NJC
Letter

π-Bonded organometallic building blocks for supramolecular chemistry†

Reinaldo Atencio, Lee Brammer,* Shiyue Fang and F. Christopher Pigge

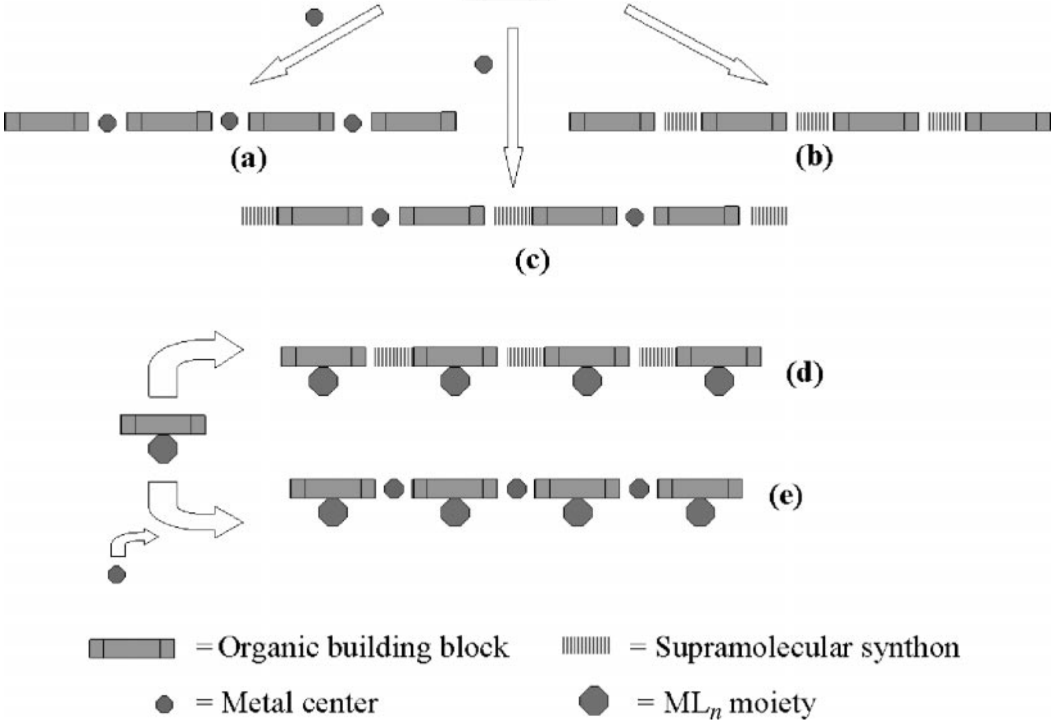
Department of Chemistry, University of Missouri-St.Louis, 8001 Natural Bridge Road, St. Louis, MO 63121-4499, USA. E-mail: lee.brammer@umsl.edu

Received 24th December 1998, Accepted 10th March 1999

Metal–arene complexes with suitable substituents on the π-bound arene represent a new class of organometallic building blocks for use in supramolecular chemistry. They provide a conceptually versatile avenue for construction of discrete assemblies and extended arrays, as is illustrated by the examples presented in which assembly occurs *via* hydrogen-bonded connections between carboxyl substituents.

Harmonizing in a supramolecular network the functionality of organic compounds with the versatility of transition metals is a current challenge in the field of supramolecular chemistry and crystal engineering.[1] In addition to the possibility of introducing electrochemical, magnetic, or optical properties, the presence of metal atoms can contribute structural elements (*e.g.*, various co-ordination geometries) to the supramolecular assembly that may facilitate the design of functional materials.[2] The fruitful combination of organic and metal components is nicely illustrated by the class of materials known as co-ordination polymers, in which the metal co-ordination environment is propagated into an infinite 1D, 2D or 3D framework by using a multitopic organic ligand [see Scheme 1(a) for a linear 1D example].[3] Recently, reports describing a strategy of combining hydrogen-bonded supramolecular assemblies common in organic systems [Scheme 1(b)] with the orienting ability of well-known metal co-ordination geometries to construct molecular arrays [Scheme 1(c)] have appeared.[4] The two general cases illustrated in Scheme 1(a) and 1(c) involve a metal center acting as an "*active*" component (combined with an organic connector) in the construction of the assembly.

Here we describe a strategy applicable, in principle, to the construction of either infinite or finite supramolecular assemblies that uses a new class of organometallic building block. The approach is based on the modification of arene-containing organic building blocks, of the types represented in Scheme 1(a)–(c), by their π-co-ordination to a metal–ligand



Scheme 1 Schematic representation of supramolecular assembly involving (a) multitopic organic compounds linked *via* co-ordinative bonds to (transition) metals, (b) organic compounds linked by hydrogen bonding (or other intermolecular bonding *synthon*), (c) an approach combining features of (a) and (b), (d) a new approach combining metal–ligand π-bonding with intermolecular bonding supramolecular synthons of (a) (illustrated in the present work using hydrogen bonding), and (e) a proposed new approach combining metal–ligand π-bonding with the co-ordinative bonded linkages of (b).

---

† *Supplementary material available*: synthesis of **1** and molecular structures and packing diagrams of **1** and **2**·^{n}Bu$_2$O. For direct electronic access see http://www.rsc.org/suppdata/nj/1999/461/, otherwise available from BLDSC (No. SUP 57514, 9 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).

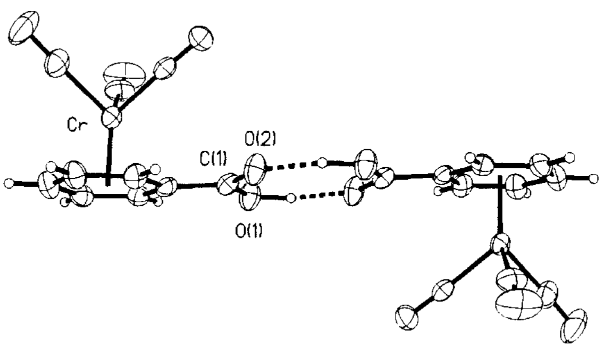


Fig. 1 Dimeric arrangement of molecules in the crystal structure of **1** (shown with 50% probability ellipsoids). Selected intramolecular distances (Å): carboxyl C1–O1 1.289(4), C1–O2 1.245(4).

molecular fragment (ML_n). The resulting organometallic complexes should, in principle, preserve the fundamental capacity for supramolecular assembly derived from the original organic component. In this sense the metal fragment can play a more "*passive*" role in the assembly process, while still serving a vital role in establishing the properties of the final material.[5] One may envisage the π-bound ML_n moiety as a potentially functional metal-containing appendage to an otherwise organic assembly.

A convenient route to many new networks or to discrete molecular arrays based upon such organometallic building blocks is envisaged. Assembly could occur *via* hydrogen bonds [Scheme 1(d)], co-ordination bonds [Scheme 1(e)] or other supramolecular *synthons*,[6] depending on the choice of π-co-ordinated organic ligand. Although there has been recent attention focused on the area of organometallic crystal engineering,[7] the overall design strategy proposed above has not previously been fully articulated in the literature.[8] The feasibility of this approach is illustrated here with organometallic derivatives of benzenecarboxylic acids assembled *via* hydrogen bonds.

It is well established that polycarboxylic acids can form extended architectures sustained by hydrogen-bonded carboxylic acid dimers.[9] Benzene-1,3,5-tricarboxylic acid (trimesic acid, TMA), for instance, forms honeycomb networks using all three acid residues or extended zigzag hydrogen-bonded ribbons using the acid groups in the 1,3-positions.[10] Here the crystal structures‡ of the complexes $[Cr(\eta^6\text{-}C_6H_5CO_2H)(CO)_3]$ **1** and $[Cr\{\eta^6\text{-}C_6H_3(CO_2H)_3\}(CO)_3]\cdot{}^nBu_2O$, **2**·$^nBu_2O$ are reported. The latter forms an extended organometallic supramolecular arrangement sustained by hydrogen-bonded carboxylic acid dimer motifs, whereas **1** utilizes the same *synthon* to form discrete dimeric species.

Compound **1** was prepared§ using a literature procedure.[11] The dimeric units in the crystal structure exhibit a coplanar arrangement of the arene rings and the hydrogen-bonded carboxyl groups (Fig. 1). The $Cr(CO)_3$ moieties adopt an *anti* configuration. The importance of this structure from a crystal engineering standpoint is that it represents the simplest case for which the strategy can be tested (*i.e.* one carboxyl group on the arene and no other substituents). Thus, **1** may be seen as a zero-dimensional network model that allows examination of the supramolecular parameters of a potential family of $[\{(\eta^6\text{-}C_6H_{6-x})(CO_2H)_x\}ML_n]$ building blocks. In this regard it should be noted that the carboxylic acid dimer is also formed in the crystal structure of benzoic acid,[12] and shows a very similar geometry [intermolecular O···O distance 2.627(1) at 295 K *vs.* 2.617(3) Å in **1** at 208 K]. The dimeric unit in **1** is further propagated in three dimensions *via* stacking between arene groups and through multiple C–H···O hydrogen bonds (see SUP 57514).

Complex **2** was obtained§ by direct reaction between $Cr(CO)_6$ and TMA in THF–$^nBu_2O$. The crystal structure of **2**·$^nBu_2O$ contains two independent formula units. The organometallic components form extended zigzag ribbons connected *via* hydrogen bonding between the carboxyl groups in the 1- and 3-positions [O132···O253 2.607(9), O133···O252 2.625(9), O153···O232 2.624(10), O152···O233 2.619(9) Å]. The third carboxyl group anchors a dibutyl ether molecule through an O–H···OBu_2 hydrogen bond [Fig. 2; O172···O105 2.692(11), O272···O205 2.580(11) Å for the two independent acid–ether pairs]. Such a ribbon, while common in isophthalic acid and its derivatives,[13] is less common for TMA,[14] and has not previously been observed in an organometallic π-arene system.[15] At first, it may seem surprising that the honeycomb network of the parent TMA was not observed for **2**. However, it should be recognized that such an arrangement has only been observed either for

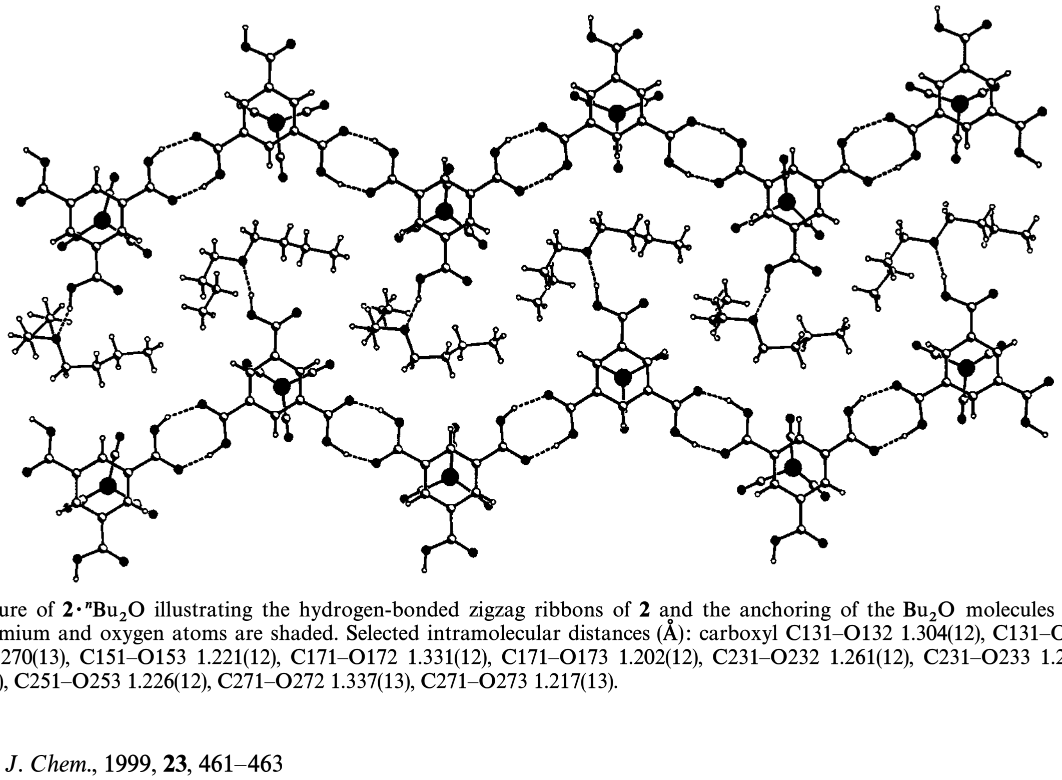


Fig. 2 Structure of **2**·$^nBu_2O$ illustrating the hydrogen-bonded zigzag ribbons of **2** and the anchoring of the Bu_2O molecules in the solvent channel. Chromium and oxygen atoms are shaded. Selected intramolecular distances (Å): carboxyl C131–O132 1.304(12), C131–O133 1.220(12), C151–O152 1.270(13), C151–O153 1.221(12), C171–O172 1.331(12), C171–O173 1.202(12), C231–O232 1.261(12), C231–O233 1.268(12), C251–O252 1.292(13), C251–O253 1.226(12), C271–O272 1.337(13), C271–O273 1.217(13).

unsolvated TMA, which adopts a concatenated structure to fill the voids in the hydrogen bonded rings, or for structures in which typically long-chain solvents thread short channels of stacked TMA honeycomb sheets.[10]

As in **1**, the hydrogen-bonded carboxyl groups and arene rings are mutually co-planar. However, in **2**·^{n}Bu$_2$O adjacent Cr(CO)$_3$ moieties adopt a *syn* disposition,[15a] indicating the absence of steric impediment to such an arrangement. The tethered ether molecules form well-ordered solvent channels between the ribbons of **2**. The stacking arrangement of adjacent ribbons, and formation of carbonyl-containing bilayers into which the ether molecules are partially intercalated, is illustrated in SUP 57514.

A strategy for supramolecular assembly using a new class of organometallic building blocks has been described. This approach elaborates upon existing approaches that use arene-containing units connected *via* intermolecular interactions (*e.g.* hydrogen bonds) or *via* co-ordinative bonds to metals. The elaboration is in the form of π-co-ordination of the arenes to an ML$_n$ moiety. Illustrative examples are presented.

Currently the formation of both finite and extended organometallic networks based upon substituted arenes combined with a variety of π-bound ML$_n$ moieties is being explored.

Acknowledgements

Support from University of Missouri-St.Louis Research Initiative Award, "Inorganic Crystal Engineering" (L.B.), from the Instituto Venezolano de Investigaciones Científicas and CONICIT (R.A.), and NSF grant CHE-9309690 (Siemens SMART diffractometer) is gratefully acknowledged. We thank Professor A. G. Orpen (Bristol) for helpful comments.

Notes and references

‡ Crystal structure analyses: **1**: $M = 258.15$, triclinic, $P\bar{1}$, $a = 7.0349(3)$, $b = 7.2332(3)$, $c = 11.1518(5)$ Å, $\alpha = 88.710(1)$, $\beta = 81.733(1)$, $\gamma = 63.012(1)°$, $U = 499.82(4)$ Å^3, $Z = 2$, $D_c = 1.716$ Mg m^{-3}, $\mu = 1.145$ mm^{-1}, $T = 208(5)$ K, $R_1(F) = 0.0449$, $wR_2(F^2) = 0.0981$, $S(F^2) = 1.032$ for 1868 $F^2 > 2\sigma(F^2)$. **2**: $M = 476.39$, triclinic, $P\bar{1}$, $a = 11.6029(3)$, $b = 13.0537(2)$, $c = 15.2638(2)$ Å, $\alpha = 87.472(1)$, $\beta = 75.734(1)$, $\gamma = 86.752(1)°$, $U = 2235.89(7)$ Å^3, $Z = 4$, $D_c = 1.416$ Mg m^{-3}, $\mu = 0.564$ mm^{-1}, $T = 173(5)$ K, $R_1(F) = 0.110$, $wR_2(F^2) = 0.267$, $S(F^2) = 1.33$ for 3651 $F^2 > 2\sigma(F^2)$. CCDC reference number 440/106. See http://www.rsc.org/suppdata/nj/1999/461/ for crystallographic files in cif format.

§ Syntheses: complex **1** [Cr(η^6-C$_6$H$_5$CO$_2$H)(CO)$_3$] was prepared by saponification of the corresponding η^6-methylbenzoate complex using a slight modification of a literature procedure[11] (see SUP 57514), and isolated as an orange crystalline solid that contained crystals suitable for X-ray diffraction. ^{1}H NMR (500.1 MHz, DMSO-d$_6$–CDCl$_3$, 298 K): δ 5.22 (t, 6.5 Hz, 2H), 5.48 (t, 6.3 Hz, 1H), 6.05 (d, 6.5 Hz, 2H). ^{13}C NMR (125.7 MHz, DMSO-d$_6$–CDCl$_3$, 298 K): δ 89.95, 91.11, 94.79, 95.11, 167.03, 231.20. IR (KBr, cm^{-1}): ν(C≡O) 1964s, 1894vs; ν(C=O) 1682m. Complex **2** [Cr{η^6-C$_6$H$_3$(CO$_2$H)$_3$}(CO)$_3$]. A heterogeneous mixture of TMA (720 mg 3.4 mmol) and Cr(CO)$_6$ (1500 mg 6.8 mmol) in deoxygenated THF (20 mL) and ^{n}Bu$_2$O (100 mL) was refluxed for 24 h under N$_2$. The mixture was filtered to remove unreacted and oxidized chromium compounds, and the yellow liquid was left at −20 °C overnight. After further filtration and concentration of the solution, orange crystals of **2**·^{n}Bu$_2$O were obtained by slow crystallization over several weeks at −20 °C. Following crystallographic characterization, crystals from the same batch were dissolved for spectroscopic characterization.^{1}H NMR (500.1 MHz, DMSO-d$_6$, 298 K): δ 0.82 (t, 12.3 Hz, CH$_3$), 1.29 (m, CH$_2$), 1.45 (m, CH$_2$), 3.32 (t, 10.8 Hz, OCH$_2$), 5.69 (s, CH), 6.88 (s, CO$_2$H). ^{13}C NMR (125.7 MHz, DMSO-d$_6$, 298 K): δ 13.8 (CH$_3$), 19.0 (CH$_2$), 31.4 (CH$_2$), 69.7 (OCH$_2$), 95.4 (CH), 133.6 (*C*–CO$_2$H), 166.0 (C–*C*O$_2$H), 213.3 (Cr–*C*O). IR (KBr, cm^{-1}): ν(C≡O) 1973s, 1906vs; ν(C=O) 1709m.

1 (*a*) I. G. Dance, in *Perspectives in Supramolecular Chemistry: The Crystal as a Supramolecular Entity*, ed. G. R. Desiraju, Wiley, Chichester, 1996, vol. 2, ch. 5; (*b*) A. D. Burrows, C.-W. Chan, M. M. Chowdry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, **24**, 329; (*c*) D. Braga and F. Grepioni, *Chem. Commun.*, 1996, 571; (*d*) J. C. Mareque Rivas and L. Brammer, *Coord. Chem. Rev.*, 1999, **183**, in the press.

2 (*a*) J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinhein, 1995; (*b*) C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289; (*c*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417.

3 (*a*) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architectures*, ACS, Washington, DC, 1992; (*b*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*c*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.* 1995, **117**, 4562; (*d*) P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779.

4 (*a*) C. B Aakeröy and A. M. Beatty, *Chem. Commun.*, 1998, 1067; (*b*) C. B Aakeröy, A. M. Beatty and D. S. Leinen, *J. Am. Chem. Soc.*, 1998, **120**, 7383; (*c*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801; (*d*) J. C. Mareque Rivas and L. Brammer, *New J. Chem.*, 1998, **22**, 1315.

5 From the structural point of view, the π-co-ordinated metal–ligand fragment is obviously important in defining the final solid-state structure (the tertiary structure), but should not necessarily modify the secondary structure (*e.g.* ribbon or sheet arrangement), which may still be defined exclusively by the π-bound organic component.

6 (*a*) The term *supramolecular synthon*[6b] is hereafter contracted to *synthon*; (*b*) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.

7 (*a*) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375, and refs. therein; (*b*) D. Braga, F. Grepioni and G. R. Desiraju, *J. Organomet. Chem.*, 1997, **548**, 33; (*c*) D. Braga and F. Grepioni, *J. Chem. Soc., Dalton Trans.* 1999, 1, and refs. therein.

8 (*a*) It should be noted that assemblies consistent with this design strategy can be seen in a few previously reported structures of 1,1′- and 1,2-substituted metallocenes with substituents capable of hydrogen bonding,[8b,c] and that similarities between hydrogen-bonded organic compounds and π-bound organometallic analogues have been noted in a few cases as a consequence of crystallographic database studies,[8d] most pertinent being for *p*-^{t}BuC$_6$H$_4$CO$_2$H–[Cr(η^6-*p*-^{t}BuC$_6$H$_4$CO$_2$H)(CO)$_3$] and for C$_2$H$_2$(CO$_2$H)$_2$–[Fe{η^2-C$_2$H$_2$(CO$_2$H)$_2$}(CO)$_4$]; (*b*) F. Takusagawa and T. F. Koetzle, *Acta Crystallogr., Sect. B*, 1979, **35**, 2888; (*c*) M. Scherer, J. L. Sessler, M. Moini, A. Gebauer and V. Lynch, *Chem. Eur. J.*, 1998, **4**, 152; (*d*) D. Braga, F. Grepioni, P. Sabatino and G. R. Desiraju, *Organometallics*, 1994, **13**, 3532.

9 L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1976, **32**, 775.

10 F. H. Herbstein, in *Comprehensive Supramolecular Chemistry*, eds. D. D. MacNicol, F. Toda and R. Bishop, Elsevier, Oxford, 1996, vol. 6, ch. 3.

11 B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551.

12 R. Feld, M. S. Lehman, K. W. Muir and J. C. Speakman, *Z. Kristallogr.*, 1981, **157**, 215.

13 (*a*) R. Alcala and S. Martinez-Carrera, *Acta Crystallogr., Sect. B*, 1972, **28**, 1671; (*b*) J. L. Derissen, *Acta Crystallogr., Sect. B*, 1974, **30**, 2764; (*c*) S. Valiyaveetil, V. Enkelmann and K. Müllen, *J. Chem. Soc., Chem. Commun.*, 1994, 2097.

14 (*a*) F. H. Herbstein and R. E. Marsh, *Acta Crystallogr., Sect. B*, 1977, **33**, 2358; (*b*) S. V. Kolotuchin, E. E. Fenlon, S. R. Wilson, C. J. Loweth and S. C. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2654.

15 (*a*) A similar ribbon is observed in one polymorph of [Fe(η^2-fumaric acid)(CO)$_4$],[8d] but with an *anti* arrangement of Fe(CO)$_4$ moieties; (*b*) A chain with a different hydrogen bonding pattern is also seen for [Fe(η^2-maleic acid)(CO)$_4$].[8d]

Letter 9/01925A