1.580, Ir—O 2.057, O—H 0.964 Å and the angles H—Ir—O 90.5, Ir—O—H 108.5°. The agreement with the observed structure is not particularly good, so that in the following calculation the PF$_6^-$ anion was included, at a fixed distance, all other conditions being the same. The presence of the anion leads to a significant improvement in the distances and angles, which are now Ir—H 1.571, Ir—O 2.047, O—H 0.969 Å, and the angles are H—Ir—O 88.3°, Ir—O—H 107.0°. The Ir—O—H angle is, however, still far from the experimental value of 104.4(7)°, so that a third optimization procedure was carried out, in which the axial phosphines were allowed to bend and any symmetry element removed. The new distances and angles are Ir—H 1.572, Ir—O 2.075, O—H 0.969 Å, and the angles are H—Ir—O 88.3°, Ir—O—H 106.8°. The hydride—H(O) distance decreases as the quality of the model increases. Indeed, in the first one, this distance was 2.469 Å. The addition of the anion leads to a shorter distance (2.374 Å), an effect that is enhanced by the more flexible model without symmetry constraints (2.361 Å). This trend is shown in Chart 2, where the H···H distances and the Ir—O—H angle (italics) are given.

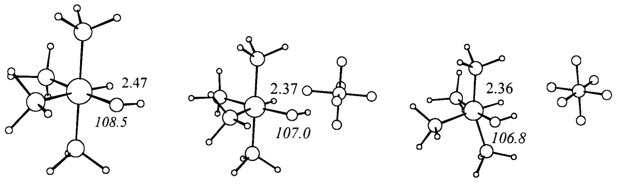

Chart 2

Notice that after the geometry optimization, the H—Ir—O—H torsion angle is 0°, as found in the structure. This rather important aspect ought to be analysed in some more detail, as it is central to our discussion. Single point calculations on idealized geometries with C_s symmetry were performed for H—Ir—O—H torsion angles of 0° and 180°, in the absence and in the presence of the PF$_6^-$ anion. The results are collected in Table 2. The arrangement where the two hydrogens, the hydride, and the H(O) are close (torsion angle 0°) is always more stable, but the relative stability increases when the counter ion is included in the calculations. The observed geometry is reproduced by the calculations and the charge distribution is compatible with an attractive electrostatic interaction. This interaction has been described before as arising from a weak dipole-dipole interaction.[14c] The hydrogen atoms occupy the positions leading to the lowest energy arrangement, according to the calculations. The presence of the counter ion is important in enhancing the trend and stabilizing the conformation.

We can now compare this complex with the related sulfur derivative, [IrH(SH)(PMe$_3$)$_4$][PF$_6$], where a H—Ir—S—H torsion angle of 180° is observed [Fig. 1(*b*)]. First, the geometry of the [IrH(SH)(PH$_3$)$_4$]$^+$ cation was optimized under C_s symmetry, but allowing the axial phosphines to bend. The H—Ir—S angle was 86.7°, the Ir—S—H angle 97.7°, and the angle between axial phosphines 165.2°. The preferred conformation was that with a torsion angle of 1.4°, close to 0° (Chart 3, left).

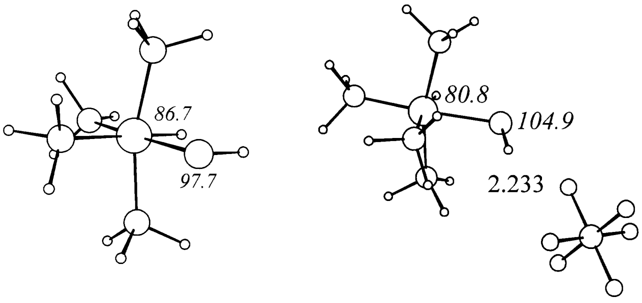

Chart 3

Table 2 Results of single point calculations on *cis*-[IrH(OH)(PH$_3$)$_4$]$^+$, without and with PF$_6^-$.

	No PF$_6^-$	No PF$_6^-$	With PF$_6^-$	With PF$_6^-$
H—Ir—O—H	0°	180°	0°	180°
Relative energy[a]	0.00	4.98	0.00	10.56
Charges				
Ir	0.182	0.190	0.176	0.193
Hydride	−0.157	−0.156	−0.072	−0.073
O	−0.730	−0.725	−0.740	−0.714
H(O)	0.278	0.279	0.304	0.274

[a] kcal mol^{-1}.

Inclusion of the PF_6^- anion in the energy optimization resulted in a reorientation of the sulfur hydrogen toward one of the fluorines and in a very different torsion angle of 166.1° (Chart 3, right). The Ir—S—H angle opened up from 97.7° to 104.9°, closer to the experimental value of 111(3)°, while the H—Ir—S angle became 80.8° (experimental 76°), and the angle between the axial phosphines 163.8° (experimental 164°). The Ir—P distances were all slightly affected by the introduction of the counter ion, changing from 2.275 to 2.269 Å (axial ones), 2.358 to 2.348 Å (*trans* to hydride), and 2.258 to 2.252 Å (*trans* to sulfur). The Ir—H distance did not change significantly (1.573 to 1.575 Å), but the Ir—S distance shortened by *ca.* 0.1 Å (2.436 to 2.344 Å). The experimental distances are, for comparison, Ir—H 1.642, Ir—S 2.487, Ir—P 2.354, 2.343, 2.378 and 2.298 Å (axial, *trans* to H, *trans* to S). The charge distribution is different from that in the previous *cis*-$[IrH(OH)(PH_3)_4]^+$ complex, reflecting the smaller electronegativity of sulfur. The hydride carries a −0.244 charge, the H(S) +0.209, sulfur −0.347 (in the presence of the anion). Instead of a short H···H contact, a S—H···F interaction is found. Again in this compound, the observed geometry is consistent with the results of the DFT calculations, and maximizes the interaction with the counter ion.

The compound $[IrH_2(CO)(PPh_3)_2(pzH—N)][BF_4][C_6H_5Me]$[22] is also cationic and contains a short 1.998 Å distance between one hydride and a pyrazole hydrogen [see Fig. 5(*a*)]. The geometry of $[IrH_2(CO)(PH_3)_2(pz)]^+$ was optimized under C_s symmetry, keeping the pyrazole ring in the mirror plane, and afterwards, in a second calculation, it was optimized in the presence of the BF_4^- anion. Although bond distances were essentially maintained unaltered (Ir—N 2.136/2.137, Ir—H(2) 1.591/1.583, Ir—H 1.555/1.561, N—N 1.353/1.359 Å), some angles changed significantly with the introduction of the anion. The H(2)—Ir—N angle closed from 89.9° to 74.3°, while the angle between the two phosphines changed from 170.2° (constrained by symmetry) to 164.1° (no symmetry when the anion is present). As a consequence, the two hydrogens, the hydride H(2) and the H(N), approached from 2.474 to 2.106 Å, as shown in Chart 4. One fluorine atom from the anion is involved in a hydrogen bond with the two hydrogens.

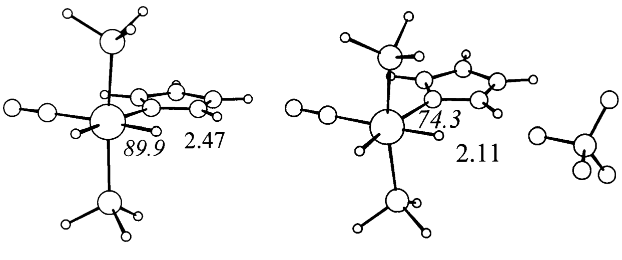

Chart 4

This seems to imply that the presence of the BF_4^- anion is the driving force for moving the two atoms together. Single point calculations on an idealized geometry under C_s symmetry were also performed in the absence and in the presence of the counter ion; the results are shown in Table 3. These values indicate that the preferred conformation is more stabilized when BF_4^- is considered. The charge distribution is consistent with an attractive electrostatic interaction, the hydride carrying a negative charge and the H(N) a positive one. The hydride charge becomes less negative when the conformation of the pyrazole ring is changed from the 0° situation to the 180° one. Interestingly, the proximity of the anion has a strong influence on H(N), its charge being the most significantly affected among those shown. This suggests that a N—H···F hydrogen bond is being formed.

Table 3 Results of single point calculations on $[IrH_2(CO)(PH_3)_2(pz)]^+$, without and with BF_4^-.

	No BF_4^-	No BF_4^-	With BF_4^-	With BF_4^-
H—Ir—N—H	0°	180°	0°	180°
Relative energy[a]	0.00	1.76	0.00	7.68
Charges				
Ir	0.594	0.592	0.591	0.592
Hydride	−0.239	−0.219	−0.149	−0.135
N(H)	−0.476	−0.478	−0.477	−0.486
H(N)	0.236	0.245	0.276	0.233

[a] kcal mol^{-1}.

Conclusions

In this paper we have systematically investigated the occurrence and characteristics of H···H interactions between metal bound hydrogen atoms and hydrogen atoms bound to electronegative main group elements (C, N, O, and S) and which can, in principle, be donated in hydrogen bond formation. The structures extracted from the CSD have been investigated by means of DFT calculations and the results discussed for three compounds where interesting conclusions could be drawn.

Indeed, for *cis*-$[IrH(OH)(PMe_3)_4][PF_6]$, *cis*-$[IrH(SH)(PMe_3)_4][PF_6]$[20] and $[IrH_2(CO)(PPh_3)_2(pzH—N)][BF_4][C_6H_5Me]$,[22] the geometrical arrangement leading to the formation of H···H contacts results from the overall optimization of the structure of the cation. More importantly, the inclusion of the counter ion in the model for geometry optimisation led to a significant improvement of the results. This indicates that the anions are not innocent spectators but can influence the extent of H···H interaction.

For the other compounds, the results of the calculations were not particularly enlightening so as to deserve detailed discussion. In particular, the neutral compound $[IrH(Cl)(PEt_3)_2(NHPhC_7H_{10})]$, which could be directly compared, as it is also an iridium complex exhibiting a short H···H(N) distance, is difficult to model accurately. What can be said is that in general the charge distribution is compatible with an electrostatic interaction for all the terminal hydride species. For bridging hydride derivatives, this ligand usually carries a positive charge and is forced to close proximity to other protons by steric constraints.

Experimental

Cambridge Structural Database[17] analysis: data were retrieved from the October 1997 version of the CSD for all crystal structures with an exact match between chemical and crystallographic connectivity. Both neutral and charged species were considered. Only entries where $R < 0.10$ and where atomic coordinates (including those of the hydride atoms) are given were considered. Geometrical calculations were performed on these hydride subsets for M—H···H hydrogen bonds with H···H distances between 1.5 and 2.5 Å. Duplicate hits (identified by the same REFCODES) were manually removed by eliminating the structure with the highest R values (for the X-ray determinations). Unique contacts were considered up to an H···H distance of 2.34 Å (van der Waals sum). M—H bond lengths were taken as such and not normalized (see below). A representative example of a geometrical question is given in the electronic supplementary material. All the examples were taken from the search outputs and were investigated by computer graphics.[28a] The computer program PLATON[28b] was used to analyse the metrical features of the hydrogen bonding patterns.

The DFT calculations[18] were based on the LCAO density functional programme system by Baerends *et al.*[29] A new numerical integration scheme allowed for the accurate and efficient evaluation of the matrix elements appearing in the secular equation.[30] The core orbitals were frozen for Ir ([1–5]s, [1–5]p, [3,4]d, 4f), Zr, Rh ([1–4]s, [1–4]p, 3d), P (1s, 2s, 2p) and O, C, N, F (1s). Triple ζ basis sets were used for H 1s; O, C, N, F 2s, 2p; P 3s, 3p; Ir 5d, 6s, 6p, and were augmented with one polarization function for H, O, C, N, F, P. Relativistic effects were incorporated for iridium and phosphorus in the calculations as proposed by Ziegler *et al.*[31] Bond energies were evaluated by the generalized transition state method.[32] The Vosko, Wilk, Nusair[33] parametrization for the electron gas was used and Perdew and Wang's non-local exchange and correlation corrections were included in the gradients calculations.[34]

Acknowledgements

Financial support from the University of Bologna (project "*Innovative Materials*") and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (project "*Supramolecular Devices*") is acknowledged (DB and FG). DB, FG, and MJC acknowledge CNR (Italy) and JNICT (Portugal) for joint financial support. PEML acknowledge funding from JNICT (BD2527/93). MJC and PEML thank the HCM European network *Quantum Chemistry of Transition Metals Compounds* for funding.

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Paper 8/09073D