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C–H $\cdots$ O Hydrogen bonding in crystalline complexes carrying methylidyne (μ_3-CH) and methylene (μ-CH$_2$) ligands: a database study [§]

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The relationship between the molecular and crystal structures of organometallic complexes carrying methylidyne (μ_3-CH) and methylene (μ-CH$_2$) ligands has been investigated on data retrieved from the Cambridge Structural Database. It has been shown that μ_3-CH and μ-CH$_2$ groups participate in intermolecular hydrogen-bonding networks of the C–H $\cdots$ O type involving, in most cases, the oxygen atoms of CO ligands as acceptors. The order of decreasing acidity, judged on purely geometrical grounds from the average length of the hydrogen-bonding interactions, is roughly μ_3-CH > μ-CH$_2$. These ligands establish C–H $\cdots$ O interactions which are comparable in length to those established by hydrogen atoms bound to sp- and to sp^2-hybridized carbon atoms consistent with experimental and theoretical evidence.

Our most recent research efforts have been aimed at the understanding of intermolecular interactions in inorganic and organometallic solids in the context of crystal engineering and supramolecular synthesis.[1] We are carrying out a systematic investigation of the way neutral and charged organometallic molecules and clusters self-recognize and self-assemble in the solid state.[2] The objective is that of achieving sufficient basic knowledge to be able to *choose* intermolecular interactions to project the synthesis of novel crystalline materials on the basis of shape, size and structural functionality.[3]

As a part of our study of hydrogen bonding in organometallic crystals[4] we have shown that organometallic complexes and clusters afford both 'new' hydrogen-bonding acceptors and 'new' hydrogen-bonding donors.[5] Carbon monoxide, for example, affords hydrogen-bonding accepting sites of *tunable* basicity thanks to the possibility of varying the co-ordination mode of the ligand with the metal centres in polymetallic systems.[6] We have shown,[7] both on the basis of Cambridge Structural Database (CSD) analysis[8] and by examining families of closely related complexes,[9] that the CO ligand participates in C–H $\cdots$ OC interactions the strength of which follows roughly the order μ_3-CO > μ-CO > η^1-CO which corresponds to the order of decreasing basicity of the ligand. Metal-bound hydrogen atoms, on the other hand, possess an amphoteric behaviour: μ_3- and μ-H ligands, for example, can act as hydrogen-bonding donors in M–H $\cdots$ OC interactions,[10] whereas terminal M–H systems may behave, depending on the coligands in the complexes, as weak hydrogen-bonding acceptor sites with suitable donor groups.[11]

In this paper we report our observations on the participation of methylidyne (μ_3-CH) and methylene (μ-CH$_2$) ligands in hydrogen-bonding interactions. We have found that the hydrogen atoms of these ligands behave very much like those bound to sp^2 carbons in cyclopentadienyl or arene ligands in the formation of intermolecular hydrogen bonds with soft bases such as carbon monoxide.[6,9] This study is part of the debate about whether the carbon atoms in μ_3-CH and in μ-CH$_2$ ligands should be better described as 'distorted' sp^3 hybrids or as more closely related to ≡CH (sp) and =CH$_2$(sp^2) systems.

Great efforts have been made in an attempt to rationalize the bonding mode of μ-CH$_2$ ligands to transition-metal clusters, while less work has been done on the μ_3-CH system. On theoretical grounds,[12] extended Hückel and Fenske–Hall calculations are consistent with a model of methylene bridges bound to transition metals by σ donation from a filled orbital of CH$_2$ and back donation from the metals to the ligand π^* empty orbital, this resulting in the formation of a small negative charge on the ligand C atom. The interaction of methylidyne ligands with metal clusters has been described in a similar manner. Back donation occurs to two empty and mutually perpendicular π^* orbitals.[12c] Therefore, these models describe methylene and methylidyne ligands as sp^2 and sp hybrids, respectively. However, somewhat different conclusions have been reached from experiments. For example, accurate electron-density determinations[13a,b] of CH$_2$-bridged complexes did not show negative charge accumulation on the C atom, while IR spectroscopy appears to indicate some sp^3 character.[13c] On the other hand, ^{59}Co nuclear quadrupole resonance spectroscopy results[13d] obtained for μ_3-CH complexes were found to be in accord with a ≡CH bonding picture of the organic moiety in methylidyne clusters.

We have obtained indirect information about the nature of the bonding of these ligands with metal centres from an analysis of the environment in the solid state, *viz*. of the patterns of intermolecular C–H $\cdots$ O hydrogen bonds established by these groups in the solid state. The most common acceptor groups are the CO ligands, which are also the most common coligands in methylidyne and methylene clusters. The behaviour of the methylydyne and methylene ligands ought to be compared with those of the same groups of atoms in organic crystals. The participation of ≡CH and =CH$_2$ donor types in hydrogen bonding in organic crystals has been studied,[14a] as has the effect of hydrogen bonding on the atomic displacements of atoms involved in ≡CH $\cdots$ O and =CH $\cdots$ O interactions.[14b]

Methodology

As in previous papers in this series we have retrieved the structural information on the geometry of intermolecular C–H $\cdots$ O interactions by searching the CSD.[8] The April 1996 update version was employed for all crystal structures with an exact match between chemical and crystallographic connectivity. Both neutral and charged species were considered. Only entries presenting atomic coordinates of the H atoms were considered. The results of the CSD searches are discussed below and presented in Table 1, crystal structures being identified by their respective

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[§] *Supplementary data available* (No. SUP 57234, 6 pp.): compound REFCODES, names and references. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

Table 1 Compound formulae, REFCODES and relevant geometrical parameters for C−H···O intermolecular interactions for transition-metal complexes carrying methylidyne and methylene ligands

Compound	REFCODE		C−H···O	C···O/Å	H···O/Å	C−H···O/°	Ref.
$[Co_3(\mu_3\text{-}CH)(CO)_9]$	MEDYCO01	μ_3-CH	C(10)−H(1)···O(11)	3.21	2.53	120.0	16
		μ_3-CH	C(10)−H(1)···O(33)	3.39	2.50	139.3	
		μ_3-CH	C(10)−H(1)···O(31)	3.30	2.62	120.6	
$[Rh_3(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CH)(\mu\text{-}CO)_2]$-$[O_2CCF_3]$	CMCPRH10	μ_3-CH	C(1)−H(1)···O(5)	3.24	2.25	151.7	17
		C_5H_5	C(14)−H(14)···O(5)	3.25	2.19	166.9	
		C_5H_5	C(18)−H(18)···O(5)	3.20	2.45	125.8	
		C_5H_5	C(15)−H(15)···O(6)	3.29	2.49	130.1	
		C_5H_5	C(16)−H(16)···O(6)	3.62	2.58	162.0	
		C_5H_5	C(18)−H(18)···F(1)	3.52	2.53	152.6	
		C_5H_5	C(15)−H(15)···F(3)	3.50	2.51	151.6	
$[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CH)(PrCNO)]$-$[BF_4]$	DIPMEU	μ_3-CH	C(20)−H(23)···O(1)	3.12	2.30	131.1	18
		C_5H_5	C(5)−H(5)···O(1)	3.30	2.47	132.3	
		C_5H_5	C(11)−H(11)···O(1)	3.39	2.51	138.8	
		C_5H_5	C(9)−H(9)···F(3)	3.25	2.17	173.8	
		C_5H_5	C(13)−H(13)···F(4)	3.34	2.27	171.8	
		C_5H_5	C(7)−H(7)···F(1)	3.30	2.37	142.6	
		C_5H_5	C(1)−H(1)···F(3)	3.59	2.51	176.2	
		C_5H_5	C(17)−H(17)···F(1)	3.56	2.52	161.2	
		C_5H_5	C(4)−H(4)···F(4)	3.59	2.53	164.9	
		C_5H_5	C(8)−H(8)···F(4)	3.37	2.54	133.3	
$[AsPh_4][Fe_3(\mu_3\text{-}CH)(CO)_{10}]$	CAXTUQ	μ_3-CH	C(998)−H(998)···O(11)	3.57	2.53	162.0	19(*a*)
		Ph	C(132)−H(132)···O(12)	3.62	2.55	168.4	
		Ph	C(112)−H(112)···O(21)	3.42	2.57	135.8	
		Ph	C(142)−H(142)···O(13)	3.53	2.58	146.6	
		Ph	C(145)−H(145)···O(33)	3.45	2.60	135.4	
$[WOs_3(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}CH)(CO)_{11}]$	YARCEZ	μ_3-CH	C(2)−H(2a)···O(1)	3.50	2.52	149.4	20
		CH_3	C(43)−H(29)···O(9)	3.42	2.43	152.3	
		CH_3	C(19)−H(2)···O(18)	3.21	2.48	123.6	
		CH_3	C(22)−H(2)···O(20)	3.15	2.59	111.7	
		CH_3	C(19)−H(4)···O(21)	3.65	2.57	176.6	
$[Fe_3(\mu_3\text{-}CH)(CO)_9Bi]$	KEMVIH	μ_3-CH	C(1)−H(1)···O(8)	3.52	2.48	161.5	21
$[Mn_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)(CO)_4]$	BANGIG10	μ-CH_2	C(3)−H(3)···O(1)	3.57	2.56	154.7	22(*a*)
		C_5H_5	C(7)−H(7)···O(12)	3.45	2.50	146.1	
$[Os_3(\mu\text{-}CH_2)(CO)_9(PhCCPh)]$	BEFKEC	μ-CH_2	C(20)−H(201)···O(8)	3.47	2.41	168.3	23
		μ-CH_2	C(10)−H(102)···O(16)	3.65	2.58	171.7	
		Ph	C(48)−H(48)···O(8)	3.21	2.44	127.3	
		Ph	C(314)−H(314)···O(18)	3.35	2.55	130.3	
$[MnFe_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$-$(\mu\text{-}CH_2)(\mu_3\text{-}COMe)(CO)_5]$	FIDSAM	μ-CH_2	C(2)−H(2)···O(5)	3.45	2.46	169.1	24
		C_5H_5	C(17)−H(11)···O(2)	3.31	2.40	149.2	
		CH_3	C(19)−H(17)···O(4)	3.29	2.57	128.8	
		CH_3	C(18)−H(13)···O(4)	3.35	2.58	133.1	
$[SnOs_3Cl_2(\mu\text{-}CH_2)(CO)_{11}]$	DUJYAI	μ-CH_2	C(20′)−H(21′)···Cl(2)	3.76	2.70	165.8	25
		μ-CH_2	C(20′)−H(21′)···Cl(1)	3.82	2.77	163.4	
		μ-CH_2	C(20)−H(21)···O(8)	3.41	2.72	121.4	
$[Re_2Me_4O_3(\mu\text{-}CH_2)]$	SIGGIY	μ-CH_2	C(5)−H(13)···O(3)	3.55	2.48	172.5	26
		CH_3	C(1)−H(3)···O(1)	3.29	2.33	147.8	
		CH_3	C(2)−H(3)···O(1)	3.31	2.28	143.6	
$[Ir_2(\mu\text{-}Me)(CO)_2\{(PMe_2)_2(CH_2)\}_2]$-$[O_3SCF_3]$	JAZMIG	μ_3-CH_3	C(5)−H···O(3)	3.63	—	—	27
		$6P(CH_3)$	C−H···O	<3.6	<2.6		

REFCODES. Unless stated otherwise, all structural parameters were calculated on the basis of C−H distances normalized to the corresponding neutron diffraction values. Selection criteria, beside those on the quality of the structural data, have been based on (C)H···O interatomic separations falling between 1.5 and 3.0 Å. Geometrical questions are given in SUP 57234 as representative examples. All relevant crystals structures were selected from the search outputs and investigated by computer graphics.[15a] The computer program PLATON[15b] was used to analyse the metrical features of the hydrogen-bonding patterns.

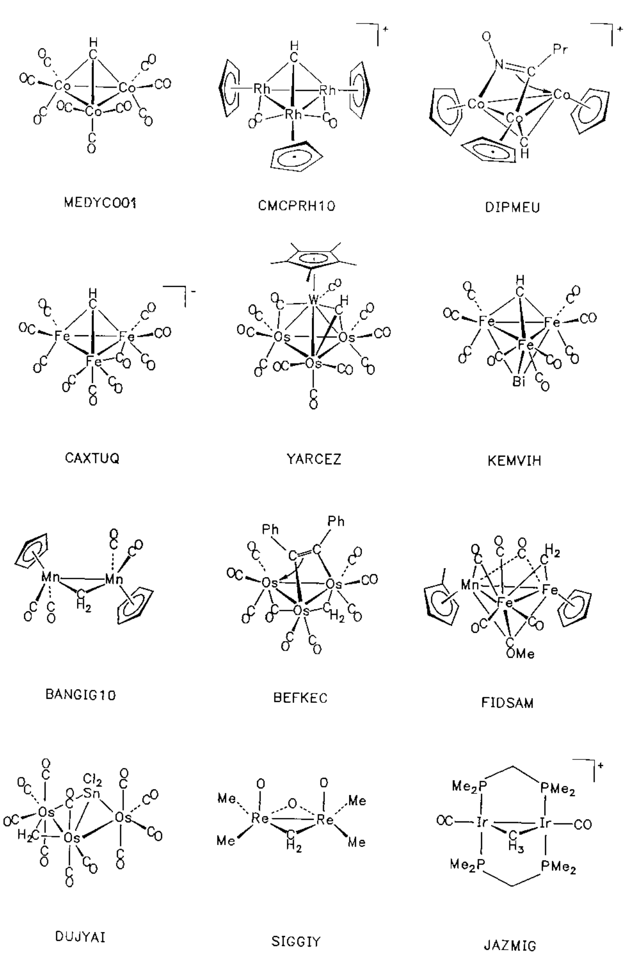
Results and Discussion

General information on the crystal structures discussed in this paper is reported in Table 1 together with CSD REFCODES, chemical formulae and references to the original structural papers.[16–27] Given the complexity of the species, their molecular structures are presented in Scheme 1 together with CSD REFCODES. Intermolecular C···O and (C)H···O separations are given, as well as the values of the C−H···O angles. Methylidyne and methylene ligands are compared with other typical donors such as cyclopentadienyl ligands.

It can be immediately appreciated from Table 1 that both methylidyne and methylene hydrogen atoms do indeed participate in hydrogen-bonding interactions with CO acceptors or other bases. These interactions are comparable in terms of intermolecular separations and angularity with those established by hydrogen atoms belonging to cyclopentadienyl and arene ligands with CO ligands (average H···O separations are 2.44, 2.57 and 2.62 Å for triply bridging, doubly bridging and terminal bonding modes of CO respectively). The (C)H···O distances reported in Table 1 tend towards the smaller values for such interactions in organometallic[6] and organic[28] crystals.

Some complexes afford a sort of internal comparison between C−H···O bonds formed by methylidyne and methylene and those formed by CH groups belonging to other ligands. Methyl groups also form C−H···O interactions though usually longer than those established by μ_3-CH and μ-CH_2 ligands in accord with the lower acidity of these groups.

The clusters $[Rh_3(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CH)(\mu\text{-}CO)_2]^+$, CMCPRH10, and $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CH)(PrCNO)]^+$, DIPMEU, and [$Fe_3$-



Scheme 1

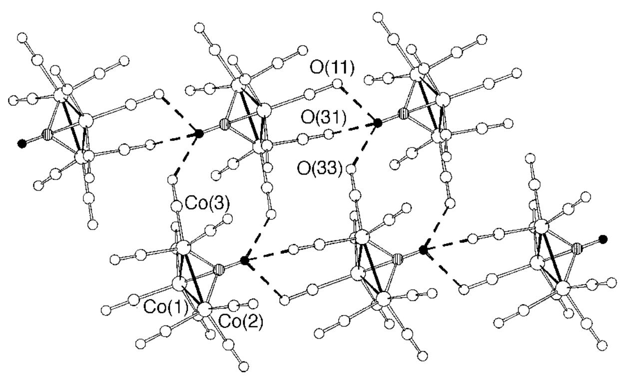


Fig. 1 Hydrogen-bonding networks in crystalline $[Co_3(\mu_3\text{-CH})(CO)_9]$, MEDYCO01. The methylidyne ligand participates in a trifurcated interaction with two neighbouring molecules. Note the large 10-atom ring

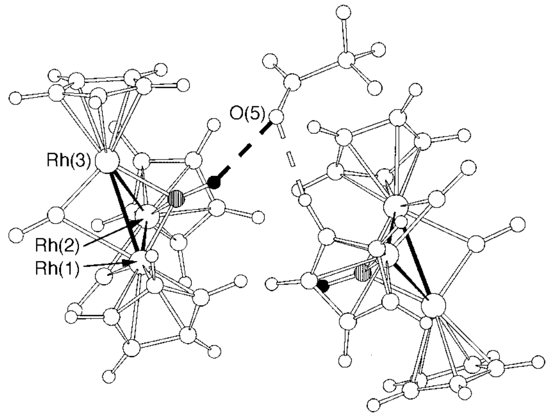


Fig. 2 Hydrogen-bonding in crystalline $[Rh_3(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-CH})(\mu\text{-CO})_2][O_2CCF_3]$ (CMCPRH10). The methylidyne as well as the cyclopentadienyl hydrogens interact with the trifluoroacetate anion forming an intricate network of C−H · · · O interactions. The two shortest C−H · · · O intermolecular contacts are shown for clarity

$(\mu_3\text{-CH})(CO)_{10}]^-$, CAXTUQ, are ionic, *i.e.* their crystals are constituted of charged systems and the interaction between anions and cations, as well as those between ions of the same charge have also to be taken into account. The effect of the ionic charge is, as expected, the same as observed in other charged organometallic species, *i.e.* the interactions between ions of opposite charge are 'reinforced' with respect to neutral species.

Intermolecular organization and hydrogen bonding in methylidyne clusters

The cluster $[Co_3(\mu_3\text{-CH})(CO)_9]$ (MEDYCO01) has been characterized by both X-ray and neutron diffraction.[16] The molecular structure is simple, with only terminal CO ligands (three on each Co atom) and the methylidyne ligand symmetrically spanning the triangular cluster. The methylidyne ligand participates in a trifurcated interaction with two neighbouring molecules, as shown in Fig. 1. This compound is particularly interesting because, contrary to the other species listed in Table 1, it is the only case in which no other donor or acceptors groups beside μ_3-methylidyne and CO ligands are present.

The crystal structure can be described as formed of parallel molecular rows. Each molecule participates in two main types of hydrogen-bonding interactions: (*i*) a dimer, recalling the carboxylic, or amide dimer, based on a 10-atom ring formed by molecules in centrosymmetric orientations; and (*ii*) a chain motif involving two axial CO ligands and the apical methylidyne ligand. Although the H · · · O distances (2.50–2.62 Å) are long compared with those observed in other systems (see also below) it is important to keep in mind that the methylidyne ligand is involved in a trifurcated interaction.

In the crystal of the trifluoroacetate salt of $[Rh_3(\eta^5\text{-}C_5H_5)_2(\mu_3CH)(\mu\text{-CO})_2]^+$, CMCPRH10,[17] all hydrogen-bonding interactions involve the anion. The F atoms interact with the cyclopentadienyl hydrogens, which also participate in links to the oxygen atoms of the anion. One of the shortest C−H · · · O interactions [(C)H · · · O 2.25 Å] is established by the methylidyne H atom with one O atom of the anion (see Fig. 2), very likely because the bond is reinforced by the opposite charges of the donor and acceptor partners. Owing to the variety of acceptor groups, the hydrogen-bonding pattern is fairly complicated. It is worth mentioning that the crystal structure of this compound also allows an 'internal' comparison between $H(C_5H_5)$ and $H(\mu_3\text{-CH})$. As shown in Table 1, the μ_3-CH · · · O distance is somewhat in between the minimum and maximum values of $(C_5H_5)H$ · · · O distances, *viz.* one can speculate, *though purely on geometric grounds*, that the polarization of the C−H bond in the methylidyne complex is more similar to that of an sp^2- or sp-hybridized atom. The average values of the μ_3- and μ-C · · · O intermolecular distances collected in Table 1 [3.36(15) and 3.59(14) Å, respectively] are tendentially shorter than the corresponding C≡C · · · O and C=C · · · O separations in organic crystals (3.46 and 3.64 Å, respectively).[14a] The average C−H · · · O distance involving the other sp^2 carbon atoms in Table 1 is 3.41(13) Å, *i.e.* somewhat in between the μ_3- and μ-C · · · O separations.

The presence of C−H · · · F interactions as one dominating factor in crystal packing is found again in the crystal of the BF_4^- salt of $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-CH})(PrCNO)]^+$, DIPMEU.[18] The only *competitor* in hydrogen-bond formation is the nitrosyl oxygen O(1), which is capable of accepting three H atoms, two from C_5H_5 ligands and one from the methylidyne ligand, the latter being the shortest (2.30 *versus* 2.47, 2.51 Å). These inter-

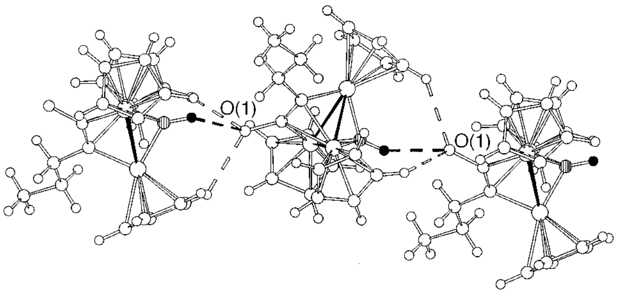


Fig. 3 Hydrogen-bonding interactions in the BF_4^- salt of $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CH)(PrCNO)]^+$, DIPMEU. The nitrosyl oxygen O(1) accepts hydrogen bonds from three hydrogens

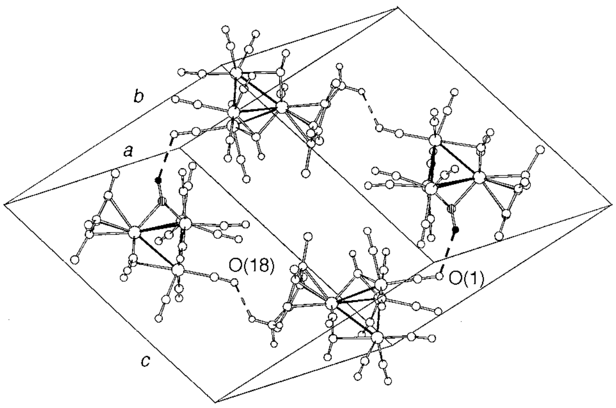


Fig. 4 The μ_3-CH ··· O interaction linking the two independent molecules in crystalline $[WOs_3(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}CH)(CO)_{11}]$ (YARCEZ)

actions are shown in Fig. 3. Besides the interactions with the nitrosyl and methylidyne ligands, there is a diffuse network involving the BF_4^- anions with the F atoms forming a total of seven C–H ··· F links shorter than 2.6 Å. These bonds are responsible for holding together the anion chain.

Carbonyl oxygens accept hydrogen bonds from both the phenyl CH systems in the tetraphenylarsonium cations as well as from the methylidyne ligand in the anion $[Fe_3(\mu_3\text{-}CH)(CO)_{10}]^-$ in crystalline CAXTUQ.[19a] The μ_3-CH ··· O intermolecular hydrogen bond links the anions in a row along the *b* axis. In the $N(PPh_3)_2^+$ salt of this anion[19b] (CACSAA) there are two independent molecules, one of which is disordered. The packing is dominated by the very big cation which prevents interaction between clusters so that only (Ph)H ··· O links are observed.

In the case of crystalline $[WOs_3(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}CH)(CO)_{11}]$ (YARCEZ)[20] the asymmetric unit contains two independent molecules which are connected by a single CH ··· O interaction [C(2)–H(2a) ··· O(1) 2.52 Å] as shown in Fig. 4. Additional CH ··· O interactions are established between the CO ligands and the CH_3 (C_5Me_5) groups.

Let us now examine the three cluster species $[Fe_3(\mu_3\text{-}CH)(CO)_9(\mu_3\text{-}E)]$ (KEMVIH, E = Bi; KEMVON, E = Sb; KEMVED, E = As).[21] These three cluster species are isostructural and the antimony and arsenic derivatives are also isomorphous in their crystalline forms. The latter crystals reveal the existence of interactions between the capping main-group atoms. This aspect, which goes beyond that of the subject matter of this paper, needs further investigation and will not be discussed in the context of this study. It will be the subject of a future investigation. At the moment we focus on KEMVIH because the methylidyne group interacts as in the case discussed above with the carbonyl oxygen atoms [(C)H ··· O 2.48 Å] thus forming chains in the crystal structure as shown in Fig. 5. The bismuth atoms are at 3.71 Å from the carbonyl oxygens.

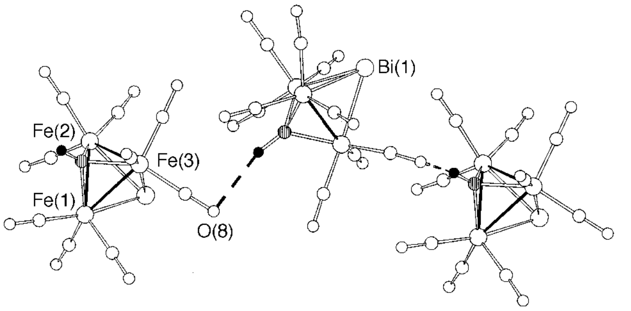


Fig. 5 Hydrogen-bonding involving the methylidyne hydrogen atom in crystalline KEMVIH. Chains of molecules are formed *via* CH ··· OC interactions (2.48 Å).

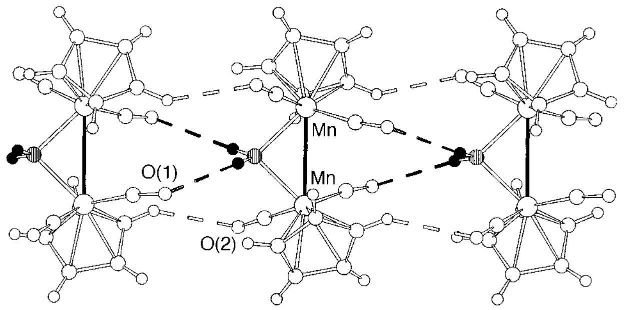


Fig. 6 Hydrogen-bonding in crystalline $[Mn_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)(CO)_4]$ (BANGIG10). The molecules form piles along the *c* axis and are held together by two HCH ··· O and two (C_5H_5)H ··· O interactions of comparable length

Intermolecular organization and hydrogen bonding in methylene complexes

Several examples are also available of organometallic complexes carrying the μ-CH_2 group. The hydrogen bonding between the methylene hydrogen and carbonyl oxygens in crystalline $[Mn_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)(CO)_4]$, BANGIG10,[22a] is shown in Fig. 6. The molecules are held together in piles along the *c* axis by two HCH ··· O and two (C_5H_5)H ··· O interactions of comparable length [C(3)–H(3) ··· O(1) 2.56, C(7)–H(7) ··· O(12) 2.50 Å]. This compound affords an internal comparison of hydrogen-bond length since the C–H ··· O distances relative to methylene and cyclopentadienyl ligands are of comparable lengths, while they are longer than most CH ··· O discussed above. Interestingly, if the C_5H_5 ligands are replaced by C_5Me_5 such as in crystalline $[Mn_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CH_2)(CO)_4]$ (not discussed here),[22b] the methylene ligand becomes encapsulated within the ligand sheath and is no longer capable of approaching the CO ligands of neighbouring molecules.

There are two independent molecules in the asymmetric unit of crystalline $[Os_3(\mu\text{-}CH_2)(CO)_9(PhCCPh)]$, BEFKEC,[23] with both CH_2 groups forming relatively short H ··· O bonds with CO ligands [H(201) ··· O(8) 2.41 and H(102) ··· O(16) 2.58 Å]. Additional interactions are established between the CO ligands and the phenyl hydrogens (see Table 1).

Crystalline $[MnFe_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)(\mu\text{-}CH_2)(\mu_3\text{-}COMe)(CO)_5]$, FIDSAM,[24] shows three types of interactions: one $H(CH_2)$ ··· O interaction [H(2) ··· O(5) 2.46 Å], one $H(C_5H_4Me)$ ··· O link [H(13) ··· O(4)] and two $H(C_5H_5)$ ··· O bonds [H(11) ··· O(2)].

The crystal structure of $[SnOs_3Cl_2(\mu\text{-}CH_2)(CO)_{11}]$, DUJYAI,[25] shows the effect of an alternative acceptor, the Cl ligand, with respect to CO. The two independent molecules present in the asymmetric unit form two different types of CH ··· Cl interactions (2.70 and 2.77 Å) as shown in Fig. 7. The shortest HCH ··· O distances (2.71 Å) in the crystal structure are much longer than any discussed so far.

The dinuclear rhenium complex $[Re_2Me_4O_3(\mu\text{-}CH_2)]$ (SIGGIY)[26] is noteworthy since the hydrogen-bonding acceptor sites

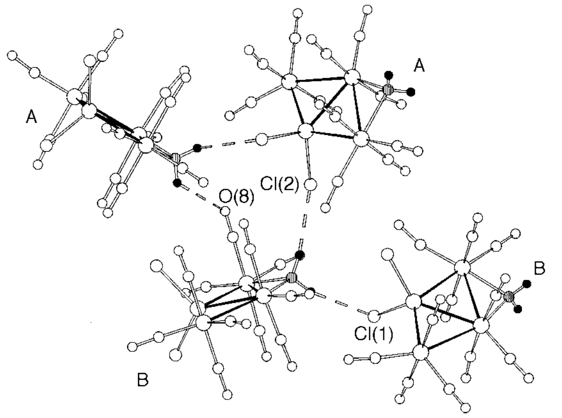


Fig. 7 Hydrogen-bonding of the HCH···Cl type in crystalline $[SnOs_3Cl_2(\mu\text{-}CH_2)(CO)_{11}]$, DUJYAI. Note how the two independent molecules (A and B) are linked by C–H···Cl interactions

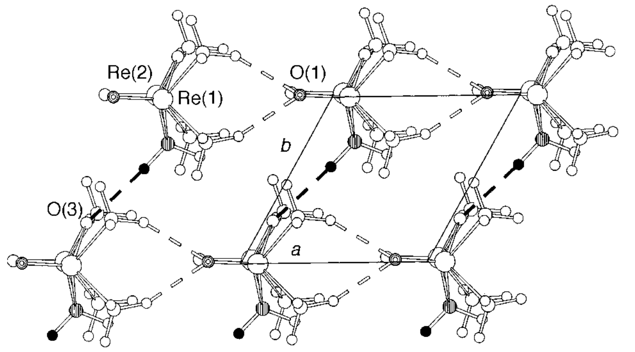


Fig. 8 Hydrogen-bonding interaction in crystalline $[Re_2Me_4O_3(\mu\text{-}CH_2)]$ (SIGGIY). The C–H···O interactions between methyl hydrogens and oxide ligands (shaded) organize molecules in a row along the *a* axis, while methylene C–H···O contacts link these rows

are afforded by the oxide ligands, two of which are terminally bound and one is spanning the Re–Re bond together with the μ-CH_2 ligand (see Scheme 1). A $(CH_2)H\cdots O$ (oxo) hydrogen bond connects molecules in pairs [H(13)···O(3) 2.48 Å] which form chains along the *a* axis *via* H(methyl)···O bonds as shown in Fig. 8. These bonds are slightly shorter (2.33 and 2.38 Å) than that involving the methylidyne group. The structure affords additional support to one of the classical empirical rules of crystal packing, namely that, in the presence of hydrogen bonding, molecules are organized so as to make maximum use of all acceptor and donor groups in the structure. In this case methyl groups are also used to satisfy the requirement of the oxygen acceptors. In the case of $[Re_2Me_4(\mu\text{-}O)(\mu\text{-}CH_2)(PMe_3)_2]$ (SIGGEU)[26] the substitution of two phosphine groups for the oxo ligands makes the C–H···O link no longer possible.

Finally, the crystal structure of $[Ir_2(\mu\text{-}Me)(CO)_4\{(Me_2P)_2(CH_2)\}_2][O_3SCF_3]$ (JAZMIG),[27] where the complex carries a bridging methanido group, needs some discussion. The participation of the μ-CH_3 group in C–H···O bonds can only be evaluated from the C···O distances as hydrogen-atom coordinates are not available [C(5)···O(3) 3.63 Å]. As in previous cases of ionic systems, the interaction connects the cation with the anion. Participation of the methyl groups of the $(Me_2P)_2(CH_2)$ ligand in several C–H···O bonds is also observed.

For the sake of completeness, it should be mentioned that the CSD search yielded six other compounds carrying either methylidyne or methylene ligands which do not show the presence of μ_3-CH···O or μ-CH_2···O interactions of importance,[29–34] see SUP 57234. In the case of $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)(CO)_3]$[29] and *cis*-$[Ru_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_2)(CO)_3]$,[31] the hydrogen-bonding patterns are dominated by $(C_5H_5)H\cdots O$ bonds as described previously.[6] Similarly, in crystalline $[Rh_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CH)(CO)_2][PF_6]$[32] all short-range interactions involve either the PF_6^- anion as acceptor sites or the C_5H_5-ligands as donors, whereas in $[Fe_3(\mu_3\text{-}CH)(\mu_3\text{-}COCOMe)(CO)_9]$ all short interactions involve the methoxy-groups. These ‘negative’ examples are also useful as they indicate that, when dealing with weak non-covalent interactions, there is no hard and fast rule but only general behaviours. It is important, for instance, to keep in mind the steric–electronic balance that, in some cases, may require the ‘sacrifice’ of small cohesive intermolecular contributions if this allows optimization of van der Waals interactions.

The case of nonacarbonyltris(μ-hydrido)(μ_3-methylidyne)triosmium (COTPOQ01[34]) is admittedly much more intriguing because, while there is no short C–H···O bond in the crystal, the solid-state structure shows the existence of a very short intermolecular H···H contact between the two independent molecules in the asymmetric unit. Whether these interactions are related to the ‘dihydrogen bond’ that is attracting much interest at the moment,[35] or are the result of some more subtle packing compromise between competing intermolecular interactions and packing efficiency, will be the subject of a forthcoming investigation.

Conclusion

In this paper we have examined the crystal structures of organometallic complexes carrying either methylidyne or methylene ligands with the aim of establishing whether these ligands are sufficiently acidic to form intermolecular hydrogen-bonding interactions with suitable acceptors. Structural information has been retrieved from the CSD. Although the sample of structures is admittedly limited, one can still recognize some important structural features. The main outcomes of this work can be summarised as follows.

(*i*) Methylidyne (μ_3-CH) and methylene (μ-CH_2) ligands form hydrogen bonds of the C–H···O type chiefly with the oxygen atoms of the CO ligands, which are almost invariably present as coligands in complexes of this type.

(*ii*) In terms of metrical features, the two groups are comparable with the alkyne and alkene groups in organic crystals, hence behaving as sp- and sp^2-hybridized C atoms, respectively.

It is important to stress that we have come to this conclusion from a purely structural source of information. We *observe* the effect of the different extent of C–H polarization in the two types of ligands with respect to CH_3 groups within the same crystal environment (structures carrying both μ_3-CH and μ-CH_2 ligands and CH_3 groups in the presence of the same acceptor) and between different crystalline environments (organometallic and organic structures).

(*iii*) The presence of ionic charges on the organometallic complexes is one of the most important differences between organic and organometallic systems since very few organic compounds are in ionic form as opposed to organometallics. As expected, the charge difference reinforces the hydrogen-bonding interactions leading to shorter (C)H···O separations than in the case of neutral species. This is in keeping with the general idea that hydrogen bonds, also of the C–H···O type, have a large component of electrostatic contributions. ‘Charge assistance’ in the formation of hydrogen bonding in organic molecules is a well ascertained effect.[36]

(*iv*) The effect of competitors with the CO ligand as acceptor of CH donation is well evident in the cases of ionic clusters where counter ions carrying F atoms are used for the crystallization. It seems that charge-assisted C–H···F interactions in ionic crystals play an important role in crystal cohesion. The effect of these interactions in the stability and phase-transitional behaviour of organometallic salts has recently been discussed.[37]

Non-covalent intermolecular interactions established by organic and organometallic molecules show not only many fundamental analogies but also several substantial differences.

One may concede that intermolecular interactions in organic systems are a subset of those afforded by organometallic complexes and clusters. With this study we have demonstrated that the interaction of μ_3-CH and μ-CH_2 ligands with metal atoms generates highly polarized C−H bonds which behave, at least in terms of the length of intermolecular C−H···O bonds, as sp- and sp^2-hybridized C atoms.

Clearly, the understanding of how non-covalent interactions can be tuned and controlled when metal atoms are involved represents a fundamental challenge. It may help to understand the mechanism of many homo- and hetero-geneous catalytic processes as well as to develop some synthetic strategy in the field of supramolecular organometallic chemistry.

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