J. Am. Chem. Soc. **1995,** *117,* 3156−3166

Hydrogen Bonding in Organometallic Crystals. 2. $C-H\cdots O$ Hydrogen Bonds in Bridged and Terminal First-Row Metal Carbonyls[1]

Dario Braga,[*,†] **Fabrizia Grepioni,**[†] **Kumar Biradha,**[‡] **V. R. Pedireddi,**[‡] **and Gautam R. Desiraju**[*,‡]

Contribution from the Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, and School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

Received July 22, 1994. Revised Manuscript Received December 30, 1994[⊗]

Abstract: $C-H\cdots O$ hydrogen bonding interactions in crystalline organometallic complexes and clusters have been investigated. The analysis takes the form of retrieval from the Cambridge Structural Database of all intra- and intermolecular $H\cdots O$ distances less than 2.80 Å, associated with appropriate $C-H\cdots O$ angular geometry, in organometallic crystal structures of the first-row transition elements containing terminal and bridging CO ligands. Individual crystal structures have also been examined to evaluate the role of $C-H\cdots O$ hydrogen bonds in determining the supramolecular arrangement. There is a definite manifestation of $C-H\cdots O$ hydrogen bonding in this group of crystalline substances. In general, the bridging CO ligands form shorter and more linear hydrogen bonds than do the terminal CO ligands, reflective of their higher basicity. This effect is especially pronounced for intermolecular hydrogen bonds, the intramolecular ones being expectedly more dependent on the details of the molecular structure. $C-H\cdots O$ hydrogen bonds formed by both bridging and terminal CO ligands are also directional. In both cases, there is a tendency for the $CO\cdots H$ angle to be around 140°, hinting that there is oxygen lone pair density in these ketonic directions. Examination of specific structures shows that bifurcated acceptors (several C−H groups pointing toward a single O atom) are common and that the anisotropic displacement parameters of atoms involved in $C-H\cdots O$ bonding are smaller than those of other atoms. It is suggested that the $C-H\cdots O$ hydrogen bond is an example of a soft intermolecular interaction as compared to the hard $O-H\cdots O$ hydrogen bond.

Introduction

The assembly of mononuclear and polynuclear organometallic complexes in the solid state[2] is governed, as is the packing of organic crystals,[3] by a balance between nondirectional close-packing forces[4] and directional interactions between metal atoms[5] or charged groups.[6] However, the crystallisation behavior of organic and organometallic molecules is also contradistinctive. The flexibility of the typical organometallic molecule means that crystal packing and molecular shape are interlinked and influence each other in a manner which is much more intricate than what is observed in the majority of organic crystals.[7] Flexible shapes and the availability of different bonding modes which differ little in energy for the same type of ligands result in structural non-rigidity for most organometallic molecules. This, in turn, is responsible for the many fluxional processes organometallic molecules undergo in solution and for the existence of polymorphism in the solid state.[8]

Given these premises, our efforts have this far been directed to the understanding of intermolecular interactions acting among organometallic molecules, the effect of these interactions on the structure and conformation of the individual molecule, and the control exerted by these interactions on the molecular packing in the crystal. An appreciation of these aspects is of importance for the understanding of the solid state properties of organometallic materials. Both physical (conductivity, diffusion, magnetic susceptibility, reorientation and second harmonic generation) and chemical (solid state reactivity, racemisation, resolution) properties depend on the ways in which molecules are organized in the crystal and on the forces which hold them together.[3b] Along these lines, we have recently investigated the role played by "strong" or conventional hydrogen bonds in organometallic crystals and have studied the molecular organization in crystals of transition metal complexes and clusters containing hydrogen bond donor and acceptor groups such as −COOH, −OH, and −COOR as well as CO ligands.[1,9]

The ability of carbon atoms to act as proton donors in hydrogen bonding situations has been a matter of debate and

---

[†] Università di Bologna.

[‡] University of Hyderabad.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1995.

(1) For Part 1 of this series, see: Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju, G. R. *Organometallics* **1994**, *13*, 3532.

(2) (a) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1994**, *27*, 51. (b) Braga, D.; Grepioni, F. *Organometallics* **1991**, *10*, 2563.

(3) (a) Kitaigorodskii, A. I. *Molecular Crystal and Molecules*; Academic Press: New York, 1973. (b) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989. (c) Gavezzotti, A.; Simonetta, M. *Chem. Rev.* **1982**, *82*, 1.

(4) (a) Braga, D.; Grepioni, F. *Organometallics* **1992**, *11*, 711. (b) Braga, D.; Grepioni, F.; Sabatino, P.; Gavezzotti, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1185.

(5) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 2505.

(6) (a) Braga, D.; Grepioni, F.; Milne, P.; Parisini. E. *J. Am. Chem. Soc.* **1993**, *115*, 5115. (b) Braga, D.; Grepioni, F. *Organometallics* **1992**, *11*, 1256. (c) Mingos, D. M. P.; Rohl, A. R. *Inorg. Chem.* **1991**, *30*, 3769. (d) Mingos, D. M. P.; Rohl, A. R.; Burgess, J. *J. Chem Soc., Dalton Trans.* **1993**, 423.

(7) Braga, D. *Chem. Rev.* **1992**, *92*, 633.

(8) Braga, D.; Grepioni, F.; Dyson, P. J.; Johnson, B. F. G.; Frediani, P.; Bianchi, M.; Piacenti, F. *J. Chem. Soc., Dalton Trans.* **1992**, 2565.

(9) Throughout this paper, the term "strong" when applied to hydrogen bonding refers to $O-H\cdots O$ and $N-H\cdots O$ interactions while the term "weak" refers to $C-H\cdots O$ interactions. This is a subjective criterion but one which is generally justified because the vast majority of $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds are stronger than the strongest of $C-H\cdots O$ interactions (*ca.* 5 kcal/mol).

0002-7863/95/1517-3156$09.00/0

controversy in the past.[10] At present, there seems to be hardly any dispute about the use of the term "hydrogen bond" to describe these interactions.[11] Their potential as delicate yet accurate links for systematic supramolecular construction is only just beginning to be realized[12] and a number of recent books and papers have addressed different aspects of these weak interactions.[13] As far as purely organic structures are concerned, there is very little doubt that C−H···O hydrogen bonds (energy 1−5 kcal mol^{-1}) are major determinants of crystal packing, especially when strong O−H···O and N−H···O hydrogen bonds (energy 5−10 kcal mol^{-1}) are absent.[11,13a] Even in the presence of strong hydrogen bonds, C−H···O hydrogen bonds may distort the geometry and topology of the strong hydrogen bond network in specific instances.[14] Conversely, the absence of C−H···O hydrogen bonding which can be caused by molecular features (for instance a lack of a critical number of H atoms) leads on occasion to unexpected topologies for the strong hydrogen bond network.[15] Anomalies and puzzles in the strong hydrogen bond patterns of certain crystal structures are (with belated hindsight) being explained on the basis of the interplay of strong (O−H···O, N−H···O) and weak (C−H···O) hydrogen bonds.[9,16] In general, the strength and effectiveness of a C−H···O hydrogen bond depends on C−H carbon acidity[17] and on O-atom basicity,[18a] which is enhanced *via* cooperative effects.[19]

It is remarkable that, inspite of the interest that the C−H···O hydrogen bond has attracted, little has been done in this context with regard to organometallic solids. This is surprising because the number of organometallic species characterized by diffraction methods, to date, is counted in terms of the tens of thousands. Most of these structures are deposited in the Cambridge Structural Database (CSD),[20] thus providing direct access to fundamental information on both molecular and crystal structures. A further reason for interest arises from the presence in organometallic molecules of an additional and different type of potential hydrogen bonding acceptor, namely the CO ligand. The CO ligand can bind to metal centers in a terminal or bridging fashion, this latter bonding mode being found in polynuclear complexes. We have already observed the capacity of the CO ligand to form intermolecular C−H···O hydrogen bonds which, though weak, are significant.[1,13d,g,h] However, this ligand takes part in hydrogen bonding networks only when stronger acceptor groups are absent.

In this paper we report results of an extensive study of intramolecular and intermolecular C−H···O hydrogen bonds in organometallic crystal structures of the first-row transition elements containing terminal and bridging CO ligands. In particular, we will try to address the following questions: (i) Does CO participate in C−H···O hydrogen bonds wherein the donor H atom belongs to a metal-coordinated organic ligand, M−C−H, or to an organic ligand, R−C−H, and the acceptor O atom belongs to a metal-coordinated CO molecule? (ii) Do C−H···O hydrogen bonds play a detectable (and if so, significant) role in the stabilization of crystals formed by neutral mononuclear or polynuclear organometallic complexes? Are these interactions important in supramolecular architecture? (iii) Is there a recognizable difference in hydrogen bonding capability between the two main bonding modes shown by CO ligands in organometallic complexes, namely terminal (CO-t hereafter) and bridging (CO-b hereafter) which could be related to the different basicity of CO in the two bonding modes?

To answer these questions, we have systematically explored the CSD in order to analyze intramolecular and intermolecular C−H···O hydrogen bonds in crystal structures of neutral complexes containing at least one atom among the series Sc to Zn (with special emphasis on the metals Mn, Cr, Fe, Co, and Ni) and at least one CO ligand whether bound in a terminal or in a bridging fashion. From the search outputs, some representative examples have been selected and discussed in detail.

Experimental Section

Cambridge Structural Database (CSD) Analysis. Data were retrieved from the 1993 update of Version 5.05 of the CSD (109816 entries) for all the ordered crystal structures with an exact match between chemical and crystallographic connectivity and containing at least one of the first-row transition metal atoms (Sc−Zn). Polymeric and charged species were excluded. No *R*-factor restriction was employed because the structures were found to be of good accuracy with *R* factors very rarely in excess of 0.10. Geometrical calculations were performed on the retrieved data for intramolecular and intermolecular C−H···O interactions separately for each metal atom using QUEST3D-GSTAT, an automatic graphics nonbonded search program of the CSD. Duplicate hits (identified by the same REFCODE) were removed manually by eliminating all but the structure with the lowest *R* value in each case. Unique contacts were considered up to an H···O distance of 2.80 Å (van der Waals sum). A bonafide C−H···O hydrogen bond was considered to be one where, in addition to this distance stipulation, the C−H···O angle lies in the range 110−180°. C−H bond lengths were normalized to 1.08 Å. The queries were constructed such that the O atom of the C−H···O bond belongs to a CO group attached to a metal atom. Calculations were performed separately for the CO-t (C−H···O≡C−M) and CO-b (C−H···O≡C<) cases. Geometrical questions constructed for the Mn case are given in

---

[10] (a) Sutor, D. J. *Nature* **1962**, *68*, 195. (b) Donohue, J. In *Structural Chemistry and Molecular Biology*; Rich, A., Davidson, N., Eds.; W. H. Freeman: San Francisco, 1968; pp 443−465. (c) Green, R. D. *Hydrogen Bonding by C−H Groups*; Wiley: New York, 1974. (d) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

[11] Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.

[12] (a) Sharma, C. V. K.; Panneerselvam, K.; Pilati, T.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1992**, 832. (b) Biradha, K.; Sharma, C. V. K.; Panneerselvam, K.; Shimoni, L.; Carrell, H. L.; Zacharias, D. E.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1993**, 1473. (c) Reddy, D. S.; Craig, D. C.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1994**, 1457.

[13] (a) Desiraju, G. R. In *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989; pp 142−173. (b) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991. (c) Seiler, P.; Dunitz, J. D. *Helv. Chim. Acta* **1989**, *72*, 1125. (d) Aime, S.; Cordero, L.; Gobetto, R.; Bordoni, S.; Busetto, L.; Zanotti, V.; Albano, V. G.; Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1992**, 2961. (e) Steiner, T.; Saenger, W. *J. Am. Chem. Soc.* **1992**, *114*, 10146. (f) Pedireddi, V. R.; Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1992**, 311. (g) Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1993**, 1223. (h) Braga, D.; Grepioni, F.; Parisini, E.; Johnson, B. F. G.; Martin, M. C.; Nairn, J. G. M.; Lewis, J.; Martinelli, M. *J. Chem. Soc., Dalton Trans.* **1993**, 1891. (i) Steiner, T.; Saenger, W. *J. Am. Chem. Soc.* **1993**, *115*, 4540. (j) Bock, H.; Dienelt, R.; Schodel, H.; Havlas, Z. *J. Chem. Soc., Chem. Commun.* **1993**, 1792. (k) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1994**, 101. (l) Steiner, T.; Saenger, W. *Acta Crystallogr.* **1993**, *D49*, 592. (m) Wadepohl, H.; Braga, D.; Grepioni, F. *Organometallics* **1995**, *14*, 24. (n) Sarma, J. A. R. P.; Dhurjati. M. S. K.; Ravikumar, K.; Bhanuprakash, K. *Chem. Mater.* **1994**, *6*, 1369.

[14] (a) This is observed in crystalline 3,5-dinitrocinnamic acid. Desiraju, G. R.; Sharma, C. V. K. *J. Chem. Soc., Chem. Commun.* **1991**, 1239. (b) The neutron diffraction analysis of this acid has been determined recently: Hoy, V. J.; Sharma, C. V. K.; Biradha, K.; Allen, F. H.; Howard, J. A. K.; Desiraju, G. R. Unpublished results.

[15] (a) Desiraju, G. R.; Murty, B. N.; Kishan, K. V. R. *Chem. Mater.* **1990**, *2*, 447. (b) Goud, B. S.; Desiraju, G. R. *Acta Crystallogr.* **1993**, *C49*, 292.

[16] Sharma, C. V. K.; Panneerselvam, K.; Pilati, T.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2209.

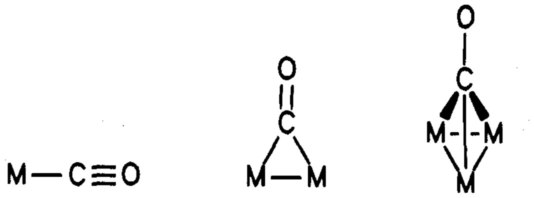
[17] (a) Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1989**, 179. (b) Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1990**, 454. (c) Pedireddi, V. R.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1992**, 988. (d) Taylor, R.; Allen, F. H. In *Structure Correlation*; Burgi, H.-B., Dunitz, J. D., Eds.; VCH: Weinheim, 1994; Vol. 1, pp 128−130.

[18] (a) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2341. (b) Steiner, T. *Ibid.* **1995**, in press.

[19] Sharma, C. V. K.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2345.

[20] Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 204.

Scheme 1. CO Bonding Modes



the supplementary material as representative examples. Key examples were then selected from the search outputs and were investigated by computer graphics.[21a] The computer program PLATON[21b] was used to analyze the geometrical features of the hydrogen bonding patterns.

Carbonyl complexes of transition metal atoms are common and almost all metals form stable complexes in the low-oxidation states with CO. Binary carbonyls (e.g. complexes containing CO as the only ligand) are known and have been structurally characterized for all transition metals in the series Ti–Ni. Most of these form clusters of various nuclearities. There are, however, relatively few complexes containing exclusively CO ligands when compared to the number of mononuclear and polynuclear complexes containing organic ligands as well as CO. In order to efficiently handle the problem under investigation, we have confined our CSD search to first-row metal complexes but with no limitations on the nuclearity of the metal core.

It is crucial in the following discussion to recall that the CO molecule can bind to polynuclear metal complexes in terminal and various bridging fashions. Bridging COs 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 Scheme 1. In all these bonding modes, CO provides two electrons to the valence electrons of the complex. CO is also known to be capable of interacting with metal centers *via* the unsaturated C–O bond. End-on (or isocarbonyl) complexes are also well-established.[22] The formation of these complexes requires strong Lewis acids such as alkali metal cations, other main groups metals, or rare earth acceptors.

The basicity of CO increases on going from the terminal to the bridging bonding geometry so that the involvement of this ligand in hydrogen bonding also increases.[1] For this reason, we have preferred to separately examine these different involvements of CO in C–H···O type interactions. For the purpose of the following discussion we have designated CO in terminal and bridging bonding geometries as CO-t and CO-b, respectively. The descriptors inter and intra will be used to discriminate between intermolecular and intramolecular interactions. The four categories we will therefore discuss are CO-t(inter), CO-b(inter), CO-t(intra), and CO-b(intra).

Studies of hydrogen bonding which rely on X-ray derived crystal structures are handicapped by the fact that the position of the most important atom in the hydrogen bond, namely H, is the one which is determined with the least accuracy. Typically, C–H distances are systematically shortened by 0.05–0.10 Å. Two approaches are commonly used to alleviate this problem. In the first approach, one considers only neutron diffraction structures wherein the H-atom positions are determined with great accuracy.[23] Because of obvious experimental difficulties, this technique cannot be used routinely.[13e,14b] In the second approach, the X-ray derived H-atom position is normalized by extending this position along the C–H vector such that the C–H distance corresponds to the typical neutron-derived value.[24] Such normalization yields hydrogen bond geometries which closely parallel neutron-derived geometries, and this is the procedure which has been employed in this study. There are situations, however, where neutron-derived structures are invaluable and we have discussed a neutron diffraction structure (HMPCIC10) to show the superiority of this technique in obtaining accurate experimental information on C–H···O hydrogen bonding.

The geometrical criteria which are selected to characterize a particular C–H···O grouping as a significant intermolecular interaction or as a hydrogen bond have also been the subject of some discussion.[11] There appear to be two distinct viewpoints: (1) use a conservative C···O threshold such as 3.25 or 3.30 Å and refer to longer separations as van der Waals interactions; (2) use a more liberal threshold. Historically, the Sutor–Donohue controversy in the 1960s arose because of the tendency to accept the first viewpoint.[10a,b] More recent analysis, however, has shown that many longer C–H···O contacts (C···O 3.50–4.00 Å) have angular characteristics and effects on crystal structures which resemble the shorter contacts (3.10–3.50 Å).[13e,14a] We emphasize that the C–H···O bond is not really a van der Waals contact but is primarily electrostatic, falling off much more slowly with distance and hence viable at distances which are equal to or longer than the conventional van der Waals limit. Therefore the outer cutoff C···O distance must be liberal. Additionally, it must be noted that the chemically meaningful distance is the H···O distance rather than the C···O distance and that this H···O distance is geometrically determined by the (experimentally easily observable) C···O distance and the hydrogen bond angle θ (C–H···O). In practice, we have employed an H···O cutoff of 2.80 Å for the H-normalized data. This value is close to the van der Waals sum and even longer values have been considered as being justified and necessary.[13k] More complex and accurate prescriptions have been suggested by us[16] and others[13e] in studies of small, homogeneous groups of crystal structures, but in this extensive study we have preferred generality with the attendant simplicity. Actually, the question is not whether this or that cutoff is correct or incorrect but rather that one uses a consistent and high value throughout. Mean geometries will inevitably depend on the particular range of H···O values chosen, but this is not a problem if comparisons are being made, say from metal to metal within the overall group of structures. Needless to say, while evaluating individual C–H···O hydrogen bonds, the greatest weight is given to those contacts wherein short H···O separations (2.00–2.30 Å) are accompanied by large θ angles (150–180°). It may be noted in this context that while short C···O separations are often accompanied by small θ angles (weak and bent hydrogen bonds), the chemically unreasonable combination of a short H···O distance and a small θ angle is observed but seldom.

Results and Discussion

All average structural parameters from the CSD search for the series Ti–Ni are listed in Table 1. All metals behave very similarly, that is there is no dependence on the nature of the metal which also means no dependence on the number of ligands since the number of electrons (that is, of ligands) required by the EAN rule decreases on moving from left to right along the transition row.[25] Plots of the C–H···O angle *versus* the C···O distance have been deposited in the supplementary material. The following general considerations can be made:

(i) Comparison between CO-t(inter) and CO-b(inter). Table 1 shows that both C···O and H···O mean distances for CO-t(inter) are generally longer than those of CO-b(inter). Although V and Cr appear to contradict this trend, the number of CO-b in these cases is too small to be of statistical relevance. The differences in mean length between CO-t(inter) and CO-b(inter) fall within the range 0.02–0.06 Å for the C···O separations and 0.04–0.08 Å for the H···O separations. For Fe and Co, the trend is clear and the confidence level in such an observation is high with the differences in mean length being at least 10σ. For Mn and Ni, the differences in mean length are not significant at the 3σ level because of the standard deviation for the CO-b(inter) values. However, the trend is toward longer distances for hydrogen bonds involving CO-t, and this general behavior very likely follows from the higher basicity of CO-b with respect to CO-t.[22]

---

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

[22] Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 218.

[23] Jeffrey, G. A. In *Accurate Molecular Structures*; Domenicano, A., Hargittai, I., Eds.; Oxford University Press: Oxford, 1992; pp 270–298.

[24] (a) Murray-Rust, P.; Glusker, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1018. (b) Kroon, J.; Kanters, J. A.; van Duijneveldt-van de Rijdt, J. G. C. M.; Vliegenhardt, J. *J. Mol. Struct.* **1975**, *24*, 109.

[25] However, many stable complexes of the early and late transition metals possess fewer electrons than predicted by the EAN rule.

Table 1. Mean Geometrical Parameters for C–H···O Hydrogen Bonds in First-Row Transition Metal Carbonyls[a]

	C···O (Å)	H···O (Å)	C–H···O (deg)	C–O···H (deg)	no. of unique REFCODES	no. of hits
			CO-t(inter)			
Ti	3.53(0.02)	2.63(0.02)	140.3(2.2)	126.5(4.0)	7	29
V	3.49(0.01)	2.65(0.01)	136.5(1.6)	124.9(2.7)	22	88
Cr	3.51(0.003)	2.64(0.002)	140.1(0.3)	124.9(0.5)	474	2415
Mn	3.51(0.004)	2.64(0.003)	139.4(0.4)	126.8(0.6)	366	1510
Fe	3.51(0.002)	2.62(0.002)	139.8(0.2)	128.3(0.3)	1137	4205
Co	3.52(0.005)	2.64(0.004)	140.3(0.5)	128.3(0.7)	291	916
Ni	3.52(0.02)	2.64(0.02)	141.2(3.0)	125.2(3.4)	12	30
			CO-b(inter)			
Ti					0	0
V	3.51(0.1)	2.61(0.06)	145.4(11.9)	125.8(6.7)	1	4
Cr	3.56(0.05)	2.56(0.04)	155.3(3.6)	131.7(6.3)	4	9
Mn	3.48(0.02)	2.58(0.02)	144.0(2.4)	132.5(2.7)	23	51
Fe	3.45(0.009)	2.57(0.008)	142.5(1.1)	132.9(1.2)	129	285
Co	3.47(0.01)	2.59(0.008)	141.4(1.0)	132.2(1.2)	110	257
Ni	3.50(0.02)	2.59(0.02)	145.4(2.5)	128.3(3.4)	20	47
			CO-t(intra)			
Ti	3.45(0.04)	2.62(0.05)	135.3(7.0)	80.3(1.2)	2	4
V	3.40(0.04)	2.66(0.03)	127.7(3.9)	82.2(2.0)	10	21
Cr	3.52(0.007)	2.64(0.005)	140.1(0.7)	84.6(0.8)	218	456
Mn	3.50(0.007)	2.65(0.006)	137.3(0.7)	79.8(0.7)	212	429
Fe	3.50(0.004)	2.64(0.003)	138.0(0.4)	82.0(0.4)	599	1272
Co	3.50(0.01)	2.67(0.006)	135.8(0.9)	82.7(0.9)	138	261
Ni	3.60(0.04)	2.69(0.02)	143.7(3.8)	80.5(3.2)	8	15
			CO-b(intra)			
Ti					0	0
V	3.46(0.06)	2.62(0.08)	136.2(12.1)	86.3(2.5)	1	3
Cr	3.46(0.08)	2.70(0.08)	128.1(9.0)	104.4(8.1)	1	2
Mn	3.34(0.03)	2.55(0.03)	132.4(4.0)	98.7(2.6)	10	22
Fe	3.35(0.01)	2.56(0.01)	130.4(1.4)	94.7(1.2)	45	99
Co	3.32(0.01)	2.52(0.01)	131.0(1.2)	96.1(0.9)	51	128
Ni	3.39(0.03)	2.59(0.03)	132.0(2.7)	96.2(3.1)	13	24

[a] Values obtained from the Cambridge Structural Database (standard deviation values are in parentheses).

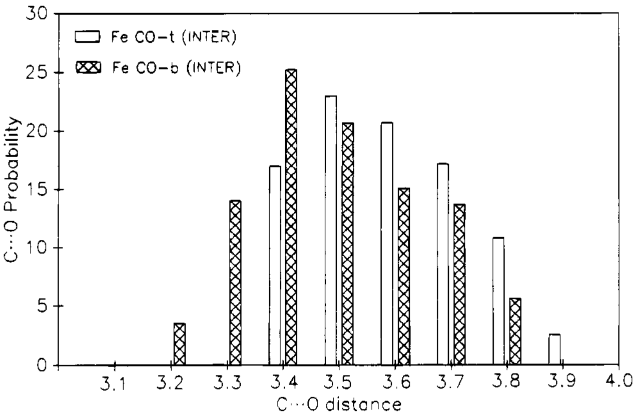


Figure 1. Histograms of C···O distances for the Fe CO-t(inter) and CO-b(inter) complexes. The populations are expressed as probabilities to facilitate comparison. The bars at, say, 3.40 Å represent contacts between 3.30 and 3.40 Å. Notice the offset of the CO-t histogram toward longer C···O distances.

Although these distance differences are small, there is adequate evidence that mean C···O and H···O distances accurately reflect C–H···O acidity–basicity properties.[17,18] C–H···O distance distributions will *always* be broad. This is inherent in the very weakness of the interaction.[17a] However, when as in this case the sample sizes run into the several thousands, the values of the means are less likely to be affected by outliers and comparison of mean C···O and H···O distances becomes a reliable exercise,[17d] inasmuch that these distances have been shown to even correlate properly with solution pK_a values.[17c] In support of such an argument, Figure 1 shows histograms of C···O distances for the Fe CO-t(inter) and CO-b(inter) complexes with the populations of structures expressed as probabilities in both cases to facilitate comparison. These histograms represent 4205 and 285 hits, respectively. Notice that the entire histogram for CO-t(inter) is offset toward longer C···O distances. Such behavior has been observed previously for acidity series involving chloroform and dichloromethane[17a] and involving alkynes and alkenes.[17b] The less basic the CO ligand, the longer the C···O distance. This shows that a consideration of mean C···O and H···O values is a valid approach to monitor O-atom basicity in organometallic complexes.

Similarly, C–H···O angles for CO-t(inter) are smaller than those of CO-b(inter), 139–140° *versus* 142–146°. This difference is small and indeed the trend is again fully satisfactory only for Fe and to some extent Co, but strengthens the idea that CO-b(inter) forms, on the average, more linear and stronger intermolecular bonds than CO-t(inter). This is noteworthy also because steric factors favor CO-t(inter) over CO-b(inter), the former type of ligands protruding more from the molecular surface. Similar arguments and caveats also hold for the C–O···H angles (see Table 1) although these angles are, on the whole, smaller, approaching 120°. With regard to metals other than Fe and Co, it should be recognized that the interaction being studied is really weak and thus the significance level may be low for some of the distance and angle differences. Inasmuch, however, as one would like to make some chemical interpretations from these geometrical results for Cr, Mn, and Ni structures, it should be stated that though the trends are not statistically significant at the 3σ level, they appear similar and more reliability may be placed in these results at a future time when a larger sampling of data becomes available. Along these lines, we have calculated mean C–H···O angles for *all* metals for CO-t(inter) and CO-b(inter) to be 139.8(0.3)° and 142.5-

(1.2)°, respectively. Similar C−O···H angles are 127.1(0.5)° and 132.2(1.5)°, respectively.

(ii) Comparison between CO-t(inter) and CO-t(intra). C···O and H···O distances for CO-t(intra) and CO-t(inter) have similar mean values. Both C−H···O and C−O···H angles are larger for CO-t(inter) than CO-t(intra). The average value for C−H···O angles is 139 *versus* 137°. The difference in C−O···H angles is even more striking being of the order of 40−50°. These differences are probably due to the common octahedral coordination of ligands around the metal centers with ligands forming L−Me−L′ angles of *ca.* 90°.

(iii) Comparison between CO-b(inter) and CO-b(intra). The relationship observed between CO-t(inter) and CO-t(intra) is also maintained between CO-b(inter) and CO-b(intra). Again, the results for Fe and Co are the most reliable while those for Mn and Ni (though following the same trend) are equivocal. The C−H···O angle difference is more appreciable while CO···H angles are larger than for CO-t(intra). This is very probably due to the fact that CO-b are more embedded in the ligand shell and can get closer to neighboring ligands.

(iv) CO···H Directionality and O-Atom Lone Pair Orientations. Plots of CO···H angles *versus* H···O distances in the nearly 1500 Fe-atom-containing crystal structures are presented in Figure 2a. Similar plots for Mn, Co, Ni, and other metals have been deposited. We will discuss intramolecular and intermolecular angles separately.

(a) Intramolecular Angles. CO···H angles for both CO-t(intra) and CO-b(intra) cluster around 70−100° with only a very few outliers which exceed 100°. It appears that, as the O···H distance increases, the CO···H angles for CO-t(intra) tend to span a larger range than at shorter distances. The reason for this is perhaps to be found in the normal geometry of a complex or cluster; if ligands have O and H atoms at short contact distances (less than 2.80 Å) they must belong to ligands which are bound to the same metal atom or, at most, to two adjacent metal atoms in a dinuclear or higher nuclearity complex, as shown in Scheme 2, left. Only when the ligand carrying the CH unit we are considering is very flexible and capable of folding back toward the CO ligand (Scheme 2, right) can the CO···H angle be larger.

This is perhaps why intramolecular six-, seven-, and higher-membered rings are formed rather than five-membered rings. In order to have five-membered rings, the C atom carrying the H atoms of interest must be bound directly to the metal. This bond could be of the uncommon σ-type (M - - CH) or be due to the presence of a π-ligand (cyclopentadienyl, arenes, etc.) which is found more frequently. In this latter case, however, the H atom must be at less than 2.80 Å (to fall within our search cutoff) and intramolecular repulsions between C(π-ligand) and C(CO) arise as shown in Scheme 3. As a matter of fact, in all the examples we have examined where this latter situation is present, short interactions between, say, Cp or arene H atoms and COs are never observed.

(b) Intermolecular Angles. Far more interesting is the situation presented by the CO···H angles in the CO-t(inter) case. These angles provide information on O-atom directionality, a subject which has not been studied rigorously for C−H···O bonding. For strong hydrogen bonds, the directionality of X−H···O (X = N, O), that is the preference of the X−H vector to point toward the lone pair direction of the O atom, has been found to depend on whether the O atom is sp^2 or sp^3 hybridized.[10d] For carbonyl acceptors, there is a marked preference for the hydrogen bond to lie in the lone pair direction, or in other words with an X−H···O=C< angle of around 120°. For ethereal acceptors, however, the directionality is not so pronounced; while there is some preference for hydrogen bonding in the plane containing the O lone pairs ("rabbit ears" plane), there is no favored trajectory within the plane.[24a] In general, C−H···O directionality has been found to be similar, that is C−H···O hydrogen bonds to carbonyl O are more directional than those to ether O. The extent of CO···H−C directionality among the organometallic compounds studied here is therefore of relevance because it may be used to adduce evidence for the shapes of lone pairs on the O atoms of terminal (CO-t) and bridged (CO-b) CO ligands.

In this context, let us examine the CO-t(inter) plot in Figure 2a (top left). The most significant feature here is that data on as many as 4205 hits from 1137 Fe-atom-containing crystal structures are included. The distribution of intermolecular CO···H angles is unexpected. There is a large angular distribution (90−180°) at long O···H separations (>2.60 Å) which narrows as the O···H separation decreases, focussing around 125−135° for the strongest C−H···O hydrogen bonds. This feature is quantified in Figure 2b which is a plot of the percentage (probability) of hits in the range 125−135° *versus* the H···O distance. Note that 25% of the hits have CO···H angles in this range when the H···O distance is around 2.30 Å whereas this percentage falls to around 16% at a distance of 2.80 Å. Is this result significant and does Figure 2b really confirm that the CO···H approach is angular? This question may be studied further by using the approach of Kroon et al., who have shown that for purely geometrical reasons, hydrogen bond angles, θ, which tend to linearity cover smaller solid angles than do bent angles.[24b] Actually, Kroon et al. discussed O−H···O angles but the argument is just as valid for CO···H angles, ϕ. Figure 2c is a histogram of observed CO···H angles. The populations in each 10 deg range of ϕ were then normalized for the above geometrical bias by division by sin ϕ, and the corrected histogram is shown in Figure 2d. *Significantly, the maximum population for ϕ occurs around 140−160° and not around 180°*, though the preference for such a bent approach is only just discernible. This is in contrast to the results of Kroon et al. and also of Taylor and Kennard (who applied a similar geometrical correction on C−H···O angles),[10d] who found that the "observed" maximum for θ at around 150° became, in effect, a true maximum at 180° (showing incidentally the linearity of the O−H···O and C−H···O approaches). All our results and especially Figure 2d reveal a tendency for a bent CO···H approach. However, the analysis as is the nature of the interaction we are studying is delicate. This effect is somewhat less pronounced for CO-b(inter) as is seen in Figure 2a (bottom left). The situation with the other metals is similar. It is significant that the CO-t cases display an O-atom directionality suggestive of a ketonic >C=O group because in a naive valence bond picture, this should be true only for the bridging CO group where there are presumably two lone pairs on the **O** atom available to accept H bonds at around 120°. According to such a depiction there should be a potential for the formation of only one hydrogen bond in a terminal CO group, that is toward the single lone pair along the M−C≡O vector (CO···H angle ~180°). So, while the observed directionality of the CO-b(inter) bonds may be thus rationalized, that of the CO-t(inter) bonds (which seems to be more reliably determined in this study than the CO-b directionality) is unexpected and warrants further study.

(v) Hard and Soft Hydrogen Bonds. A further issue merits discussion. This study has shown that CO ligands of both terminal and bridging varieties form a profusion of C−H···O hydrogen bonds. However, we have noted earlier[1] that CO ligands do not seem to act as efficient hydrogen bond acceptors

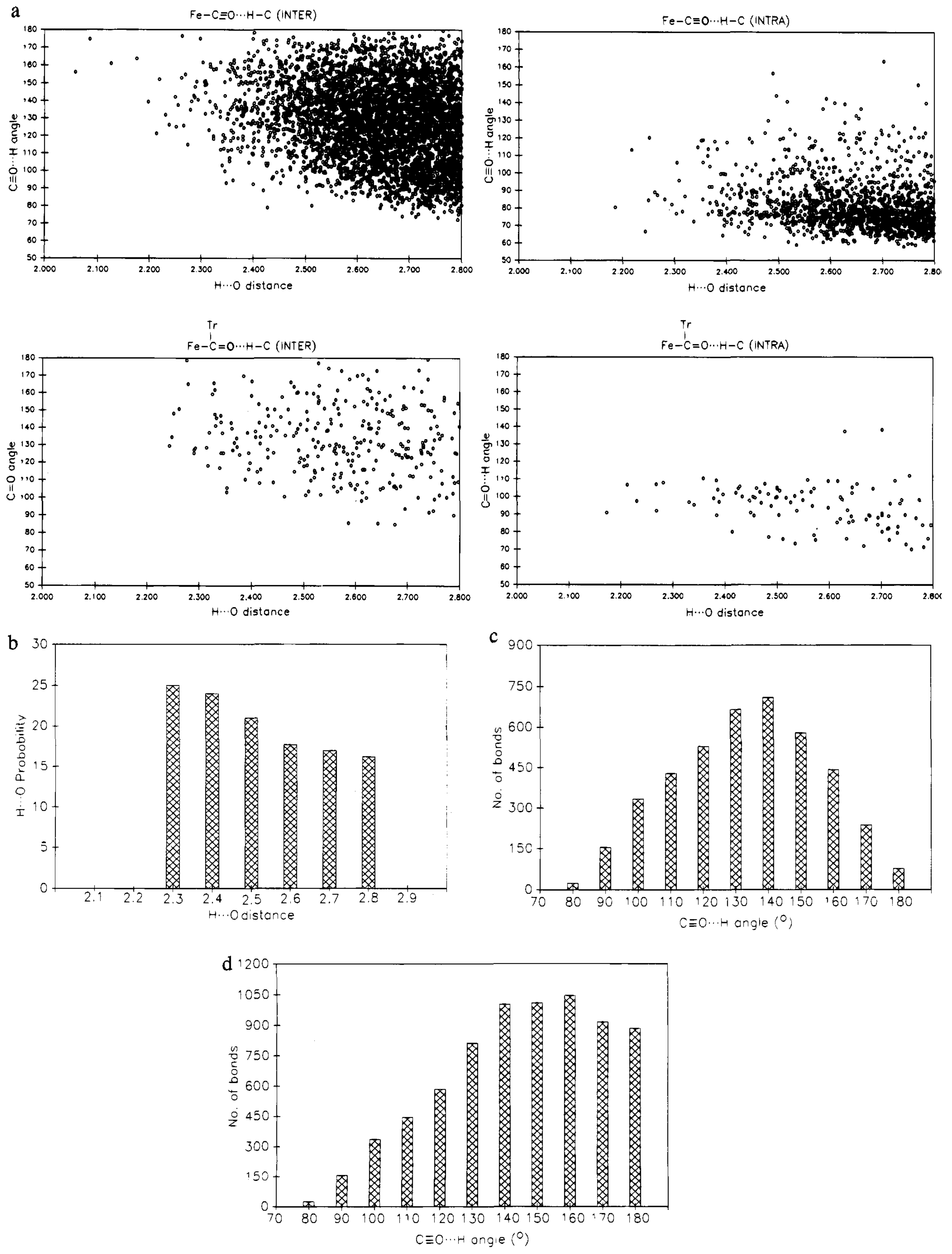
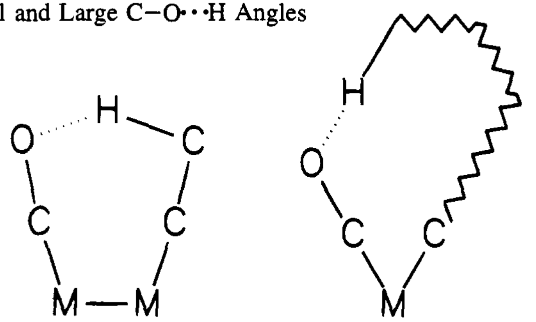
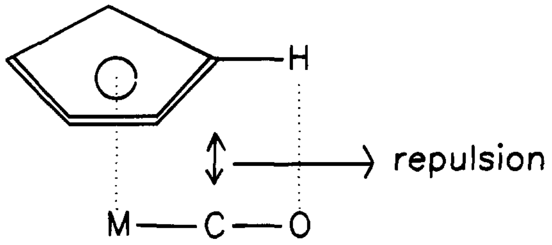


Figure 2. (a). Plots of CO$\cdots$H angle *versus* H$\cdots$O distance for intra- and intermolecular C—H$\cdots$O hydrogen bonds in Fe carbonyl complexes. (b) Populations of CO$\cdots$H angles (expressed as probabilities) in the 125–135° range as a function of H$\cdots$O distances for Fe CO-t(inter). Notice that the probability decreases smoothly from 25% to 15% as the H$\cdots$O distance increases. (c) Histogram of CO$\cdots$H angles, ϕ for Fe CO-t(inter). (d) Histogram of CO$\cdots$H angles, ϕ for Fe CO-t(inter) with the populations corrected by a factor of sin ϕ.

Scheme 2. Intramolecular C−H···O Bonding, Showing Small and Large C−O···H Angles



Scheme 3



in strong hydrogen bonding situations. The reason for this observation could lie in the hardness and softness of these interactions. Concepts of hardness and softness can be profitably extended from molecular to supramolecular chemistry and one might consider O−H···O and N−H···O as hard hydrogen bonds and C−H···O, O−H···C, and C−H···C[18b] as soft hydrogen bonds with perhaps N−H···N being a borderline case. Accordingly, it might be argued that the soft acceptor CO prefers to hydrogen bond with the soft donor C−H or alternatively the hard donor O−H prefers to form bifurcated or solvated hydrogen bonds with hard acceptors rather than waste itself on the soft acceptor CO. As in molecular chemistry, hardness and strength need not always be correlated. A recent study of C−H···Se hydrogen bonding shows that this interaction can affect molecular structure and conformation significantly.[26] We suggest that the unexpected formation of such a hydrogen bond may be understood in terms of the relative softness of both donor and acceptor species. However, as in molecular chemistry, the relevance of the HSAB principle (hard *versus* soft) to intermolecular interactions can be justified not from numerical data (which would reveal differences between strong *versus* weak bonding situations) but from unusual and unexplained observations, and we believe that the formation of C−H···O bonds by the CO ligand in preference to O−H···O and N−H···O bonds is one such occurrence.

Discussion of Selected Examples

Selected examples will now be described. Useful structural information is listed in Table 2, including chemical formulae, REFCODES, and references to the original structural papers.[27−32] Only those C−H···O hydrogen bonds which appear explicitly in Figures 3a−7b are mentioned in Table 2. The selection of crystal structures was based on simplicity and typicality. The examples chosen do not therefore necessarily correspond to the average geometrical situations discussed in the statistical analysis above.

***cis*- and *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$, CPFECO10 and CYPFEC01.** We begin with the cis and trans isomers of the above dinuclear complex (CPFECO10 and CYPFEC01, respectively). These two complexes are of interest because they carry two terminal and two symmetrically bridging CO ligands each. The C−H···O hydrogen bonding patterns are shown in Figures 3a and 3b for the crystals of cis and trans complexes, respectively. The results of a neutron diffraction study at 74 K are also available for the trans isomer (CYPFEC03). A comparison of the room and low temperature structures (with the X-ray determined H-atom positions being normalized) allows one to see the effect of temperature on the hydrogen bonding interactions.

Figure 3a clearly shows that both CO-t and CO-b are involved in the C−H···O network. The strongest interaction involves selectively O1 and H8 bound to the Cp atom C10 (H···O 2.34 Å; C−H···O 157.9°) between two molecules related by the inversion center. These two molecules form dimers which show some resemblance to O−H···O dimers in carboxylic acids and C−H···O dimers in α,β-unsaturated carbonyl compounds. A secondary CO-t interaction is established by O4 with H3 of the second Cp ring on the molecule (H···O 2.36 Å) whereas the second CO-b is involved in a somewhat looser interaction with the same Cp ring. This is an important difference between the packing environments around the two Cp rings and accounts clearly for the different librational and reorientational motion shown by the two ligands in the solid state. This dynamic process has been studied by ^{13}C CPMAS NMR, ^{1}H spin−lattice relaxation time measurements, packing potential energy barrier calculations, and thermal motion analysis.[6]

The situation is different in the crystal of the trans isomer, the hydrogen pattern of which is given in Figure 3b. At both room temperature and 74 K only the CO-b ligands are involved in somewhat loose interactions (O···H 2.53 2.42 Å and C−H···O 131.5° and 124.8° at room temperature at 74 K, respectively). Because of the site symmetry (the molecule is located on a crystallographic center of inversion placed midway along the Fe−Fe bond) both Cp ligands have crystallographically identical surroundings and experience the same type of interactions. Each molecule interacts with four other surrounding molecules *via* identical CO-b···H(Cp) interactions. The shortest H···O interaction involving the terminal CO is above our threshold of interest (2.81 Å) at room temperature but shortens significantly on going down to 74 K (2.65 Å).

$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$, CMCPFE10. Figure 4 shows the bifurcated-acceptor interaction established by the bridging CO in crystalline CMCPFE10. Because of the crystallographic and molecular symmetry, the unique bridging CO is at equal interaction distance from both Cp ligands of a neighbouring molecule along the *c*-axis (H···O 2.48 Å, C−H···O 123.6°) and in such a way the crystal can be pictorially described as being formed by chains of molecules linked *via* C−H···O interactions. This is a common motif in crystals of "pure" organics and is found with both strong and weak hydrogen bonds. For example, very similar bifurcated-acceptor C−H···O hydrogen bonds may be observed in the crystal structure of 2,5-dibenzylidenecyclopentenone[33] while the N−H···O topological equivalent may, of course, be identified in the crystal structure

---

[26] Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 4463.

[27] Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* **1970**, 3068.

[28] (a) Bryan, R. F.; Greene, P. T. *J. Chem. Soc. A.* **1970**, 3064. (b) Mitschler, A.; Rees, B.; Lehmann, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 3390.

[29] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1427.

[30] Adams, R. D.; Collins, D. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

[31] Marchino, M. L. N.; Sappa, E.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1984**, 1541.

[32] Teller, R. G.; Wilson, R. D.; McMullan, R. K.; Koetzle, T. F.; Bau, R. *J. Am. Chem. Soc.* **1978**, *100*, 3073.

[33] Desiraju, G. R.; Bernstein, J.; Kishan, K. V. R.; Sarma, J. A. R. P. *Tetrahedron Lett.* **1989**, *30*, 3029.

Table 2. Some Features of C−H···OC Hydrogen Bonds in Selected Organometallic Crystals

REFCODE	ref	space group, Z	type	D−H···A	D···A	H···A	D−H···A
CPFECO10	27	$P2_1/c$, 4	CO-t	C(4)−H(3)···O(4)	3.24	2.36	137.7
			CO-b	C(6)−H(5)···O(2)	3.48	2.53	145.7
			CO-b	C(10)−H(8)···O(1)	3.36	2.34	157.9
CYPFEC01	28a	$P2_1/c$, 2	CO-b	C(5)−H(5)···(O2b)	3.34	2.53	131.5
CYPFECO (74 K)	28b	$P2_1/c$, 2	CO-b	C(6)−H(4)···(O2)	3.16	2.42	124.8
CMCPFE10	29	$Pnma$, 4	CO-b	C(5)−H(5)···O(3)	3.21	2.48	123.6
CPCOCR	30	$P2_1/c$, 2	CO-t	C(2)−H(1)···O(3)	3.55	2.50	164.0
			CO-t	C(6)−H(5)···O(2)	3.40	2.49	141.7
COBGEF	31	$P\bar{1}$, 2	CO-t	C(12)−H(7)···O(4)	3.60	2.55	162.0
			CO-b	C(15)−H(10)···O(1)	3.49	2.46	158.9
			CO-b	C(20)−H(15)···O(1)	3.47	2.41	166.6
HMPCIC01 neutron	32	$P2_1/c$,4	INTRACO-b	C(10)−H(4)···O(6)	3.45	2.52	150.1
			INTRACO-b	C(13)−H(13)···O(5)	3.26	2.51	126.2
			CO-b	C(18)−H(28)···O(5)	3.57	2.56	158.3
			CO-t	C(10)−H(3)···O(9)	3.40	2.54	140.1
			CO-t	C(11)−H(7)···O(8)	3.32	2.48	135.8
			CO-t	C(13)−H(11)···O(2)	3.12	2.59	109.2

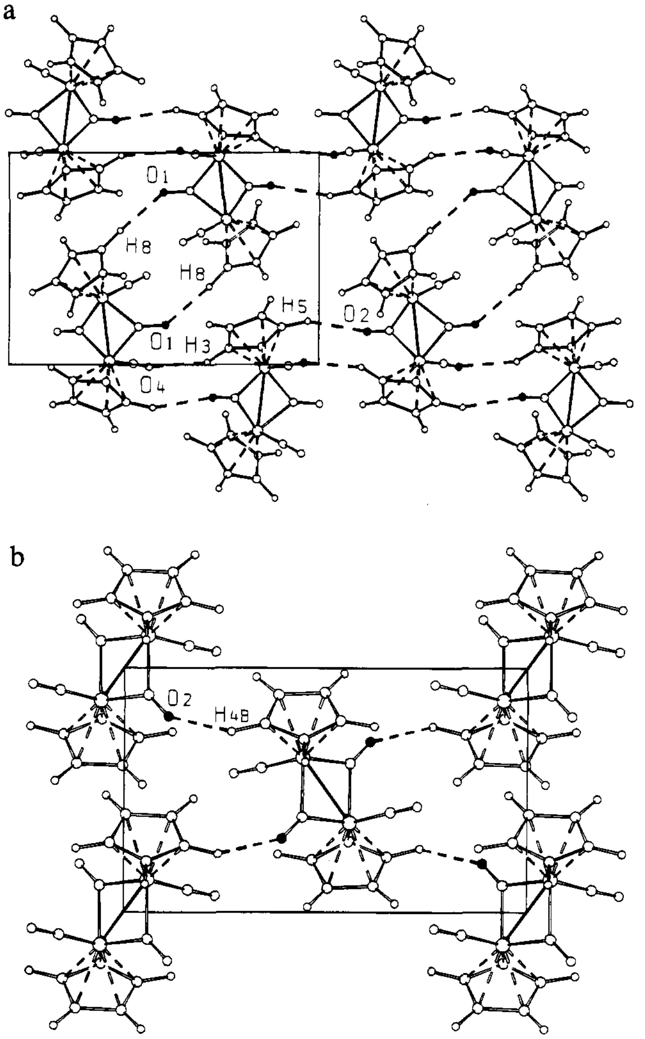


Figure 3. Hydrogen bonding networks in the cis (a) and trans isomer (b) of the dinuclear complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$, CPFECO10 and CYPFEC03, showing that both CO-t and CO-b are involved in the C−H···O network. Note how the two Cp rings in (a) are involved in a different number of interactions. The letter labels indicate symmetry-related atoms as obtained from the CSD files.

of urea.[34] As in the case of CYPFEC, the shortest distance involving the terminal CO is much longer (2.88 Å) than it is for CO-b, even though the latter forms a bifurcated interaction.

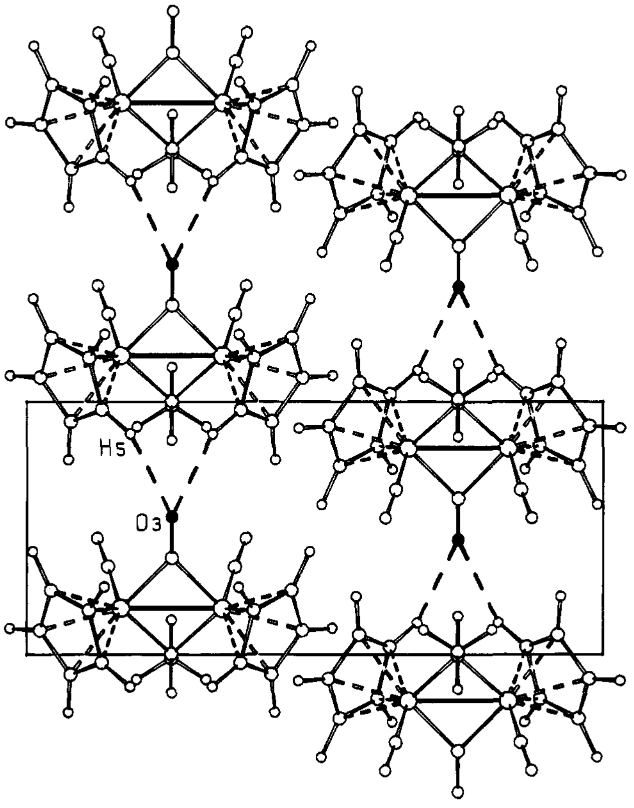


Figure 4. The bifurcated interaction established by the bridging CO in $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$, CMCPFE10.

$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$, CPCOCR. This complex possesses only terminal CO ligands. Intermolecular C−H···O interactions are clearly detectable and are shown in Figure 5. The network is based on centrosymmetric dimers linked by pairs of C−H···O interactions. A second type of interaction is also present linking dimers in an extended network. Such extended dimer structures are known in strong hydrogen bond networks, and a general conclusion of this study is that the basic packing motifs (rings and chains) adopted by strong hydrogen bonds are also established by these weaker interactions.

$(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(\mu_3\text{-}CO)(CO)_5(\mu_4\text{-}\eta^3$-Methylbutenyl-1-1′-ylidine), COBGEF. The triply bridging CO ligand in crystalline COBGEF participates in a bifurcated hydrogen bonding interaction with H atoms belonging to the Cp ligands of a neighboring molecule related by a crystallographic center of inversion (see Figure 6). Both interactions are quite short (H···O 2.46 and 2.41 Å) and linear (158.9 and 166.6°).

---

[34] Mak, C. W. M.; Zhou, G.-D. *Crystallography in Modern Chemistry*; Wiley: New York, 1992; pp 175−181.

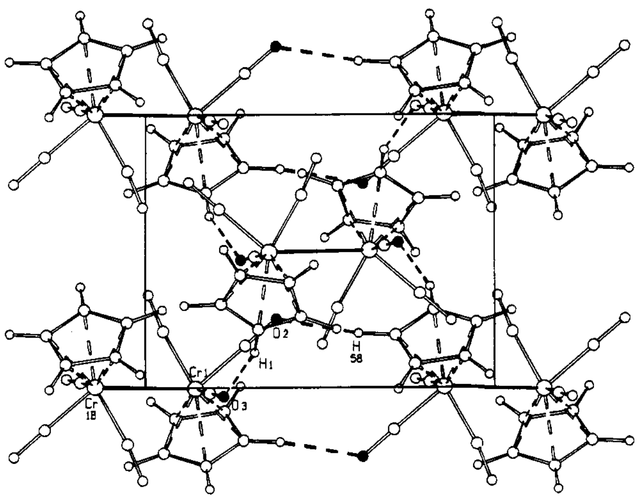


Figure 5. Intermolecular C−H···O interactions in crystalline (η^5-C_5H_5)$_2$$Cr_2(CO)_6$, CPCOCR. The network is based on centrosymmetric "dimers" linked by pairs of C−H···O interactions.

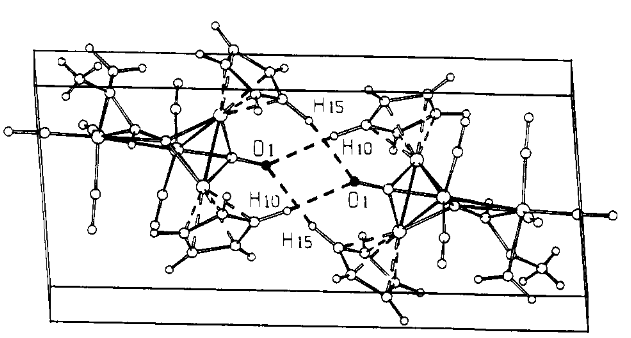


Figure 6. The triply bridging CO ligand in crystalline (η^5-C_5H_5)$_2$$Ni_2Fe_2(\mu_3\text{-}CO)(CO)_5(\mu_4\text{-}\eta^3$-methylbutenyl-1-1′-ylidine), COBGEF, links the Cp ligands of neighboring molecules related by a crystallographic center of inversion.

Although the terminal ligands are also involved in C−H···O interactions (Table 2), the triply bridging CO is sufficiently effective to form the strongest interactions despite their bifurcated nature.

(μ_3-H)$FeCo_3(CO)_9(P(OMe)_3)_3$, HMPCIC01. We discuss now the crystal structure of HMPCIC01 which has been determined by neutron diffraction at 90 K.[32] The C−H···O bond network in this crystal is of interest because it contains all four of the bond types we have been discussing in this paper so far, namely CO-t(inter), CO-b(inter), CO-t(intra), and CO-b(intra), and also because all the C−H···O hydrogen bonds involve only methoxyl H atoms. Of the nine CO ligands in the molecule, only one is not C−H···O hydrogen bonded. The individual molecule ORTEP is given in Figure 7a and the packing diagram in Figure 7b, which essentially shows only the intermolecular contacts. All three terminal CO ligands on Fe are intermolecularly C−H···O bonded. The ligands on Co are weakly hydrogen bonded; one of them forms an intramolecular bond (H···O 2.69 Å), another is intermolecularly bonded (2.71 Å), while the third is the free C−H group. As for the bridging CO ligands, while all three form intramolecular hydrogen bonds, two of them are additionally involved in intermolecular bonds (Table 2). Because neutron data are available for the C−H···O hydrogen bonds in this structure and in particular because we know the anisotropic displacement parameters (ADP) accurately (see the ORTEP diagram), additional information on the bonding nature of C−H···O interactions can be extracted. This was done with a modification of the method of Steiner, who showed in a recent study of C−H···O bonded alkyne C≡C−H groups that while the ADPs of the terminal alkyne C atom are generally larger than those of the internal alkyne C-atom, the *ratio* of these parameters decreases with decreasing C···O distance.[13k] This is presumably the case because the terminal atom is more constrained by the hydrogen bonding. In any event, we assumed that the stronger the C−H···O bonding, the less would be the thermal vibration of atoms in the vicinity of the bond. In particular, we concentrated on the U_{eq} values for the C and O atoms of the ligand (unlike Steiner, who examined the U_{eq} values in the donor moiety). Our results, however, are equally satisfying and are given in Table 3 and Figure 8.

Table 3 gives the values of the $U_{eq}(O)/U_{eq}(C)$ ratio (U ratio) for the nine CO ligands in the molecule while Figure 8 is a plot of these ratios versus the 14 H···O distances formed by 8 of these ligands. The plot and the table show that there is a separation between CO-t and CO-b. The CO-b ratios are lower, in the range 1.42−1.53, while the CO-t ratios are higher, in the range 1.59−1.78. This means that there is lower relative motion of O with respect to C for CO-b as compared to CO-t as might be expected since CO-t protrude more from the surface and have a larger soft bending motion. More interestingly, for the non-bifurcated-acceptor CO-t bonds, there is a very good correlation between the U ratio and the H···O distance with the non-hydrogen bonded ligand (U ratio 1.81) also following the same trend. This demonstrates clearly that as the C−H···O bond gets stronger, the O atom is able to vibrate less. The bifurcated-acceptor CO-t bonds are shifted to longer H···O distances as would be expected, and yet convincingly, the O atoms are still relatively immobile. All the CO-b bonds are of the bifurcated-acceptor variety (intra- and intermolecular), and they follow a trend similar to the bifurcated CO-t case. This exercise, which becomes highly reliable with neutron data, shows that an analysis of ADPs is effective in assessing the bonding character of a C−H···O interaction.[35] In this respect, subtle differences between CO-t and CO-b bonds and between bifurcated and non-bifurcated bonds are revealed. Significantly, these shades of difference are apparent even for C−H···O hydrogen bonds formed by C(sp^3) H atoms. It is tempting to think that one need not be restricted to highly acidic H atoms as in the study of Steiner.

Conclusions

Hydrogen bonding interactions in organometallic systems are now beginning to be investigated in a systematic manner. In comparison to the thoroughly explored organic solids, organometallic solids appear to offer an even greater variability of intermolecular interactions. This is essentially attributable to the supramolecular nature of most (even the simplest) organometallic molecules. After all, an organometallic complex is describable as a supermolecule formed by organic or inorganic molecules in an extraordinary variety of combinations around one or more metal centers. The resulting structural and chemical variability is well-known.

In this paper we have explored the effect of intramolecular and intermolecular C−H···O hydrogen bonds on the crystal structures of compounds containing metal-coordinated CO ligands. To this end, we have used the large amount of structural information available in the Cambridge Structural Database. The results of our survey can be summarized as follows:

(i) Metal-coordinated CO ligands take part in the formation

---

[35] This exercise was repeated with ADP values fom the X-ray structure (134 K) published in: Huie, B. T.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 3059. However, the correlation failed and this could indicate that neutron data are a prerequisite for this sort of subtle analysis.

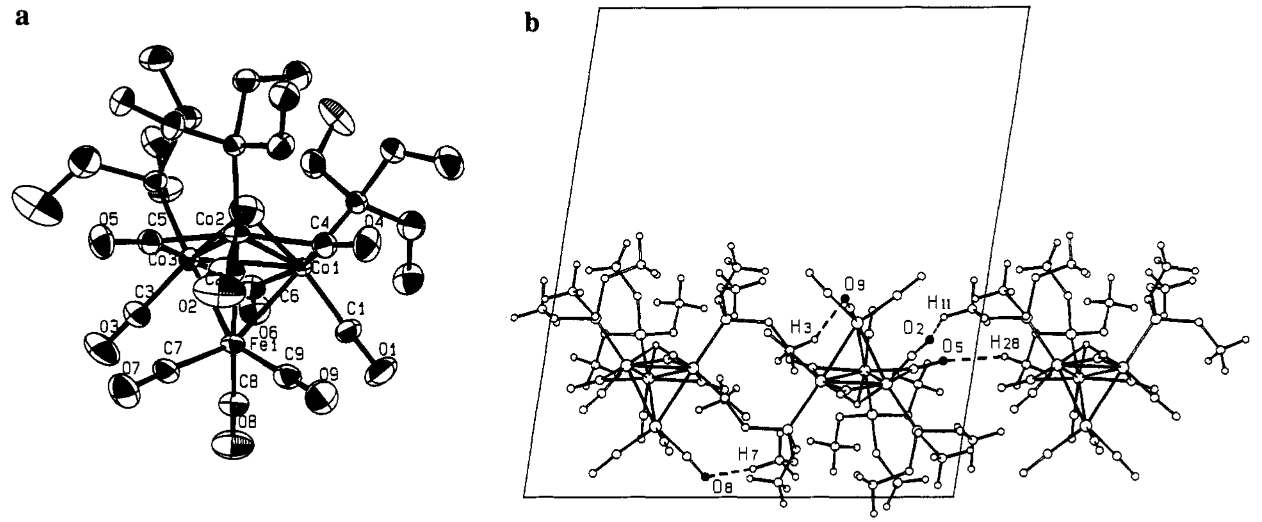


Figure 7. (a) ORTEP drawing of the neutron determined crystal structure of $(\mu_3\text{-H})FeCo_3(CO)_9(P(OMe)_3)_3$, HMPCIC01. The $P(OMe)_3$ ligands are unlabeled and the H atoms are not shown. (b) The intermolecular hydrogen bonding network in crystalline $(\mu_3\text{-H})FeCo_3(CO)_9(P(OMe)_3)_3$, HMPCIC01.

Table 3. $U_{eq}(O)/U_{eq}(C)$ and H···O Distances for C-H···O Hydrogen Bonds in the Crystal Structure of $\mu_3\text{-HFeCo}_3(CO)_9(P(OMe)_3)_3$, HMPCIC01

	H···O (Å)	$U_{eq}(O)/U_{eq}(C)$
CO-t (INTER)		
C(3)−O(3)···H(14)	2.71	1.78
C(7)−O(7)···H(14)	2.69	1.59
C(7)−O(7)···H(16)	2.72	1.59
C(7)−O(7)···H(23)	2.66	1.59
C(8)−O(8)···H(7)	2.48	1.59
C(9)−O(9)···H(3)	2.54	1.63
CO-b (INTER)		
C(5)−O(5)···H(14)	2.66	1.44
C(5)−O(5)···H(28)	2.56	1.44
C(6)−O(6)···H(2)	2.70	1.42
C(6)−O(6)···H(6)	2.64	1.42
CO-t (INTRA)		
C(1)−O(1)···H(2)	2.69	1.62
CO-b (INTRA)		
C(4)−O(4)···H(6)	2.68	1.53
C(5)−O(5)···H(13)	2.51	1.44
C(6)−O(6)···H(4)	2.52	1.42

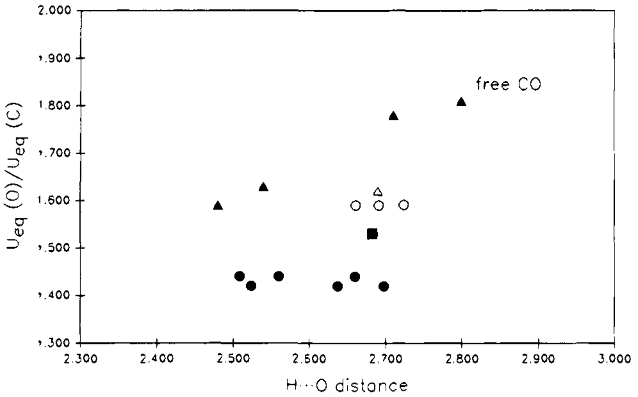


Figure 8. Plot of $U_{eq}(O)/U_{eq}(C)$, or U ratio, *versus* H···O distance for the C−H···O hydrogen bonds in crystalline $(\mu_3\text{-H})FeCo_3(CO)_9(P(OMe)_3)_3$, HMPCIC01: (▲) CO-t (inter) non-bifurcated, (△) CO-t(intra), (○) CO-t single acceptor trifurcated to three CH groups, (■) CO-b(intra), (●) CO-b(inter and intra) bifurcated.

of clearly recognizable hydrogen bonding interactions with H atoms bound to the carbon atoms of the ligands.

(ii) Bridging COs establish preferential interactions with respect to the terminal bonding mode and these H bonds are shorter and more linear. Both bridging and terminal COs seem to favor C−H···O bond formation with CO···H angles around 140° suggesting similar lone pair directionality in the two cases.

(iii) Bifurcated aceptors are quite common as would be expected in such donor-rich systems, but rather unexpectedly this phenomenon is found for both terminal and bridging bonding modes.

(iv) Triply bridging COs also form C−H···O hydrogen bonds.

(v) The effects of different metal atoms or of the nuclearity of the complex on C−H···O hydrogen bonding is not detectable.

(vi) The effectiveness of these C−H···O hydrogen bonds in the crystal structure is also reflected in a reduction of the thermal motion of the atoms involved in the bond.

(vii) The C−H···O hydrogen bond is an example of a soft intermolecular interaction.

It has been clearly demonstrated in the case of organic molecules that the presence of a large number of C−H···O contacts in crystals containing suitable atomic groupings can only be explained *via* attractive interactions between the donor and acceptor atoms exactly as in the case of conventional or strong hydrogen bonds. This holds also for complexes containing CO ligands. C−H···OC interactions afford an additional stabilization to the crystal cohesion of organometallic molecules. The H atoms bound to C atoms preferentially establish short contacts, that is intermolecular links, with the O atoms rather than with other C atoms or H atoms in the structure.

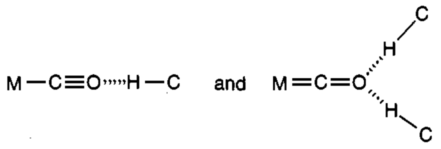
The Lewis basicity of CO is not well understood although there are a number of examples of compounds in which the CO ligand can act as a base toward a Lewis acid or a proton acid. The CO basicity will determine the effectiveness and directionality of hydrogen bonding (electrophilic attack) and depends on the degree of electron delocalization onto the CO ligand and follows the order face-bridging > edge-bridging > terminal. It should also be recalled that, end-on or isocarbonyl complexes contain CO ligands bound simultaneously through the C and O atoms. The formation of these complexes depends on the acceptor strength and on the steric bulk of the Lewis acid.

A second large category of complexes in which metal-bound CO ligands act as Lewis bases is that of the transition metal carbonylates in which the interaction is between a mononuclear or polynuclear carbonyl anion and a strong Lewis acid such as solvated or complexed alkali metal ions or main groups I, II, and III.[36] Most of these complexes show that the $M-CO\cdots M^{n+}$

---

[36] Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

interaction is not linear but angular, with angles at about 140°. Such an angularity has been taken as indicative of the presence of a directional electrostatic potential dependant on the relative contributions of the two extreme valence bond structures depicted below:



The angularity of C−H···OC hydrogen bonding interactions discussed in the present study is in keeping with this general behavior. This is suggestive of a dominance of the double bond form (sp^2 hybridization at the O atom) over the triple bond (sp hybridization).

Acknowledgment. Financial support from MURST (D.B., F.G.) , DST (G.R.D.), UGC (K.B.), and CSIR (V.R.P.) is acknowledged.

Supplementary Material Available: Sample CSD (Version 5.05) questions, bibliographic references to individual compounds in this study, and scatterplots of C−H···O hydrogen bonds in crystalline Mn, Fe, Co, and Ni complexes (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA942399V