

-Short communication

**X-RAY STRUCTURE OF HEXAMETHYL BENZENEHEXACARBOXYLATE,
[C₆(COOCH₃)₆]**

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ABSTRACT

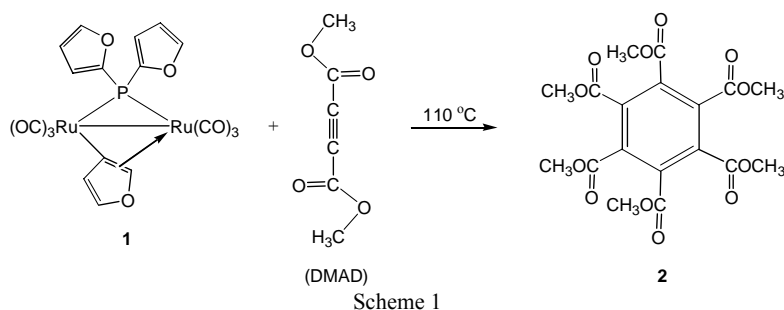
The thermal treatment of [Ru₂(CO)₆(μ-η¹,η²-C₄H₃O){μ-P(C₄H₃O)₂}] **1** with dimethyl acetylenedicarboxylate (DMAD) at 110 °C leads to cyclotrimerization of DMAD. The cyclotrimerization product hexamethyl benzenehexacarboxylate, [C₆(COOCH₃)₆] **2**, was obtained in 37% yield and characterized by a combination of spectroscopic data and single crystal X-ray diffraction study. Compound **2** crystallizes in the monoclinic space group *P1bar* with *a* = 10.3002(12), *b* = 11.0371(13), *c* = 18.781(2) Å, *α* = 76.148(2), *β* = 87.390(2), *γ* = 74.001(2)°, *Z* = 4 and *V* = 1992.2(4) Å³.

Key words: Cyclotrimerization, Dimethyl acetylenedicarboxylate, X-ray structure

The synthesis and catalytic behavior of phosphido-bridged di- and poly-nuclear complexes continued to be the subject of immense interest (Carty *et al.* 1999, Patel *et al.* 1984, Harley *et al.* 1983). The flexibility of μ-PR₂ (R = alkyl or aryl) groups despite of their strong binding with metal clusters makes them useful in catalysis. Such intriguing features of μ-PR₂ ligands support to maintain the integrity of metal cluster framework while facilitate metal-metal bond cleavage and reformation during catalytic transformation. The phosphido bridge dinuclear complexes of iron triad [M₂(CO)₆(μ-PR₂)(μ-C≡CR)] (M = iron triad; R = alkyl or aryl) have been widely investigated and found that they are capable to effect head-to-head or head-to-tail coupling of alkynyl ligands leading to polymetallic multisite-bound polycarbon materials such as [Ru₂(CO)₆(μ-PPh₂)(μ-η¹,η²-CH(C₆H₄)C(Ph)=CC≡CBu¹)] and [Ru₂(CO)₆(μ-PPh₂)(μ-η¹,η²-C=C(Ph)C=C(Ph) (C₆H₄)≡CH)] (Carty *et al.* 1983, Delgado *et al.* 1998, Chi *et al.* 1996, Davies *et al.* 1997, Blenkiron *et al.* 1996). A couple of years ago, Wong *et al.* (2001) reported the phosphido-bridged diruthenium complex [Ru₂(CO)₆(μ-η¹,η²-C₄H₃O){μ-P(C₄H₃O)₂}] **1** in which the dissociated furyl group is bonded to the Ru₂ unit in a μ-η¹,η²-coordination mode. Recently, the authors demonstrated the reactivity of **1** with various two electron donor ligands as well as the activated alkyne, dimethyl acetylenedicarboxylate (DMAD) and mentioned that the latter leads to cyclotrimerization (Begum *et al.* 2008). There the authors identified the product of this cyclotrimerization reaction by comparing the NMR data of the product with that reported by Thomas and Darkwa (1998) for [C₆(COOCH₃)₆].

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Recently hexafunctionalized benzenes are applied for various purposes. For example they have been used as a core molecule of benzene-based dendrimers (Hecht and Fréchet 1999). The cyclotrimerization of alkynes to form highly substituted benzenes continues to attract much attention and has been thoroughly investigated with group 9 transition metals to form aromatic compounds (Lautens *et al.* 1996, Frühauf 1997). Couple of years ago Uozumi and Nakazono (2002) performed cyclotrimerization of DMAD in water at 100°C using polystyrene-poly(ethyleneglycol)-supported rhodium-phosphine complexes as catalyst which give 57% of hexamethylbenzenehexacarboxylate. Recently, authors reported that $[\text{Ru}_2(\text{CO})_6(\mu-\eta^1, \eta^2\text{-C}_4\text{H}_3\text{O})\{\mu\text{-P}(\text{C}_4\text{H}_3\text{O})_2\}]$ **1** catalyzes the cyclotrimerization of DMAD in refluxing toluene (Begum *et al.* 2008). After 6 h of heating the cyclotrimerization product $[\text{C}_6(\text{COOCH}_3)_6]$ **2** was obtained in 25% yield. Authors now observe that the yield of the product increases with time and they get 37% yield after 10 h. Prolonged heating further increases the yield as well as decomposition of the catalyst which is one of the major problems in homogeneous catalysis.

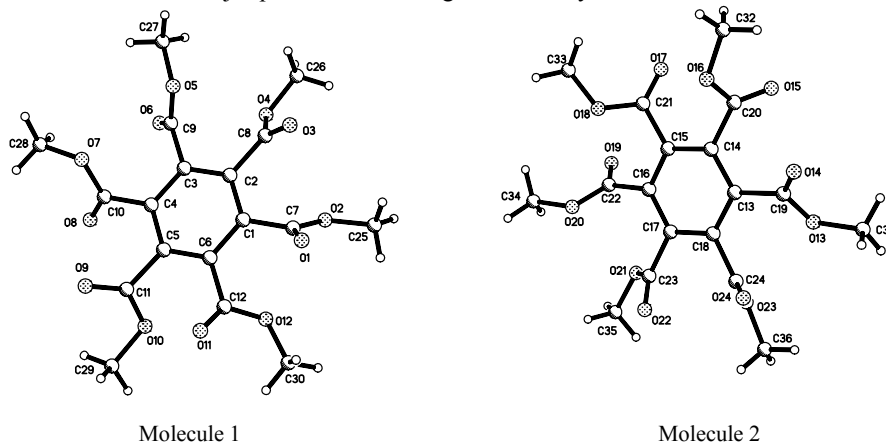


Fig. 1. A perspective drawing of the solid-state molecular structure of the two molecules of $[\text{C}_6(\text{COOCH}_3)_6]$ **2** showing the atom labeling scheme used; selected bond lengths (Å) and angles (°) for molecule 1: C(1)—C(2) 1.392(3), C(1)—C(6) 1.407(3), C(2)—C(3) 1.393(3), C(3)—C(4) 1.393(3), C(4)—C(5) 1.397(3), C(5)—C(6) 1.400(3), C(1)—C(7) 1.506(3), C(7)—O(1) 1.198(3), C(7)—O(2) 1.330(3), C(25)—O(2) 1.448(3), C(2)—C(1)—C(6) 120.0(2), C(6)—C(1)—C(7) 119.3(2), C(1)—C(7)—O(1) 123.4(2), C(1)—C(7)—O(2) 110.8(2), C(7)—O(2)—C(25) 115.2(2).

Compound **2** was previously characterized by analytical and spectroscopic data (Begum *et al.* 2008). Recently authors performed a single crystal X-ray diffraction study of **2** [Crystal data and data collection and refinement details for **2**: C₁₈H₁₈O₁₂, fw = 426.32, triclinic, *P*1bar, *a* = 10.3002(12) Å, *b* = 11.0371(13) Å, *c* = 18.781(2) Å, α = 76.148(2)°, β = 87.390(2)°, γ = 74.001(2)°, *V* = 1992.2(4), *Z* = 4, *D*_{calc.} = 1.421, λ (Mo K α) = 0.71073 Å, *T* = 150(2) K, reflections collected = 17452, independent reflections = 9179 [*R*(int) = 0.0377], θ range = 2.03–28.29, Final *R* indices [*I* > 2 σ (*I*)] = (*R*₁ = 0.0621, *wR*₂ = 0.1495), *R* indices (all data) = (*R*₁ = 0.0911, *wR*₂ = 0.1692)]. Compound **2** exists as two independent molecules in the asymmetric unit. The solid-state structures of these two molecules of **2** is shown in Fig. 1; selected bond lengths and angles are given in the figure caption for molecule **1**. The structures of each molecule possess a benzene core with six hydrogens replaced by six COOCH₃ groups. The C–C bond lengths in the central ring fall in the range of 1.392(3) – 1.407(3) Å in molecule 1 and 1.391(3) – 1.403(3) Å in molecule 2, suggesting unperturbed benzenoid character in the ring. The average H₃C–O single bond distance (1.453(3) Å in molecule 1 and 1.451(3) Å in molecule 2) is ~0.13 Å longer than the average O–CO single bond distance (1.325(3) Å in molecule 1 and 1.324(3) Å in molecule 2). This is expected since in the former a *sp*³ hybridized carbon is involved in bonding whereas a *sp*² hybridized carbon is involved in the latter. In both molecules the COOCH₃ chains are randomly oriented thus ruling out the possibility of symmetric structure. All other structural features of both molecules are within the expected range.

Supplementary data: Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 655916 (for compound **2**). Copies of this information can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.ac.uk>).

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