

Four tetrairidium carbonyl clusters linked by six diphosphino ligands: synthesis and X-ray structure of $[\{\text{Ir}_4(\text{CO})_9\}_4(\text{dppmb})_6]$ (dppmb = 1,4-bis(diphenylphosphinomethyl)benzene)

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Supporting Information

Crystal structure determination for $[\{\text{Ir}_4(\text{CO})_9\}_4(\text{dppmb})_6] \cdot x(\text{C}_7\text{H}_8)$

The single crystal X-ray diffraction experiments were carried out using a Bruker SMART APEX2 diffractometer, equipped with an Oxford Cryosystem liquid-N₂ cryostream (600 series) with the generator working at 50 kV and 30 mA. Mo K α radiation from fine focus sealed tubes, 0.5 mm collimated, was used. Crystal data are given in the text. The raw integrated intensities of all datasets were corrected for crystal anisotropies by SADABS¹ and a spherical absorption correction was then applied. Structures were solved using direct methods with SIR97² and refined based on full-matrix least squares on F² with SHELX97 (within the WINGX package³).

For both samples, the number of solvated toluene molecules is tentative and it is based on the consistent appearance of Fourier peaks in residual maps. Analysis of voids suggest that other molecules may possibly be included in these structures, but we were not able to unambiguously locate them. In fact, consideration on the unit cell volumes suggest that species *a* (monoclinic P2/c) might in fact contain more solvent molecules (up to 8-10 per each molecule of **1**) but only two (corresponding to just one symmetry independent) were located from Fourier analysis. On the other hand, it shall be considered that packing of species **1** is particularly inefficient due to the shape of the molecules itself and this explains why some phenyl groups are characterized by very large librational amplitudes. In species *b*, more toluene molecules were located (5 per each molecule of **1**), though some voids is still present (possibly occupied by other, non visible, solvent molecules).

For structure *a*, which diffraction pattern extended to higher diffraction angles, the refinement was carried out assigning anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were modelled on the riding Carbon atoms.

For structure *b*, data were of lower resolution ($2\theta \leq 40^\circ$) due to the much smaller diffraction power, even if collected at low temperature (150 K). Therefore, refinement was less stable and only Ir and P atoms were refined anisotropically. For one of the solvent molecule, the methyl group is very likely disordered over several sites, therefore scarcely visible in Fourier maps. For this reason, it was not included in the refinement.

For both structures, phenyl rings were modeled as rigid groups.

¹ Sheldrick, G. M. *SADABS 2004/1*, University of Göttingen, Germany, **2004**.

² Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giovacazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.*, **1999**, *32*, 115-119.

³ Farrugia, L. J. *J. Appl. Cryst.*, **1999**, *32*, 839.