Articles

Hydrogen Bonding in Organometallic Crystals. 4.[†] M−H- - -O Hydrogen-Bonding Interactions

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M−H- - -O hydrogen-bonding interactions in crystalline organometallic complexes and clusters of the transition metals have been investigated. Molecular and crystal structures determined by neutron and/or X-ray diffraction data have been retrieved from the Cambridge Structural Database. In a number of cases there is clear manifestation of M−H- - -O hydrogen bonding involving metal-bound H("hydride") atom(s) and oxygen atoms mainly belonging to CO groups. When the H-ligands are electronically suited to being hydrogen-bonding donors, the absence of M−H- - -O interactions is due to the steric congestion around the coordination sites of the H-ligands. Individual crystal structures have been examined in detail. It is suggested that the M−H- - -O hydrogen bond is an example of a soft intermolecular interaction and is comparable in strength to C−H- - -O hydrogen bonds.

Introduction

The great structural diversity of organometallic systems, arising from the variability of the ligands and from the ligand−metal(s) bonding, is reflected in the types and patterns of hydrogen bonding and other intermolecular interactions that are present in their crystals.[1] Hydrogen bonding is a subject of great relevance in the fields of supramolecular chemistry and crystal engineering.[2] While most efforts have been devoted to organic and biological materials,[3] not much attention has been paid to organometallic systems. Recently, we have undertaken a systematic study of the hydrogen bonds in organometallic crystals with the Cambridge Structural Database.[4] Conventional hydrogen bonds formed by strong donor/acceptor groups such as −COOH and −OH systems,[5] as well as hydrogen bonds of the C−H- - -O type, have been investigated.[6] As far as strong hydrogen bonding is concerned, organic molecules such as carboxylic acids, alcohols, or amides form the same types of hydrogen bonds whether as "free" molecules or as ligands. In weak hydrogen-bonding situations and/or when steric factors do not permit efficient approach, other bases, such as, for instance, the ubiquitous CO ligand, can become competitive and accept hydrogen bonds from donors such as O−H, N−H, and (mainly) C−H groups.[6] Although the C−H- - -OC interaction is relatively "soft" with respect to the "hard" O−H- - -O hydrogen bonds, the diffusion of C−H units and of CO ligands makes its contribution to crystal stability far from negligible. We have also shown that the order of basicity of the CO ligand follows the order of increasing back-donation onto oxygen; i.e. the μ_3-bridge is more basic than the μ_2-bridge, while the terminal CO is the least basic as reflected in the average lengths of the intermolecular H- - -O separations.[6] The survey also revealed that the C−H- - -OC bonds are quite directional, with the C−O- - -H angle around 140° indicating oxygen lone pair density in "ketonic" directions for both bridging and terminal coordination geometries.

More recently we have investigated the intermolecular hydrogen bond distribution and geometry in crystals of transition metal complexes containing primary

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[†] For part 3, see ref 7.

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(1) Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun.* (feature article), in press. Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1994**, *27*, 51.

(2) (a) Lehn J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (b) MacDonald; Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. (c) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989. (d) Sharma, C. V. K.; Desiraju, G. R. In *Perspective in Supramolecular Chemistry. The Crystal as a Supramolecular Entity*; Desiraju, G. R., Ed.; Wiley: New York, 1996.

(3) (a) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991. (b) Murray-Rust, P.; Glusker, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1018. (c) Jeffrey, G. A.; Maluszynska, H.; Mitra, J. *Int. J. Biol. Macromol.* **1985**, *7*, 336. (d) Steiner, T.; Saenger, W. *Acta Crystallogr., Sect. B* **1992**, *B48*, 819. (e) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. (f) Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1555.

(4) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Watson, D. G. *J. Chem. Inf. Comp. Sci.* **1991**, *31*, 204.

(5) Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju. G. R. *Organometallics* **1994**, *13*, 3532.

(6) Braga, D.; Biradha, K.; Grepioni, F.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156.

S0276-7333(96)00025-8 CCC: $12.00

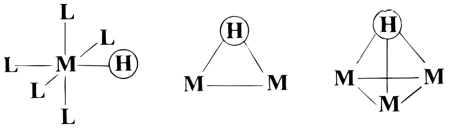

Figure 1. Hydride ligand bonding modes: left, terminal mode; middle, μ_2-bonding mode; right, μ_3-bonding mode.

$-CONH_2$ and secondary amido $-CONHR$ groups and compared with those observed in crystalline organic amides.[7]

In this paper we tackle a problem which is specific of organometallic systems and has no parallel in the neighboring organic chemistry field. We have found evidence, from a search of the CSD, for the existence of M−H- - -O cohesive interactions in which the metal atoms carrying H(hydride) ligands[8] act as donors in *intermolecular* hydrogen bonds with the oxygen atoms of the ligands, mostly CO.

The hydrogen atom can bind to mono- and polynuclear metal complexes in terminal or bridging fashions. Bridging hydrides can span a metal−metal bond (μ_2-bonding mode) or cap a triangulated metal face of an higher nuclearity cluster (μ_3-bonding mode). These principal bonding modes are shown in Figure 1. In all these bonding modes, the H(hydride) ligand can be seen alternatively as a 2 electron donor (*viz.* as H^-) interacting with a cationic complex, as H^+ (*viz.* no electron contribution) interacting with an anionic complex, or as providing 1 electron to the valence electrons of a neutral complex (*viz.* as $H^\bullet$). The terminal bonding mode is present in mononuclear complexes and rarely in polynuclear systems (metal clusters), where the bridging mode of bonding predominates.

Intermolecular hydrogen bonding to metal centers has been often invoked in organometallic reactions.[9] Direct involvement of a metal-bound hydride ligand in intermolecular interactions with the CO ligand has been reported only in very few cases such as $(\mu_2\text{-H})Fe_4(\mu\text{-}\eta^2\text{-}CH)(CO)_{11}L$ (L = CO,[10ab] PPh_3[10c]) and $[(C_5H_5)_2Mo(H)\text{-}CO][(C_5H_5)Mo(CO)_3]$.[11]

While the donor capacity of M−H systems has only be hinted in some solid-state and spectroscopic work,[12] and questioned just as well,[13] there is accumulated evidence that electron-rich metal atoms can act as acceptors toward proton donors. For example, O−H- - -M interactions have been detected spectroscopically in hydrocarbons, noble gases, and supercritical fluid solutions for systems in which alcohols interact with half-sandwich complexes of the type $(\eta^5\text{-}C_5H_5)ML_2$ [R = H, Me; M = Co, Rh, Ir; L = CO, N_2, PMe_3].[14] Evidence for an O−H- - -Ir intermolecular hydrogen bond has also been obtained by infrared spectroscopy on $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$.[15]

X−H- - -M intermolecular interactions have also been studied in crystalline salts constituted by the anion $Co(CO)_4^-$ with hydrogen-bonding cations such as $[Et_3NH]^+$ [16ab] and methylpiperazine,[16c] $[(NMP)_3H_2]^{2+}$, whereas Pt- - -H−N intramolecular interactions have been observed by neutron diffraction in the complex formed between square planar $[NPr^n_4]_2PtCl_4$ and *cis*-$[PtCl_2(NH_2Me_2)]$.[17] This matter has been recently reviewed in a comprehensive work by Brammer and coworkers.[18]

The interaction between two hydrogen atoms in M−H- - -H−X systems (X = C, N, O, S) is also attracting great interest, as demonstrated by the numerous spectroscopic,[19a−c] diffraction,[19d−f] and theoretical[19b,g] studies recently published. Though weak, M−H- - -H−X interactions are attractive in nature thus providing a further demonstration of the duality of the M−H system with regard to its participation in hydrogen-bonding interactions.

As usual, the ability of a group to participate in any specific intra− or intermolecular interaction, and hence the ability of metal hydrides to form intermolecular hydrogen bonds, depends on the interplay of steric and electronic factors. The crucial role of steric factors in hydrogen bond formation has been demonstrated in the case of organic carbon acids.[20] The steric factors depend on the ligand distribution around the metal-bound hydrogen atoms and determine to what extent these are screened from the surrounding molecules. The electronic factors (number and type of ligands, oxidation state of the metals(s), nuclearity of the complex, etc.) determine the acidity of the hydride atom and its tendency to interact with a weak base such as carbon monoxide. In general, it is not easy, if at all possible, to separate the two contributions. The Brønsted acidity of transition metal hydrides has been the subject of intense investigation in the past.[21a] Although the data

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(7) Biradha, K.; Desiraju, G. R.; Braga, D.; Grepioni, F. *Organometallics* **1996**, *15*, 1284.

(8) Kristjansottir, S. S.; Norton, J. R. *Transition Metal Hydrides*; Dedieu, A. Ed.; VCH Publisher: New York, 1992; p 309.

(9) (a) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176. (b) Teller, R. G.; Bau, R. *Struct. Bonding* **1981**, *44*, 1.

(10) (a) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4542. (b) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485. (c) Wadepohl, H.; Braga, D.; Grepioni, F. *Organometallics* **1995**, *14*, 24.

(11) Adams, M. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3020.

(12) (a) Epstein, L. M.; Krylow, A. N.; Shubina, E. S. *J. Mol. Struct.* **1994**, *322*, 345. (b) Fairhurst, S. A.; Henderson, R. A.; Hughes, D. L.; Ibrahim, S. K.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1569. (c) Peris, E.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 2179.

(13) Kristjansdottir, S. S.; Norton, J. R.; Moroz, A.; Sewany, R. L.; Whittenburg, S. L. *Organometallics* **1991**, *10*, 2357.

(14) Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069.

(15) Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1992**, 994.

(16) (a) Calderazzo, F.; Facchinetti, G.; Marchetti, F.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1981**, 181. (b) Brammer, L.; McConn, M. C.; Bullock, R. M.; McMullan, R. K.; Sherwood, P. *Organometallics* **1992**, *11*, 2339. (c) Brammer, L.; Zhao, D. *Organometallics* **1994**, *13*, 1545.

(17) Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Koetzle, T. F.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1789.

(18) Brammer, L.; Zhao, D.; Ladipo, F. T.; Braddock-Wilking, J. *Acta Crystallogr. Sect. B* **1995**, *B51*, 632.

(19) (a) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (b) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *Am. Chem. Soc.* **1995**, *117*, 3485. (c) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105. (d) Lee, J. C., Jr.; Rheingold, A. L.; Muller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021. (e) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (f) Wessel, J.; Lee, J. C., Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507. (g) Liu, Q.; Hoffmann, R., *J. Am. Chem. Soc.* **1995**, *117*, 10108.

(20) Pedireddi, V. R.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1992**, 98.

(21) (a) Bursten, B. E.; Gatter, M. G. *Organometallics* **1984**, 3, 895. (b) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231. (c) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

on p*K* values are sparse, there is a trend of increasing acidity on going from left to right along the d-metal periods.[21b,c] $HCo(CO)_4$, for example, behaves as a strong acid. In hydrogen bond formation, however, the steric factor appears to dominate since the hydride ligands are bound to the metal core of the complex and are, most often, completely embedded within the ligand sheath (see below).

In this paper we provide experimental evidence from the structural information accumulated in the CSD and discuss in detail some relevant examples. Before we proceed with the discussion, however, a word of caution is in order. When hydrogen bonding is discussed, the analysis is necessarily focused on the hydrogen atom, which, in transition metal complexes and clusters, is usually poorly located unless neutron diffraction data are available. In many complexes, and certainly in most polynuclear systems, hydride location is not even attempted and the possible position is usually inferred on the basis of the geometry of the ligands surrounding the coordination site of the hydride ligand or calculated on the basis of atom−atom potential energy minimization procedures.[22] In organic systems the lack of information on the hydrogen atom position can be tackled by using the distance between donor and acceptor atoms to guide the identification of hydrogen bonds. This is, however, not possible with metal hydrides where the geometry is much more variable and the intermolecular interlocking is influenced (if not dominated) by shape, size, and mode of coordination of the other ligands on the molecule. This is the frame in which the results of the present analysis must be judged. Nonetheless, we feel that the indications obtained from the subset of *evident* interactions are relevant because they concur with those obtained spectroscopically. All this suggests the existence of a new class of hydrogen bond in metal complexes.

Experimental Section

For the Cambridge Structural Database[4] (CSD) analysis, data were retrieved from the April 1995 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- - -O hydrogen bonds with H- - -O distances between 1.0 and 3.2 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- - -O distance of 2.80 Å (van der Waals sum). A bonafide M−H- - -O hydrogen bond was considered to be one where, in addition to this distance stipulation, the M−H- - -O angle lies in the range 110−180°. M−H bond lengths were taken as such and not normalized (see below). The queries were constructed such that the O atom of the M−H- - -O bond belongs to a CO group attached to a metal atom. H- - -O−C angles were also estimated. Geometrical questions are given in the Supporting Information as representative examples. Key examples were selected from the search outputs and were investigated by computer graphics.[23a] The computer program PLATON[23b] was used to analyze the metrical features of the hydrogen-bonding patterns. For other details of the CSD procedures, the reader is referred to earlier publications in this series.[5−7]

Results and Discussion

The CSD search yielded 962 metal carbonyl hydride structures determined by neutron and X-ray diffraction. In 204 cases, M−H- - -O intermolecular interactions shorter than 3.2 Å were observed. The compounds showing interactions shorter than 2.8 Å are listed in Table 1 together with the relevant geometrical features and the CSD REFCODES. Table 1 also reports the references to the original structural papers. Unless stated otherwise, all structural parameters are calculated on the basis of observed H(hydride) positions present in the CSD files.

On the basis of the data collected in Table 1, the following general considerations can be made:

(i) Although most structures are based on X-ray data, the M−H distances fall within a rather narrow range and are consistent with the available neutron structures.

(ii) With the exception of $[Cp_2Mo(H)CO]\cdot[CpMo(CO)_3]$ (CPCBMO), the hydride ligands forming intermolecular M−H- - -O bonds are present in all complexes as μ_2-bridges spanning M-M bonds.

(iii) The H- - -O distances can be as short as 2.446 Å in $(\mu\text{-H})_3Os_3Ni(CO)_9Cp$ (BOBTAN10) and 2.507 Å in $Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-H}))$ (VUPPAX) and appear to be strictly comparable in length with the interactions established by C−H groups and CO (also available in Table 1).

(iv) Species such as $(\mu\text{-H})(\mu\text{-}NCHCF_3)Os_3(CO)_{10}$ (BAJXIT) and $(\mu\text{-H})Os_3(CO)_9(MeCCHCMe)$ (DEVZEP) provide a direct comparison between M−H- - -O and C−H- - -O interactions.

(v) The average H- - -O−C angle is 133.6(12)° in agreement with the angularity observed for (C)H- - -O−C interactions in the solid state [127.1(5) and 132.2(1.5)° for terminal and bridging CO ligands, respectively].[6]

(vi) H atoms belonging to M−CH "agostic" systems or spanning M−B bonds also participate in short *intermolecular* H- - -O hydrogen bonds as shown by the three examples selected for Table 1.

Selected Examples of Intermolecular M−H- - -O Bonds. We now proceed to examine the hydrogen bonding pattern geometry for some of the complexes reported in Table 1. Only the most representative structures will be described (see Figures 2−6). When present, C−H- - -O hydrogen bonds will also be shown and compared with M−H- - -O hydrogen bonds. Some examples of systems which do not form M−H- - -O hydrogen bonds will also be discussed to demonstrate that steric hindrance (Figures 6−9) is most often responsible for the absence of the M−H- - -O interactions.

The structure of $(\mu\text{-H})(\mu\text{-}NCHCF_3)Os_3(CO)_{10}$ (BAJXIT) has been determined by neutron diffraction.[24] As shown in Figure 2, each cluster molecule participates in two types of hydrogen-bonding interactions. The hydrogen

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[22] Orpen, A. G XHYDEX, A Program for Locating Hydrides, Bristol University, 1980. Orpen, A. G. *J. Chem. Soc, Dalton Trans.* **1980**, 2509.

[23] (a) Keller, E. SCHAKAL93, Graphical Representation of Molecular Models, University of Freiburg, Germany. (b) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C31.

[24] Dawoodi, Z.; Martin, M. J. *J. Organomet. Chem.* **1981**, *219*, 251.

Table 1. Compound Formulas, REFCODES, and Relevant Geometrical Parameters for M−H- - -O Intermolecular Interactions for Transition Metal “Hydrides” with Intermolecular H- - -O < 2.8 Å and Comparison with C−H- - -O Interactions

compd[a]	REFCODE	diffr techn	*T* (K)	M−H (Å)	M−H- - -O (Å)	(M)H- - -O−C angle (deg)	C−H- - -O (Å)[a]	ref
$(\mu\text{-H})(\mu\text{-NCHCF}_3)\text{Os}_3(\text{CO})_{10}$	BAJXIT	neutron	20	1.837	2.594	136.4	2.571	24
$(\mu\text{-H})_3\text{Os}_3\text{Ni(CO)}_9\text{Cp}$	BOBTAN10	X-ray	296	1.972	2.446	141.0	2.613 2.626	25
$(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CH})$	BOXGUQ	X-ray	298	1.798	2.616	113.1	2.316 (intra)	26
$(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$	BUWGEF10	X-ray	297	1.798	2.576	117.5		28
$[\text{Cp}_2\text{Mo(H)CO}]\cdot[\text{CpMo(CO)}_3]$	CPCBMO	X-ray	148	1.798	2.511	131.0	2.225 2.544 2.386 2.379 2.509	11
$(\mu\text{-H})\text{Os}_3(\text{CO})_9(\text{MeCCHCMe})$	DEVPEZ	X-ray	298	1.861	2.556	166.7	2.637	29
$(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CNPr})(\text{OCOCF}_3)$	HANTIZ	X-ray	298	1.815	2.637	112.8	2.426	30
$(\mu\text{-H})\text{Fe}_4(\eta^2\text{-CH})(\text{CO})_{12}$	HMYCFE01	neutron	26	1.670 1.670 1.670 1.672	2.660 2.700	138.0 125.9	2.576[b] 2.482[b]	10b
$(\mu\text{-H})\text{Fe}_4(\eta^2\text{-CH})(\text{CO})_{12}$	HMYCFE	X-ray	173	1.670 1.834 1.637 1.730	2.680 2.702	169.9 143.3	2.718[b] 2.739[b]	10a
$(\mu\text{-H})_8\text{Pt}_2\text{Os}_7(\text{CO})_{23}$	KIWVOB	X-ray	298	1.918	2.587 2.582 (intra)	156.5		31
$(\mu\text{-H})_8\text{PtOs}_6(\text{CO})_{18}$	KIWVUH	X-ray	298	1.793	2.636	140.9		31
$\text{Os}_3(\text{CO})_{10}[\mu\text{-CH(Mo)}(\mu_2\text{-H})\text{CNMe}_2]$	VESGAB	X-ray	296	2.163	2.601	121.4	2.599	32
$\text{Os}_4(\text{CO})_{13}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})(\mu\text{-H})$	VUPPAX	X-ray	298	1.993	2.507	163.5	2.354	33
$\text{Cr(CO)}_2(\text{PMe}_3)(\eta^4\text{-C}_7\text{H}_{10})$	DEXCUE	X-ray	298	1.856	2.635[b]	130.1	2.548 2.588	34
$\text{WRh}_2\text{Au}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me}_4)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)(\eta\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)_2$	JEMDEK	X-ray	298	1.846	2.621[c]	125.3		35
$(\mu\text{-H})_6\text{H}_2\text{B}_4\text{Fe}_4(\text{CO})_{12}$	SOBTEI	X-ray	123	1.623	2.884[c]	118.35		36

[a] Based on normalized C−H distances.[6] [b] Intermolecular M−H- - -O interactions involving metal-bound hydrogen atoms participating in agostic inteeractions. [c] intermolecular M−H- - -O interactions involving hydrogen atoms spanning B−M bonds.

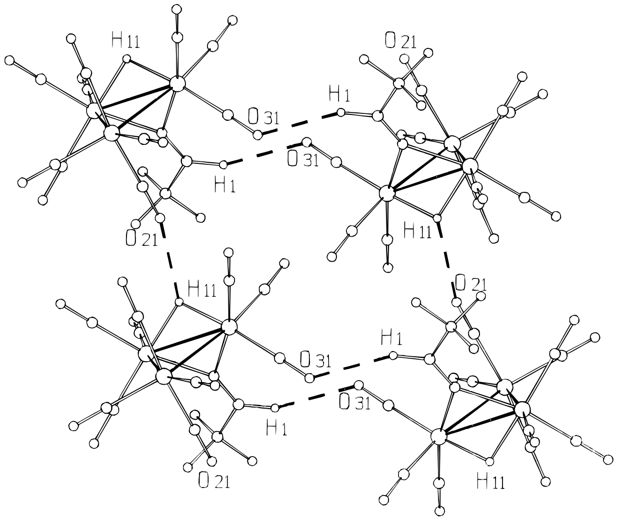

Figure 2. Crystalline $(\mu\text{-H})(\mu\text{-NCHCF}_3)\text{Os}_3(\text{CO})_{10}$ (BAJXIT). Each cluster molecule participate in hydrogen bonding interactions of the M−H- - -O and C−H- - -O types of comparable length (Os−H11- - -O21 2.594, H1- - -O31 2.571 Å). Note that the hydride−CO interactions forms molecular rows whereas the C−H- - -O bonds form rings between molecules related by a center of symmetry.

bond involving the H(hydride) effectively links molecules along a row *via* a direct interaction between the edge bridging hydride and a terminally bound CO (Os−H11- - -O21 2.594 Å). Dimers of molecules are otherwise formed *via* C−H- - -O bonds between (H1- - -O31 2.571 Å). This kind of ring is common in hydrogen-bonding patterns both in strong and in weak hydrogen-bonding situations. It is important to stress that the two types of interactions are of comparable length (hence, presumably, strength) and both involve the same type of base, *viz*. a terminally bound CO ligand.

Both M−H- - -O and C−H- - -O hydrogen bonds are important in crystalline $(\mu\text{-H})_3\text{Os}_3\text{Ni(CO)}_9\text{Cp}$ (BOBTAN10).[25] Figure 3 shows the molecular arrangements in the crystals. The M−H- - -O intermolecular bonds (H11- - -O22 2.446 Å) join molecules in chainlike fashion while a CH group belonging to a Cp ring and a terminally bound CO (H3- - -O11 2.434 Å) form a ring linking two molecules related by a center of inversion. The C−H- - -O interactions connect rows of molecules linked by the H(hydride)- - -O bonds in the crystal.

Centrosymmetric rings are formed between CO and bridging hydride ligand in crystalline $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CH})$ (BOXGUQ)[26] as shown in Figure 4. The M−H- - -O distance is 2.616 Å (H23- - -O22). No C−H- - -O intermolecular interactions are present between the methylidyne and the carbonyl ligands, whereas an intramolecular agostic interaction (H1- - -O11 2.316 Å) is detected with the CH group bent toward the metal cluster and pointing toward that oxygen atom of a nearby CO.

The trinuclear cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$ (BUWGEF10) is disordered in the solid state.[27] One of the two independent molecules has well-defined hydride positions, while the hydride ligands are disordered in the second molecule. We considered the disordered

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(25) Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1983**, *22*, 1510.

(26) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 140.

(27) Churchill, M. R.; Bueno, C. *J. Organomet. Chem.* **1990**, *396*, 327.

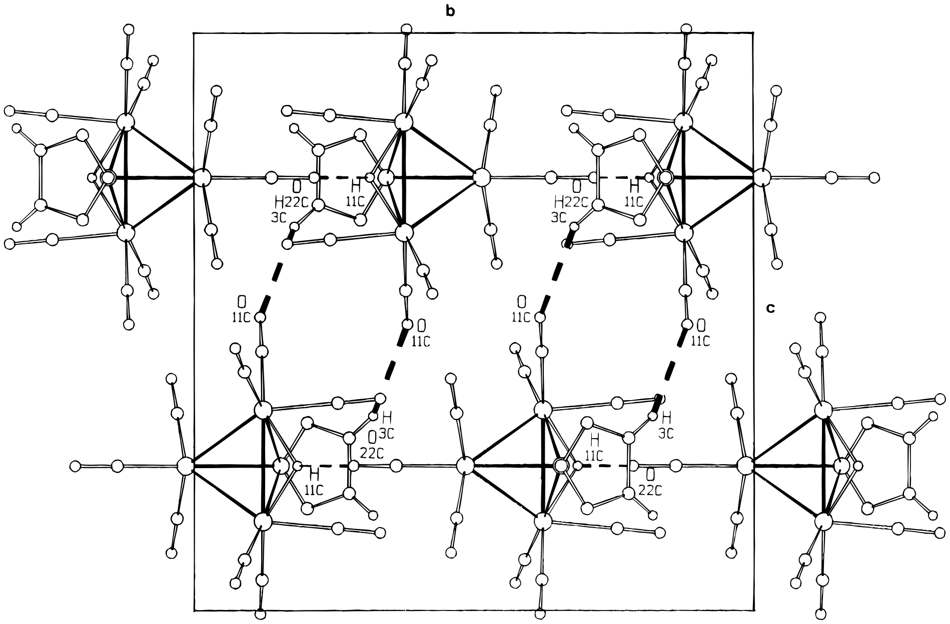

Figure 3. Molecular rows in crystalline ($(\mu\text{-H})_3Os_3Ni(CO)_9Cp$) (BOBTAN10) Note how the bonds are formed between terminally CO ligands and bridging H ligands and between CO ligands and H atoms of the Cp rings.

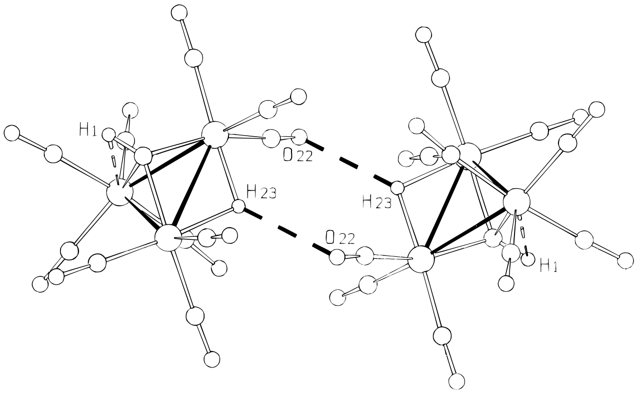

Figure 4. Centrosymmetric rings formed by CO and bridging hydride ligands in crystalline $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-}CH)$ (BOXGUQ).

crystal packing as the average of two alternative ordered models. In both models only the hydride ligands belonging to the ordered cluster appear to be involved in H-bond interactions, whereas those of the second independent molecule are not. We take this as an indication that the disorder in the hydride position around this latter molecule might be of dynamic nature while in the ordered molecule the hydrides are frozen out in one fixed conformation because of the additional constraints arising from the intermolecular bonds (see below for some additional comments on this aspect).

The crystal of $[Cp_2Mo(H)CO][CpMo(CO)_3]$ (CPCBMO)[11] contains a cationic complex, bearing the hydride ligand, and an anionic one. The presence of an intermolecular M—H- - -O interaction (H16- - -O4 2.511 Å) between two cations related by an inversion center had already been discussed in the original paper by Caulton *et al.*[11] A second crystalline form of the same complex (CPCBMO01) was discovered later.[28] The crystal packings of CPCBMO and CPCBMO01 are similar, differing in the orientation of the cations within the centrosymmetric pairs. In the latter system the M—H- - -O separation is much longer than in CPCBMO (2.876 Å) and cannot be accounted for in terms of the different Mo—H distances in the two determinations. Figure 5 shows the M—H- - -O hydrogen bonds involving the centrosymmetric dimer of cations of CPCBMO as well as the C—H- - -O bond between the CO ligands of the anion and the H atoms of the Cp ligands of the neighboring complexes (see Table 1).

An interaction between a terminal CO ligand and the bridging hydride ligand (2.556 Å) is also present in crystalline $(\mu\text{-H})Os_3(CO)_9$ (MeCCHCMe)[29] (DEVPEZ). As observed above for BOBTAN10 and BOXQUG, two different type of interactions are present in crystalline $(\mu\text{-H})Os_3(CO)_{10}(CNPr)(OCOCF_3)$[30] (HANTIZ) (see Table 1). The first link is between the unique H(hydride) and a CO ligand (M—H- - -O distance 2.637 Å), while the second, shorter, interaction is formed between an H(CH) of the CNPr ligand and an oxygen of the carboxylic ligand of a second molecule (2.426 Å).

The intermolecular organization in crystalline $(\mu\text{-H})Fe_4(\eta^2\text{-CH})(CO)_{12}$ (HMYCFE01) has been analyzed previously both by Muetterties[10a,b] and, more recently, by some of us.[10c] While the acidic nature of the agostic hydrogen atom bound to the methylidyne group is well-known, it is not so for that of the bridging hydride ligand. There are two independent molecules in the asymmetric unit of HMYCFE01. In the neutron diffraction study[10a] these molecules are linked *via* two different C—H- - -OC bonds (2.58 and 2.48 Å) and by two slightly longer Fe—H- - -O interactions (2.66 and 2.70 Å). Drawings of the crystal packing of HMYCFE01 can be seen in ref 10c. The values of both M—H- - -O and C—H- - -O distances have been estimated also for the X-ray determination of the same molecule at 173 K. The most relevant difference is in the C—H- - -O distances that increase from 2.482 and 2.576 Å at 26 K

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(28) Antsyshkina, A. S.; Dikareva, L. M.; PoraiKoshits, M. A.; Ostrikova, V. N.; Skripkin, Yu. V.; Volkov, O. G.; Pasynskii, A. A.; Kalinnikov, V. T. *Koord. Khim.* **1985**, *11*, 82.

(29) Castiglioni, M.; Giordano, R.; Sappa, E.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Dalton Trans.* **1986**, 23.

(30) Su, C. J.; Chung, M. L.; Gau, H. M.; Wen, Y. S.; Lu, K. L. *J. Organomet. Chem.* **1993**, *456*, 271.

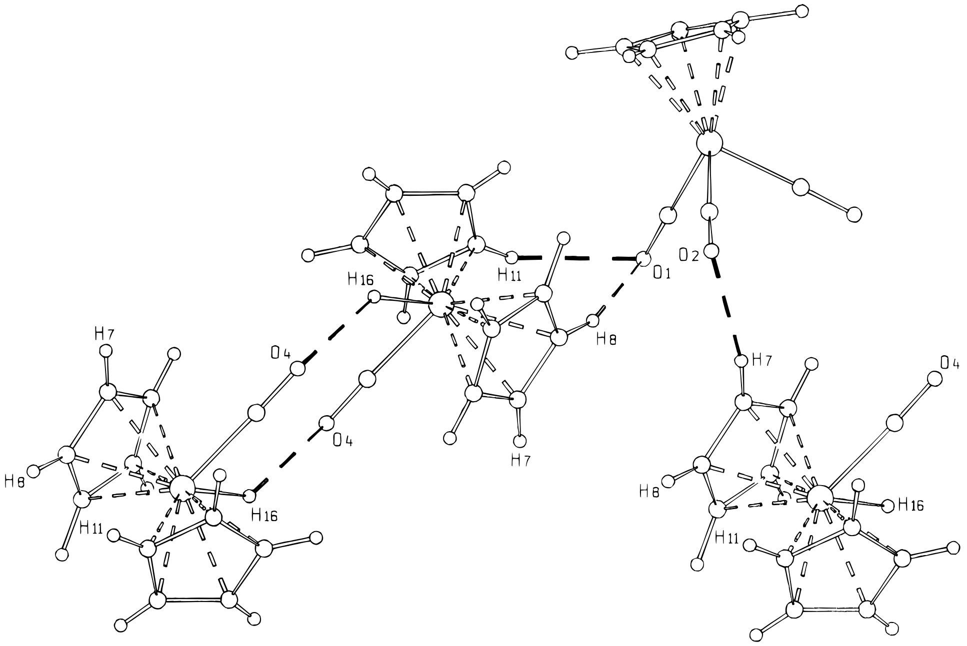

Figure 5. $[Cp_2Mo(H)CO]\cdot[CpMo(CO)_3]$ (CPCBMO). Note the M−H- - -O hydrogen bonds involving the centrosymmetric dimer of cations and C−H- - -O bonds between the CO ligands of the anion and the H atoms of the Cp ligands.

to 2.718 and 2.739 Å at 173 K, while the M−H- - -O distances are almost unaffected (2.660 and 2.700 *versus* 2.680 and 2.702 Å at 26 and 173 K, respectively). On the other hand, while the H(hydride) positions do not differ much, the C−H distances shorten from 1.191(4) and 1.176(5) to 1.00(4) and 1.09(4) Å, as usually observed on passing from the neutron to the X-ray experiments.

The molecular and crystal structures of $(\mu\text{-H})_8Pt_2Os_7(CO)_{23}$ (KIWVOB) and of $(\mu\text{-H})_8PtOs_6(CO)_{18}$ (KIWVUH) have been determined in the same study.[31] Both crystals present short M−H- - -O interactions (2.636 and 2.587 Å, respectively) in crystalline KIWVOB; however, there is simultaneous presence of both intramolecular and intermolecular M−H- - -O interactions of comparable length (2.587 and 2.582 Å) involving terminal CO ligands.

The pattern of intermolecular hydrogen bonds in crystalline $Os_4(CO)_{13}(\mu\text{-SCH}_2CMe_2CH_2Cl)(\mu\text{-H})$[33] (VUPPAX) recalls that formed by typical organic acids, namely the hydrogen-bonding ring (see Figure 6). Two molecules form a centrosymmetric dimer and are connected by two M−H- - -O interactions. The length and directionality of these interactions (H1- - -O10 2.507 Å, H1- - -O10-C10 163.5°) are strictly comparable to those observed in many crystals of carbonyl complexes where similar dimers are formed.[6] VUPPAX also presents a short C−H- - -O interaction (H5- - -O2 2.354 Å) which joins M−H- - -O “dimers” together.

Intermolecular M−H- - -O interactions are established also by metal-bound hydrogen atoms participating in agostic[33] interactions. Of course the electronic nature of the M- - -H interaction in agostic M- - -(H−C) and in hydridic M−H systems is fundamentally different. Nonetheless, as in the case of the hydride ligands, some agostic hydrogens, when not sterically screened from the surroundings by other ligands, can form intermolecular hydrogen bonds with the CO base. The H- - -O separations are comparable to those of the most acidic C−H- - -O and to some M−H- - -O interactions. The best example is most certainly HMYCFE01 discussed above. Another example is provided by the mononuclear complex $Cr(CO)_2(PMe_3)(\eta^4\text{-}C_7H_{10})$ (DEXCUE),[34] where the agostic hydrogen participates in an interaction with a neighboring CO (2.635 Å); two shorter C−H- - -O interactions are also present within the same crystal (2.548 and 2.588 Å). Intermolecular M−H- - -O interactions involving hydrogen atoms spanning B−M bonds are observed in crystalline $WRh_2Au_2(\mu_3\text{-}CC_6H_4\text{-}Me_4)(CO)_6(\eta^5\text{-}C_5H_5)(\eta\text{-}C_2B_9H_9Me_2)_2$ (JEMDEK)[35] and $(\mu\text{-H})_6H_2B_4Fe_4(CO)_{12}$ (SOBTEI).[36]

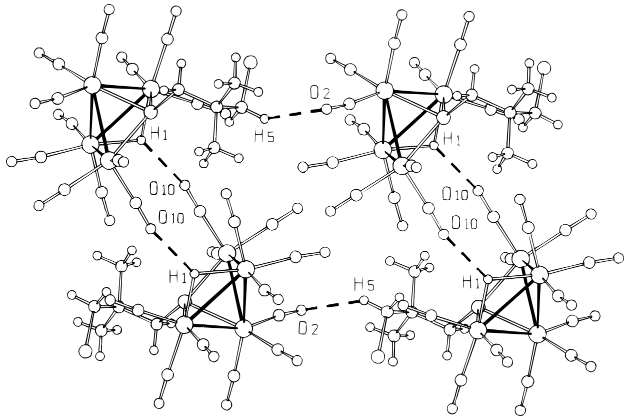

Figure 6. Cyclic dimer formed via Os−H- - -O bonds in crystalline $(\mu\text{-H})Os_4(CO)_{13}(\mu\text{-SCH}_2CMe_2CH_2Cl)$ (VUPPAX) together with the C−H- - -O bonds.

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[31] Adams, R. D.; Pompeo, M. P.; Wengan, W. *Inorg. Chem.* **1991**, *30*, 2425.

[32] Adams, R. D.; Chen, G.; Tanner, J. T. *Organometallics* **1990**, *9*, 1530.

[33] (a) Brookhart, M.; Green, M. L.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

[34] Michael, G.; Kaub, J.; Kreiter, C. G. *Chem. Ber.* **1985**, *118*, 3944.

[35] Carr, N.; Gimeno, M. C.; Goldberg, J. E.; Pilotti, M. U.; Stone, F. G. A.; Topaloglu, I. *J. Chem. Soc., Dalton Trans.* **1990**, 2253.

[36] Jun, C. S.; Meng, X.; Haller, K. J.; Fehlner, T. P. *J. Am. Chem. Soc* **1991**, *113*, 3603.

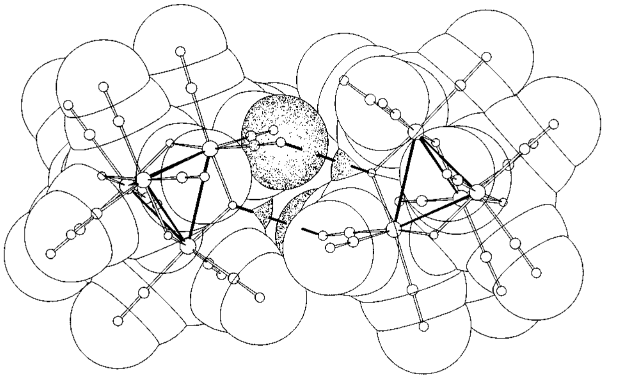

Figure 7. Space-filling representation of two first neighboring $H_4Ru_4(CO)_{12}$ molecules showing how the CO ligands are interlocked.

Sterically Hindered Hydride Complexes. We will now discuss a few examples of hydride complexes that do not form intermolecular links in order to demonstrate how steric problems can be the dominating factors in determining whether H-bonds between hydride ligands and acceptors are formed or not. It should be kept in mind that hydride ligands are, in most cases, not available to close approach by the acceptors because they are close to the metal atom(s) and embedded in the envelope formed by the other ligands.

One of the prototypical polyhydride clusters is $H_4Ru_4(CO)_{12}$ (FOKPAW).[37] This ruthenium cluster is known to have four long and two short Ru−Ru edges, the four long edges being most likely spanned by the H-bridges. A 3% disorder in the orientation of the cluster was also detected. A recent spectroscopic study of solid $H_4Ru_4(CO)_{12}$ has shown that the $^{13}C\{^1H\}$ CP MAS, ^1H-MAS, and ^1H wide-line spectral features can be interpreted in terms of a dynamic process involving either the motion of the H_4Ru_4 as a whole or the motions of the hydrides over the metal cluster.[38] H- - -O distances between hydride ligands, placed in calculated positions along bridging sites *via* XHYDEX,[22] and next neighboring CO ligands fall in the range 2.787−2.775 Å. These distances are longer than in the cases discussed above where the hydrogen atoms could be located directly. One may think that the dynamic behavior detected by NMR arises from the lack of intermolecular stabilization of the bridging sites due to the difficult intermolecular interpenetration of molecules carrying 12 terminal COs beside the hydride ligands. Figure 7 shows a space-filling representation of two interlocking $H_4Ru_4(CO)_{12}$ molecules with the modeled hydrido atom positions. The other three sites have similar interactions with neighboring molecules. All intermolecular C- - -C, C- - -O, and O- - -O interactions between first neighbor atoms correspond to "normal" van der Waals contacts; hence, shorter Ru−H- - -O distances could only be attained at the cost of CO- - -CO repulsive interactions.

Another example of hydride ligand encapsulation is shown in Figure 8, where the space-filling representation of the complex $HW_2(CO)_9(NO)$ (FUZROH) is reported.[39] The hydride ligand is surrounded by three terminal COs, which do not leave enough space to link a neighboring molecule via W−H- - -O interactions (the nearest oxygen atom is at 3.506 Å). A similar situation is seen in $HMn_2Re(CO)_{14}$ (VITMIU) (see Figure 9).[40] The hydride ligand in this mixed cluster is completely embedded within the CO-ligand envelope.

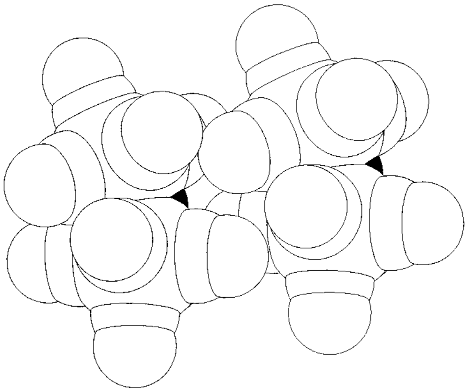

Figure 8. Space-filling representation of the molecular structures of $HW_2(CO)_9(NO)$ (FUZROH). Note how the "contact" between outer CO ligands prevents closer approach to the H atom (filled atom sphere).

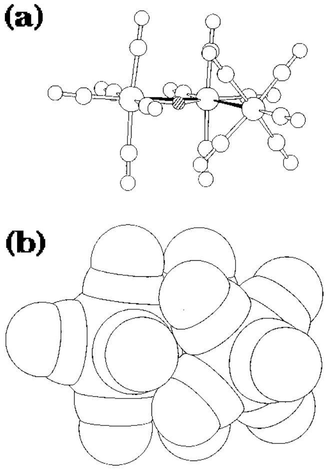

Figure 9. Ball and stick (a) and space-filling (b) representations of the molecular structures of $HMn_2Re(CO)_{14}$ (VITMIU). Note how the bridging hydride ligand (dashed atom in a) is completely embedded in the van der Waals spheres of the ligands (b).

Conclusions

Hydrogen bonding is still a source of new discoveries. In the organometallic field, the acid/base dualism, and therefore the capacity to form hydrogen bonds and their relative strength, is not confined to the "traditional" acceptor and donor groups of organic molecules. As discussed above, the M−H bonds can act as donors or acceptors in hydrogen-bonding formation.

The results discussed in this paper permit us to conclude that hydrogen atoms bound to metal atoms chiefly in polynuclear systems can be sufficiently acidic to establish hydrogen-bonding interactions in the solid state. This has been demonstrated on the basis of a CSD search which has provided evidence of the existence of M−H- - -O cohesive interactions in which the

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(37) Wilson, R. D.; Wu, S. M.; Love, R. A.; Bau, R. *Inorg. Chem.* **1978**, *17*, 1271.

(38) Aime, S.; Gobetto, R.; Orlandi, A.; Groombridge, C. J.; Hawkes, G. E.; Mantle, M. D.; Sales, K. D. *Organometallics* **1994**, *13*, 2375.

(39) Olsen, J. P.; Koetzle, T. F.; Kirtley, S. W.; Andrews, M.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc* **1974**, *96*, 6623.

(40) Albinati, A.; Bullock, R. M.; Rappoli, B. J.; Koetzle, T. F. *Inorg. Chem.* **1991**, *30*, 1414.

transition metal atoms act as donors in intermolecular hydrogen bonds with the oxygen atoms of the ligands, mostly CO. These results are in agreement with the information already available on the Brønsted acidity of the hydride atom and on its tendency to interact with weak bases (such as CO). This capacity depends on the other ligands, on the type of metal(s) forming the complex, and on the relative stability of the associated deprotonation anion. Steric factors, however important in determining hydrogen bond formation in organic systems, become crucial in the case of metal−hydride complexes in which the hydrogen ligands are bound to the metal core and, hence, are most often completely embedded within the ligand envelope. This, together with the difficulty of locating hydride ligands, accounts for the relatively small number of complexes in which M−H- - -O interactions are evident. In the cases where the donor−acceptor approach is less sterically hindered M−H- - -O bonds are clearly formed. The donor capacity of the M−H group is very much like that of the C−H group, at least toward the CO ligand. In general, M−H- - -OC bonds are comparable in distance (strength) to those formed between C−H groups, mainly belonging to sp^2-hybridized carbon atoms (as in cyclopentadienyl ligands, arenes, etc.) and CO ligands. Interactions of the C−H- - -O type are, for obvious reasons, far more abundant than M−H- - -O interactions. As pointed out by Pearson[21b] the M−H bond appears to be very similar to the C−H bond. Both bonds, for example, react as H^+, $H^\bullet$, and H^- depending on the relative stability of the resulting species. Importantly, we come to the same conclusion starting from a completely different source of data.

Another aspect of some relevance is related to the dynamic behavior of the hydride ligands in the solid state: it appears that the formation of M−H- - -O interactions is capable, in some cases, of preventing hydride fluxionality by providing additional stabilization to a given ligand arrangement. When this is made impossible by the outer ligand interlocking, the mobility of hydrogen atoms makes location of their positions more difficult, if at all possible. This is admittedly slightly speculative and needs to be substantiated with *ad hoc* experiments which are under way.

We emphasize that the word “hydride” is misleading for the type of complexes discussed here and should be replaced with a more general “hydrogen ligand” definition. In perspective, the donor−acceptor behavior of metal atoms with respect to their electronic nature and oxidation state needs to be explored in a systematic way in relation to the type of acceptor groups. Work is progressing in this direction.

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Supporting Information Available: A table listing the summary file for 276 M−H- - -O interaction hits from 204 compounds (9 pages). Ordering information is given on any current masthead page.

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