CH/π Interactions Implicated in the Crystal Structure of Transition Metal Compounds − A Database Study[‡]

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A statistical study was carried out to investigate the role of the CH/π interaction in the crystal structure of transition metal compounds. Thus, short CH/π distances were surveyed in crystal structures deposited in the Cambridge Structural Database. Among organometallic entries bearing C_6 or C_5 aromatic rings, a substantial part of the structures has been found to have intermolecular CH/π contacts shorter than the van der Waals distance. Further, in many structures short intramolecular CH/π contacts have been found. Interligand and intraligand CH/π interactions were also surveyed in coordination compounds bearing the typical ligands 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′:6′,2′′-terpyridine, as well as triphenylphosphane complexes of ruthenium, rhenium, and rhodium. The results were discussed in the context of the CH/π interaction in controlling the crystal packing and the molecular structure of transition metal compounds. The compact structure with CH/π interactions is a general aspect in coordination and organometallic chemistry.

Introduction

Sigel and his co-workers studied the conformation of a number of ternary metal complexes with aromatic and aliphatic ligands such as M(bipy)(AA), M(phen)(AA)[1] and M(ATP)(AA)[2] [M = Cu^{2+} or Zn^{2+}, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, ATP = adenosine triphosphate, AA = $RCH(NH_2)COOH$]. In every case, the alkyl group R (isopropyl, isobutyl, etc.) in AA was found to curl over the aromatic rings to form a folded rather than an extended conformation. A number of examples have been provided by these workers where, in complexes including nucleotides and amino acids as ligands, the structures displaying alkyl/arene as well as arene/arene interactions prevail in solution.[3] The results imply that an attractive interaction operates between these moieties.

Okawa first recognized the importance of CH/π interaction in the stereoselective formation of several metal complexes.[4] The relevance of the CH/π interaction[5] in coordination and organometallic chemistry has since been shown by a number of workers.[6] For instance, Brunner studied the crystal and solution structure of a series of ruthenium compounds with a cyclopentadienyl and/or benzene unit as ligand. One of the isomers in a half-sandwich complex, where a hydrogen atom of the η^5- or η^6-arene ligand points to an aromatic group in the neighboring ligand, has been shown to be more stable than the diastereoisomeric congener. They termed this the "β-phenyl effect",[7] and the phenomenon is now understood on the grounds of the CH/π hydrogen bond.[8] His finding has an obvious implication for the mechanism of enantioselective catalysis.[9]

The CH/π interaction is the weakest extreme of nonconventional hydrogen bonds[10] and is recognized to be the interaction between soft acids and soft bases,[11] in contrast to the ordinary hydrogen bond, that is the interaction between hard acids and hard bases. Though weak, the CH/π hydrogen bond plays significant roles in various fields of chemistry such as the conformation of molecules,[12] self-assembly[13] as well as chiral recognition.[14] The electronic substituent effect on the stereoselectivity of complex formation,[15] conformational equilibrium,[16] crystal packing,[17] and enantioselectivity[18] has demonstrated that the CH/π interaction is by no means merely a dispersion force. According to high-level ab initio calculations, the most important stabilization comes from the correlation energy.[19] The electrostatic interaction also contributes, but is a minor factor (ca. 20%)[20] in the CH/π interaction. Hence, the CH/π interaction is nonpolar and is effective in water unlike the conventional hydrogen bond and Coulomb force. This

[‡] CH/π Interactions − A comprehensive literature list for the CH/π interaction is available on the following website: http://www.tim.hi-ho.ne.jp/dionisio

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point is of supreme importance when considering the role of CH/π interaction in biological environments. Evidence has in fact been presented for the ubiquity of CH/π bonds in the interaction involving protein[21,22] or DNA.[23]

CH/π interactions are often reported to occur in crystal packing[24] of organometallic compounds and in clathrates.[25] Braga and co-workers reported on a Cambridge Structural Database (CSD) study of organometallic entries including XH/π (X = O, N C) bonds and demonstrated the hydrogen bond character of these interactions.[26] Previously we showed, by analyzing structures in the CSD,[27] the prominence of CH/π interactions in the packing of organic crystals[28] and host/guest compounds.[29] To investigate the significance of the CH/π interaction in coordination and organometallic chemistry, we extended our approach to the crystal structure of transition metal compounds.

Method

The CSD version 5.21 and 5.22 (April and October 2001 release) were used. The 6- and 5-membered aromatic ring systems were chosen in view of their abundance in the database. The method of exploring CH/π interactions in the CSD was described in detail in our previous papers.[12a,28,29] For surveying CH/π interactions in compounds bearing an arene ring, several kinds of distance and angle parameters were defined to cover every possibility. This is necessary since a C−H group may interact in regions where the hydrogen atom is slightly offset out of the π-plane. Figure 1 illustrates the method for a six-membered arene ring. Nonbonding contacts were sought with appropriate cut-off values for the distance and angle parameters. Interatomic distances shorter than the sum of the van der Waals radii[30] were considered as relevant for the presence of CH/π interaction.[31] In practice, the software QUEST3D was used to find CH/π contacts within the above constraints.

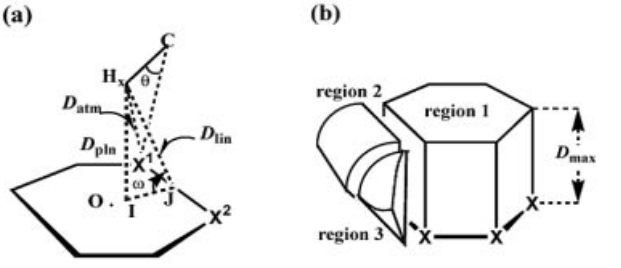

Figure 1. Method of surveying CH/π contacts with a 6-membered aromatic ring: (a) O: center of the plane; X^1 and X^2: nearest and second nearest sp^2 atoms, respectively, to H; ω: dihedral angle defined by X^1OX^2 and HX^1X^2 planes; θ: HCX^1; D_{pln}: H/π-plane distance (H/I); D_{atm}: interatomic distance (H/X^1); D_{lin}: distance between H and line X^1X^2 (H/J); (b) the program was run to search for H/π distances shorter than a cut-off value D_{max} in every region; $D_{pln} < D_{max}$, $\theta < 60°$, for the region just above the ring (region 1); $D_{lin} < D_{max}$, $\theta < 60°$, $90° < |\omega| < 130°$ for the region slightly offset from the ring (region 2); $D_{atm} < D_{max}$, $\theta < 60°$, $50° < \varphi < 90°$ for another possible region φ: HX^1I (region 3)

Results and Discussion

Intermolecular Interactions

First, coordinates determined by the neutron diffraction method were examined. Table 1 shows the results for entries bearing at least a C_6 aromatic group. The mean intermolecular CH/π distance D_{atm} increases to a larger value when the cut-off distance is longer. The proportion of hit entries, however, does not increase appreciably. The interatomic distance was then surveyed, separately, for sp^2- and sp^3-CH/π interactions. The aromatic CH groups interact with the π-system at a shorter distance than the alkyl groups.

Table 1. Intermolecular CH/π interactions in the crystal structure of organometallic compounds bearing a C_6 arene ring, determined by neutron diffraction (71 entries)

	Hit[a]	Ratio[b] (%)	D_{atm}/Å[c] (fragment)[d]
D_{max}			
3.05 Å	55	77	2.87 ± 0.13 (514)
sp^2-CH	35	49	2.86 ± 0.13 (226)
sp^3-CH	28	39	2.89 ± 0.12 (101)
3.20 Å	58	82	2.94 ± 0.17 (684)
3.50 Å	59	83	3.03 ± 0.23 (874)

[a] Number of entries with short CH/Ar contacts. [b] Proportion of hits. [c] Mean atomic distance. [d] Number of observations.

Intermolecular CH/π distances were then sought from the entire CSD (Table 2). Only error-free, nondisordered structures with $R < 10\%$ were accepted. Among 39570 organometallic entries with C_6 arene ring(s),[32] 28363 crystal structures (ca. 72%) have been found to have at least one CH/π distance shorter than 3.05 Å.[33] This proportion is a conservative estimate, since in the above 39570 entries, structures bearing no hydrogen coordinates are counted. The CH groups may also interact with nonbenzenoid π-systems such as heteroaromatics, cyclopentadienyl groups, or multiple bonds such as C≡C, C=O, etc. Further, the CH/π interaction may operate at a distance longer than 3.05 Å. D_{atm} shifted to a longer value for a larger D_{max} but the number of hits did not increase remarkably. Table 2 includes data obtained by surveying compounds with C_5 aromatic rings as the CH acceptor. D_{atm} is not appreciably distinct from the C_6 case; the results suggest that the π-donating property is not very different between these rings. The ratio of hits, on the other hand, is smaller in C_5 than in C_6 arenes. This probably reflects the smaller surface area of a cyclopentadienyl group than that of the C_6 aromatic compounds. Several database subsets were edited for 1st, 2nd, and 3rd row transition elements and surveyed. No appreciable difference has been noted between these subsets.

Figure 2 shows histograms recorded by surveying CH hydrogen atoms interacting with the C_6 aromatic ring. We see many distances shorter than the van der Waals distance. In Figure 3, positions of the hydrogen atoms are projected onto the C_6 π-plane.[34] It is remarkable that the C−H bond

Table 2. CH/π intermolecular contacts in the crystal of compounds containing transition metals (TR)

	DB[a]	Hit[b]	Ratio (%)[c]	D_{atm}/Å[d] (fragments)[e]
(a) C_6 aromatic ring as the CH acceptor				
D_{max} 3.05 Å				
All TR	39570	28363	72	2.90 ± 0.13 (> 10000)
1st row elements	15900	11361	71	2.90 ± 0.13 (> 10000)
2nd row	11366	8466	74	2.90 ± 0.13 (> 10000)
3rd row	9799	6846	70	2.90 ± 0.13 (> 10000)
D_{max} 3.20 Å	39570	29343	74	2.97 ± 0.16 (> 10000)
D_{max} 3.50 Å	39570	29922	76	3.08 ± 0.23 (> 10000)
(b) C_5 aromatic ring as the CH acceptor (D_{max} 3.05 Å)				
All TR	18198	8583	47	2.87 ± 0.13 (> 10000)
1st row elements	9496	4596	48	2.86 ± 0.14 (> 10000)
2nd row	7487	3579	48	2.87 ± 0.14 (8693)
3rd row	3946	1586	40	2.87 ± 0.14 (3302)

[a] Number of entries in the database subset. [b] Number of hits. [c] Proportion of hits. [d] Mean atomic distance. [e] Number of observations.

tends to point toward the center of the aromatic ring; this is consistent with our earlier experiences on organic crystals. Braga et al. also noticed the directionality of the XH/π-type interactions.

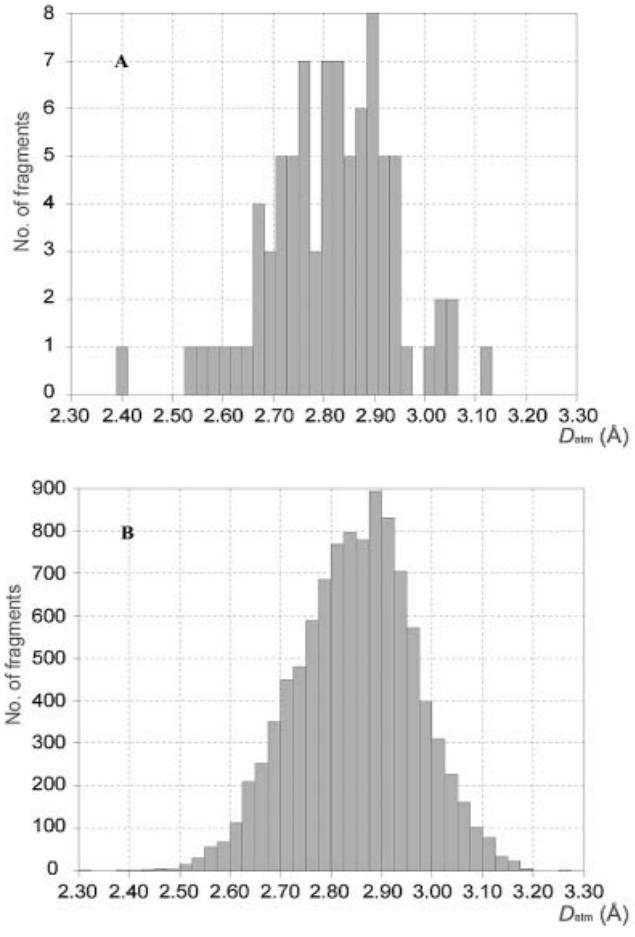

Figure 2. Histograms showing the distribution of CH/C-sp^2 interatomic distances in C_6 aromatic compounds; D_{max} 2.90 Å, region 1 (sp^2-CH); (a) neutron data; (b) X-ray data (VISTA version 2.0)

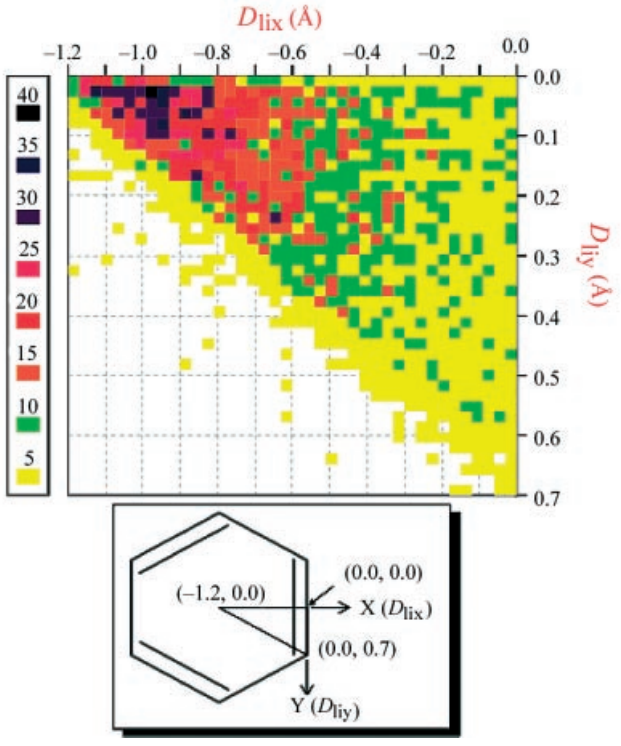

Figure 3. CH hydrogen atoms projected on the C_6 π-plane; only hydrogen atoms with D_{pln} < 2.90 Å are projected; region 1, sp^2-CH (VISTA version 2.0)

Table 3. Intramolecular CH/π interactions in the crystal structure of organometallic compounds bearing a C_6 arene ring, determined by neutron diffraction (71 entries)

	Hits[a]	Ratio (%)[b]	D_{atm}/Å[c] (fragment)[d]
N[e] = 4–999	48	67	2.70 ± 0.16 (311)
4–6	47	66	2.68 ± 0.15 (253)
7–9	23	32	2.79 ± 0.18 (54)
10	2	3	2.86, 3.06, 3.11, 3.06 Å

[a] Number of entries with short CH/Ar contacts. [b] Proportion of hits. [c] Mean atomic distance. [d] Number of observations. [e] Number of covalent bonds separating the hydrogen and carbon atoms.

Table 4. Intramolecular CH/π contacts in transition metal (TR) compounds (D_{max} 3.05 Å)

	DB[a]	Hit[b]	Ratio (%)[c]	D_{atm}/Å[d] (fragments)[e]
C_6 aromatic ring as the CH acceptor				
All TR elements	39570	20738	52	2.71 ± 0.17 (> 10000)
N[f] = 4−999				
4−6		18893	50	2.68 ± 0.16 (> 10000)
7−9		7985	39	2.83 ± 0.16 (> 10000)
10−12		2602	7	2.90 ± 0.14 (4747)
13−15		436	1	2.89 ± 0.14 (660)
> 16		60	< 0.2	2.89 ± 0.14 (86)
1st row elements	15900	7292	46	2.72 ± 0.17 (> 10000)
2nd row	11366	6890	61	2.71 ± 0.17 (> 10000)
3rd row	9799	5629	58	2.71 ± 0.17 (> 10000)
C_5 aromatic ring as the CH acceptor				
All TR elements	18198	1128	6	2.71 ± 0.19 (1845)
1st row	9496	871	9	2.70 ± 0.19 (1495)
2nd row	7487	386	5	2.70 ± 0.18 (610)
3rd row	3946	187	5	2.68 ± 0.18 (315)

[a] Number of entries in the database subset. [b] Number of hits. [c] Proportion of hits. [d] Mean atomic distance. [e] Number of observations. [f] Number of covalent bonds separating the hydrogen and carbon atoms.

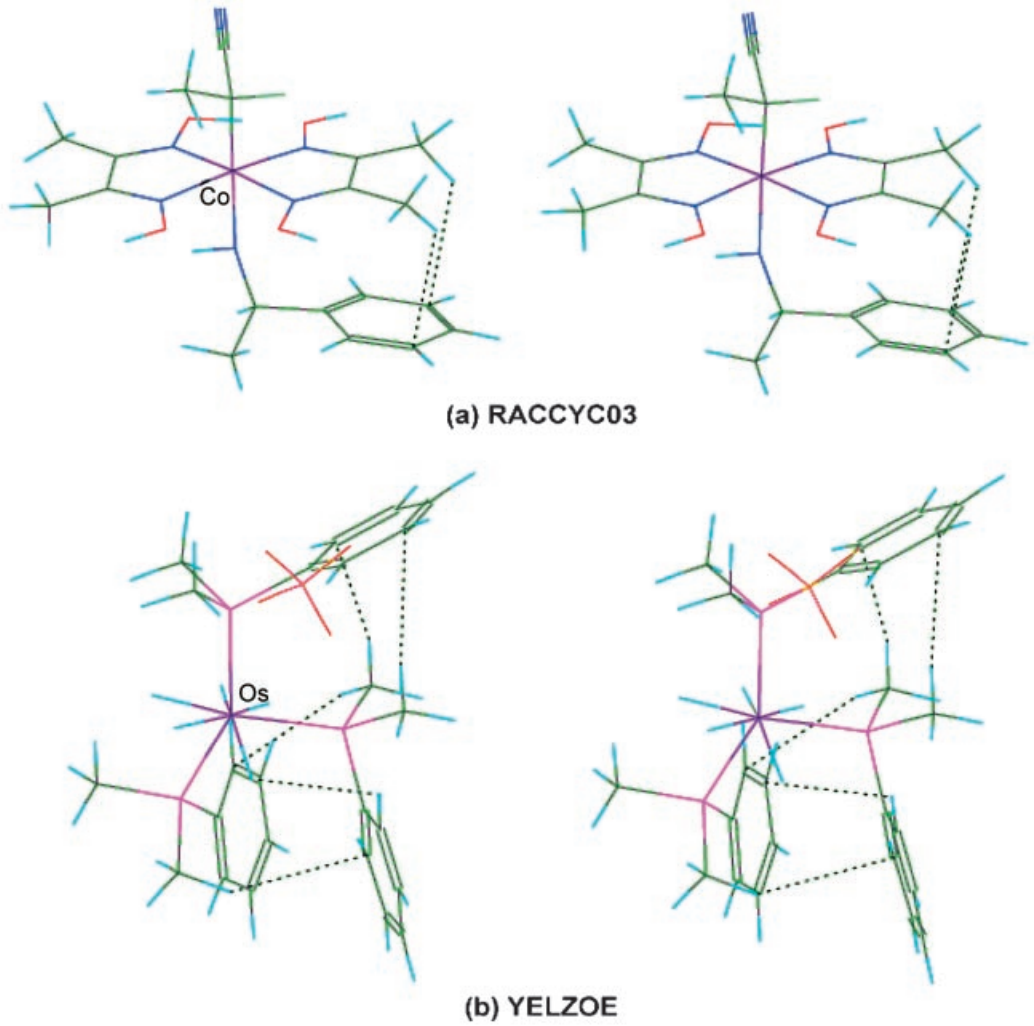

Figure 4. Intramolecular CH/π contacts disclosed in transition metal complexes (stereo view); dotted lines indicate CH/π contacts; purple: transition metal atom; (a) RACCYC03: [(*R*)-1-cyano-1-deuterioethyl][(*S*)-1-phenylethylamine]bis(dimethylglyoximato)cobalt(III); (b) YELZOE: Pentahydridotris[dimethyl(phenyl)phosphane]osmium tetrafluoroborate

Intramolecular Interactions

Table 3 gives the results obtained by examining intramolecular interactions; here the entries are limited to neutron diffraction data. We found that these structures have CH/π contacts both between and within the ligands.[35] Both the interligand and intraligand CH/π interactions seem to play an important part in controlling the shape of metal complexes.

Table 4 summarizes the results obtained by surveying the entire CSD. Among 39570 entries, 20738 crystal structures (ca. 52%) have been found to have at least one short CH/π intramolecular distance. Examples are given in Figure 4. Tables 3 and 4 show that the value of D_{atm} increases on going to a larger number of covalent bonds (N) separating the relevant H and C(sp^2) atom. The greater the value of N, the longer the CH/π interatomic distance. This is reasonable, since with a smaller N the position of CH is greatly restricted. The value of D_{atm} coalesces finally to that of the intermolecular interaction. Intramolecular interactions involving the C_5 aromatic ring as the CH acceptor are very scarce (ca. 6%). The exact reason remains unclear, but it may be pointed out that in these cyclopentadienyl compounds, ligands generally have few moieties that can make intramolecular contacts with the C_5 aromatic part.

Interactions Involved in Complexes with Certain Heteroaromatic Ligands

We then examined interactions among complexes bearing 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′:6′,2′′-terpyridine as ligands. The importance of these ligands as supramolecular motives is well known.[36] In these surveys, six-membered heteroaromatic rings also acted as the CH acceptor. Table 5 lists the results. The proportion of hits in these complexes is lower than in the general cases reported in Table 4. This is probably because such nitrogen-containing flat ligands often form an offset π/π-stacked structure.[37,38] Representative examples are given in Figure 5. CH/π contacts are often found between an *ortho*-hydrogen atom of a pyridine moiety and an sp^2 atom of a nearby ring.

Interactions Involved in Complexes with Triphenylphosphane Ligands

Rhenium, rhodium, and ruthenium compounds bearing triphenylphosphane as ligands were also examined in view of their potent use as catalysts in the enantioselective reaction. Table 6 lists the results. The ratio of hits is considerably higher in these complexes than in the other cases. This certainly reflects the propensity of PPh_3 to form CH/π bonds within the ligand or with a nearby part of the complex. Figure 6 gives representative examples. Short contacts

Table 5. Intramolecular CH/π contacts in 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′:6′,2′′-terpyridine complexes

Ligand	DB[a]	Hit[b]	Ratio (%)[c]	D_{atm}/Å[d] (fragment)[e]
Phenanthroline	789	314	40	2.79 ± 0.16 (1011)
Bipyridine	1479	592	40	2.70 ± 0.17 (2121)
Terpyridine	300	118	39	2.74 ± 0.17 (509)

[a] Number of entries in the database subset. [b] Number of hits. [c] Proportion of hits. [d] Mean atomic distance. [e] Number of observations.

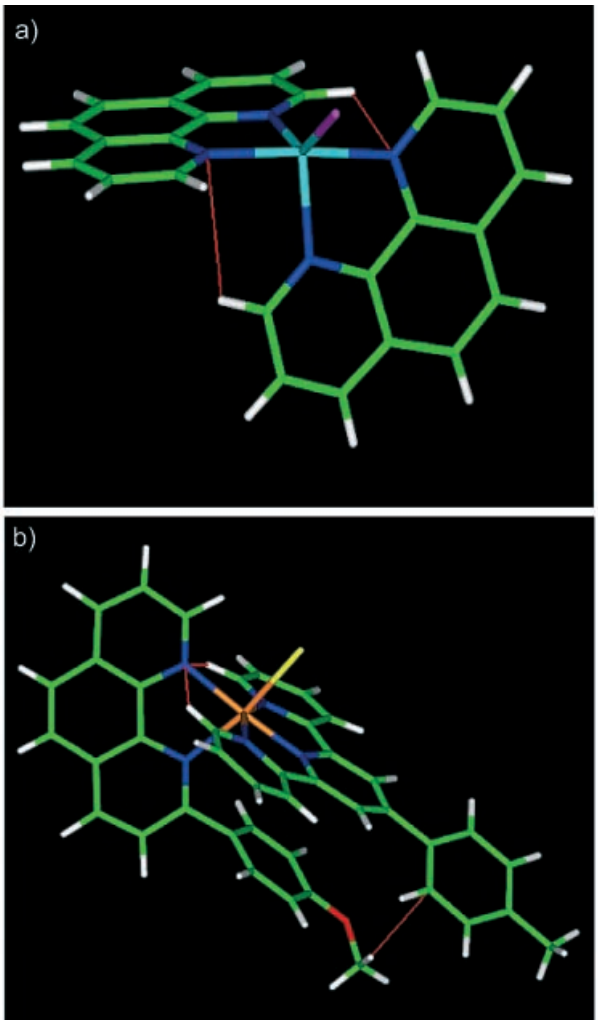

Figure 5. Interligand CH/π contacts disclosed in 1,10-phenanthroline complexes; red dotted lines indicate CH/π contacts; light blue: Cu; yellow: Cl; violet: I; orange: Ru; BASHIM: iodobis(1,10-phenanthroline)copper triiodide monoclinic polymorph; HOXLIP: chloro[4′-(*p*-tolyl)-2,2′:6′,2′′-terpyridine-*N*,*N*′,*N*′′][2-(*p*-anisyl)-1,10-phenanthroline-*N*,*N*′]ruthenium(II) hexafluorophosphate benzene solvate

Table 6. Intramolecular CH/π contacts in (triphenylphosphane)ruthenium, -rhenium, and -rhodium complexes

Metal	DB[a]	Hit[b]	Ratio (%)[c]	D_{atm}/Å[d] (fragment)[e]
Ruthenium	951	798	84	2.66 ± 0.17 (6144)
Rhenium	551	394	72	2.67 ± 0.16 (2857)
Rhodium	494	375	76	2.66 ± 0.16 (2667)

[a] Number of entries in the database subset. [b] Number of hits. [c] Proportion of hits. [d] Mean atomic distance. [e] Number of observations.

are found between CH groups of an alkyl chain as well as aromatic groups and a phenyl ring in the triphenylphosphane moiety. Dance and Scudder studied the interaction involved in both PPh_3 complexes [39] and Ph_4P^+ salts[40] in organometallic entries. They found many edge-to-face interactions and termed such a motif the "multiple phenyl embrace". These motifs seem to make the crystal structures compact and stable. Our suggestion is that this tight structure is achieved by a cooperative use of the aromatic CH/π interaction.[41]

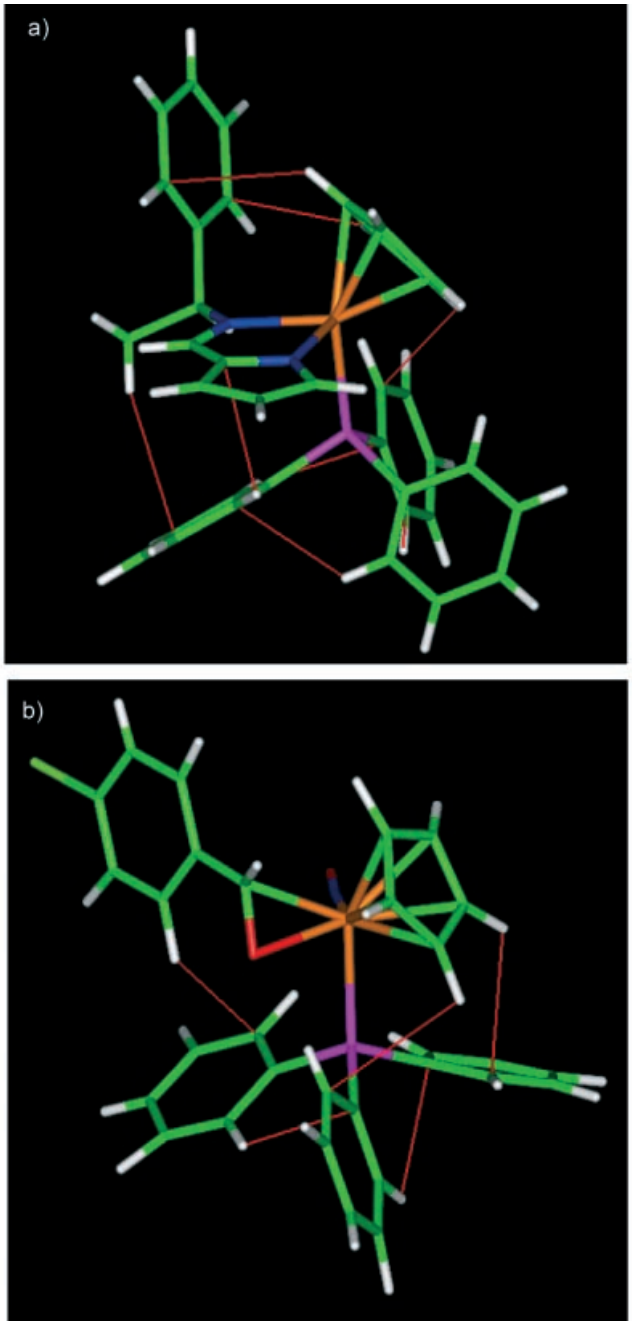

Figure 6. Intramolecular CH/π contacts disclosed in complexes bearing triphenylphosphane as a ligand; red dotted lines indicate interligand and intraligand CH/π contacts; orange: Ru or Re; violet: P; JUFQAC: η^5-cyclopentadienyl(triphenylphosphane){2-*N*-[(*S*)-1-phenylethyl]pyrrolecarbaldimine}ruthenium(II)]; ZAJSUY01: (η^5-cyclopentadienyl)nitrosyl-(η^2-*p*-chlorobenzaldehyde)(triphenylphosphane)rhenium hexafluorophosphate

Conclusion

To summarize, CH/π interactions are ubiquitously found in crystals of transition metal compounds. In other words, the CH/π-interacted crystal packing and the compact molecular structure are general aspects in coordination and organometallic chemistry. Janiak examined interactions involved in metal complexes with nitrogen-containing aromatic ligands[37] and found that the π/π-stacking[42] seldom occurs at a perfect parallel-stack geometry of the opposing parts. Nitrogen-containing flat ligands generally form an offset π/π-stacked structure. This is compatible with the present results that, for 1,10-phenanthroline complexes etc., aromatic CH/π interactions prevail but the ratio of hits is somewhat smaller than in the general cases. There are ample data in the literature demonstrating that the folded crystal conformation of metal compounds is maintained in solution.[43] The present statistical data suggest that these findings are not necessarily fortuitous, but exhibit a part of the general phenomenon. It is pertinent to point out in this regard that Taylor et al. presented unequivocal evidence by a CSD study that the so-called crystal packing forces do not provide systematic influence on molecular conformations.[44]

The enthalpy of one unit CH/π bond is certainly the smallest (around 1 kcal mol^{-1})[45] among the nonconventional hydrogen bonds. A notable feature of this molecular force, however, is that many CH groups can participate cooperatively in an interaction with π-bases. Besides, the CH/π interaction is entropically advantageous in that CH and π groups are generally arranged in a certain symmetric structure to make a persistent (stable and flexible) organization of molecules or molecular aggregates. We conclude that the concept of a CH/π hydrogen bond is vital in understanding various issues of chemistry and biochemistry of the transition metal compounds.

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[32] The entries include metal complexes as well as organometallic compounds (screen −57 in the QUEST3D program) bearing at least one C_6 aromatic ring.

[33] In the hit entries, we note crystal structures of inorganic salts such as carbonylmetal complexes pairing with Ph_4P^+ as the counter ion.

[34] D_{max} 2.90 Å: Hydrogen atoms are limited to aromatic CH groups to minimize the chemical inhomogeneity.

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