Supplementary Material (ESI) for Chemical Communications

Supplementary Information for:

Encapsulated Transition Metal Catalysts Comprising Peripheral Zn(II)salen Building Blocks: Template-Controlled Reactivity and Selectivity in Hydroformylation Catalysis

Arjan W. Kleij,[a] Martin Lutz, [b] Anthony L. Spek,[b] Piet W. N. M. van Leeuwen and Joost N.H. Reek[a*]

[a] *Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV, Amsterdam, The Netherlands. Fax: +3120-5256422; Tel: 3120-5256437; E-mail: reek@science.uva.nl*

[b] *Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH, Utrecht, The Netherlands. Fax: +3130-2533940; Tel:3130-2532538*

Contents:

Supplementary Material (ESI) for Chemical Communications

Crystal Structure Determination

X-ray intensities were measured on a Nonius KappaCCD diffractometer with a rotating anode (Mo-Kα, λ = 0.71073 Å) at a temperature of 150 K. The structures were solved with direct methods with the program SHELXS-97[a] and SIR-97[b] and refined with the program SHELXL-97[c] against F^2 of all reflections. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON[d]

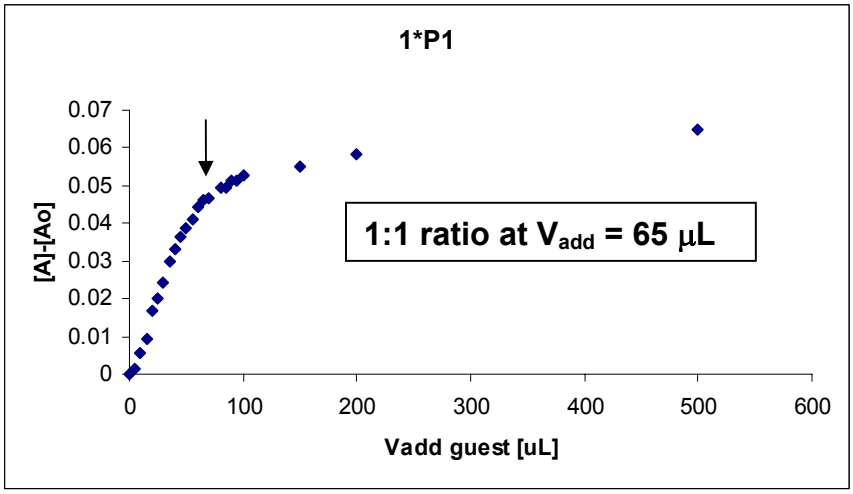
[a]G. M. Sheldrick, SHELXS-97. Program for crystal structure solution, University of Göttingen, Germany, 1997

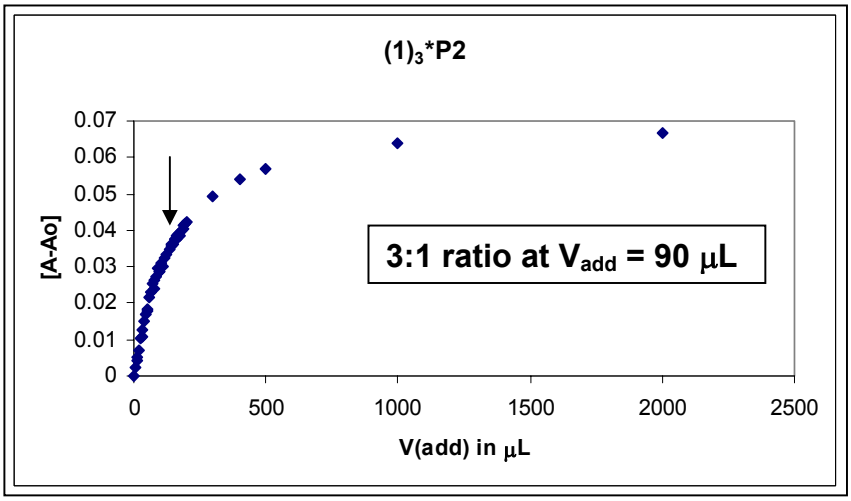
[b]A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115

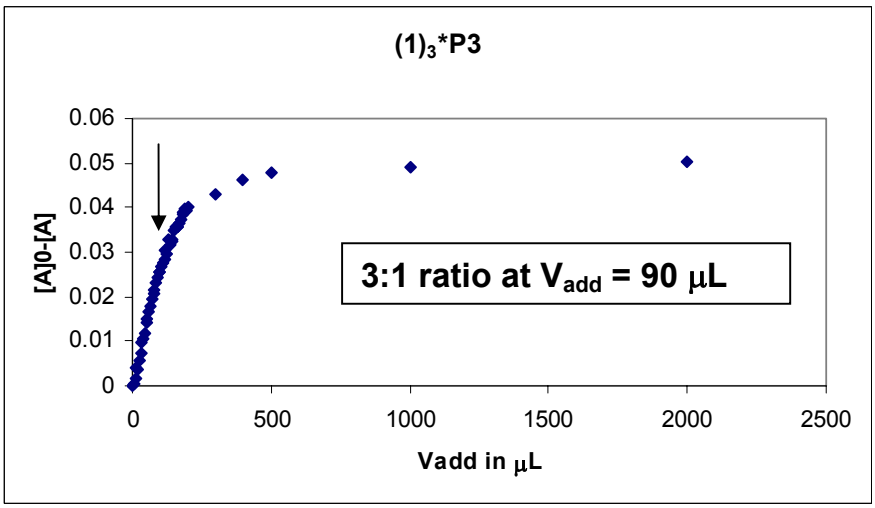
[c]G. M. Sheldrick, SHELXL-97. Program for crystal structure refinement. University of Göttingen, Germany, 1997

[d]A. L. Spek, *J. Appl. Crystallogr*., 2003, **36**, 7

UV-vis Titration curves for assemblies **1•P1**, $(\mathbf{1})_3$•**P2** and $(\mathbf{1})_3$•**P3**.

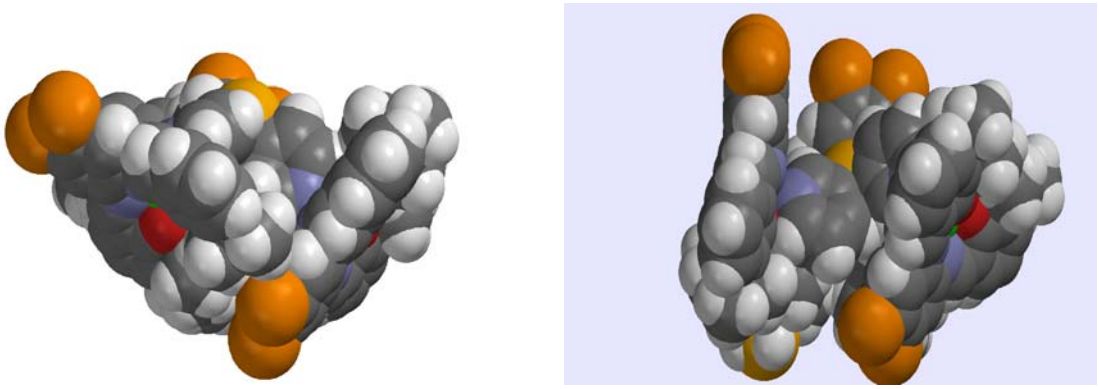






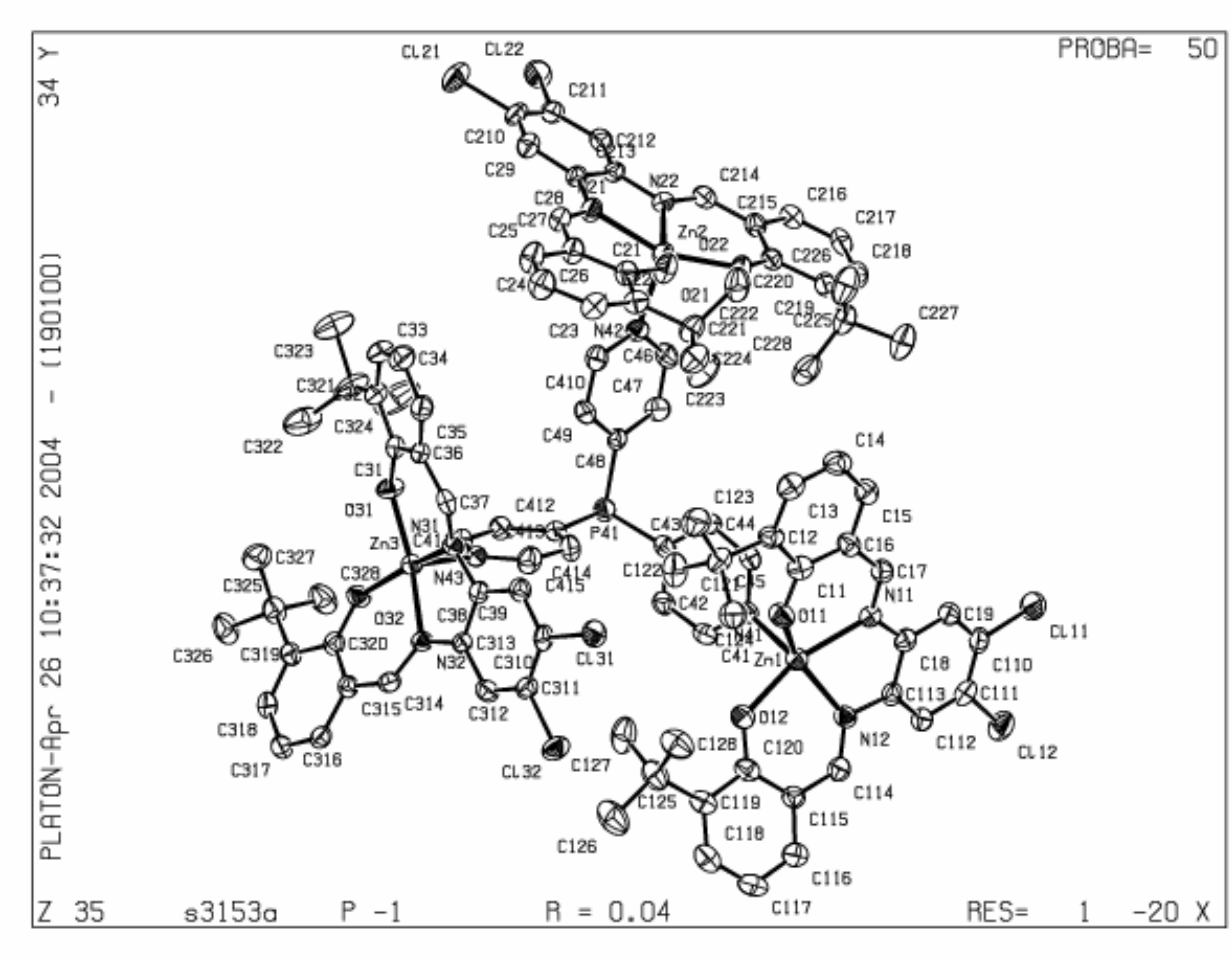
Supplementary Material (ESI) for Chemical Communications

Molecular modeling results (PM3 calculations) for assemblies (**1**)$_3$•**P2** (LEFT) and (**1**)$_3$•**P3** (RIGHT)



(Zn = red, Cl = orange, P = yellow, N = blue, C = dark grey, H = light grey)

Displacement ellipsoid plot for assembly $(\mathbf{1})_3$•**P2** with the adopted numbering scheme.



Selected bond distances (Å) and angles (°): Zn(1)-N(11) = 2.097(3), Zn(1)-N(12) = 2.076(3), Zn(1)-N(41) = 2.138(3), Zn(1)-O(11) = 1.946(3), Zn(1)-O(12) = 1.964(2), Zn(2)-N(21) = 2.085(3), Zn(2)-N(22) = 2.060(3), Zn(1)-N(42) = 2.132(3), Zn(2)-O(21) = 1.953(3), Zn(2)-O(22) = 1.949(2), Zn(3)-N(31) = 2.118(3), Zn(3)-N(32) = 2.069(3), Zn(3)-N(43) = 2.124(3), Zn(3)-O(31) = 1.948(2), Zn(3)-O(32) = 1.975(2), C(43)-P(41)-C(48) = 102.89(16), C(43)-P(41)-C(413) = 98.44(16), C(48)-P(41)-C(413) = 99.40(17).