

Heterobimetallic early–late transition-metal tetrameric metallomacrocycles *via* self assembly

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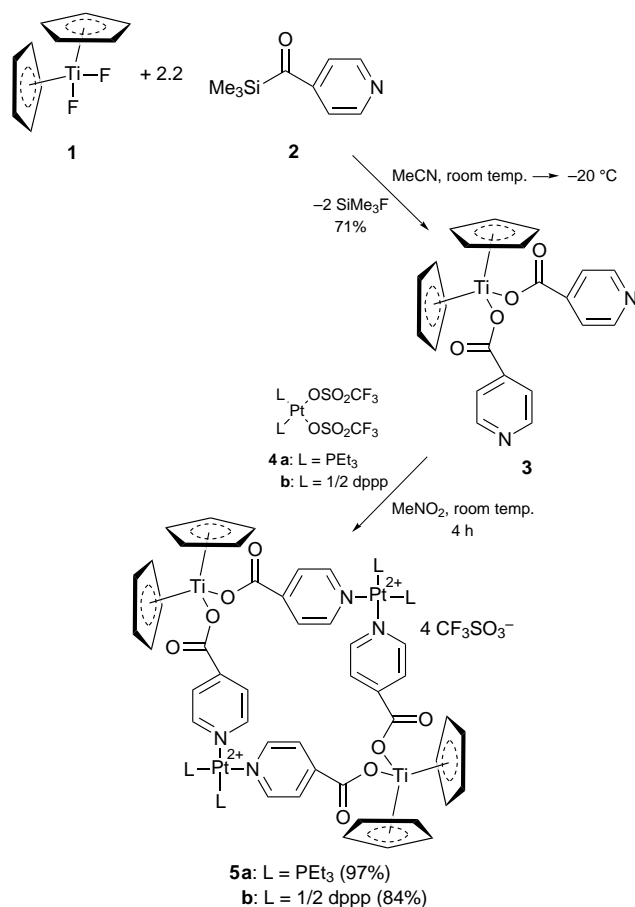
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Interaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})_2]$ with square-planar *cis*- $[\text{Pt}(\text{PR}_3)_2(\text{OSO}_2\text{CF}_3)_2]$ in MeNO_2 gives mixed Ti–Pt tetrameric metallomacrocycles, *via* self assembly, in excellent yields.

Dative metal–ligand coordination is becoming an increasingly important motif in the construction of discrete supramolecular species with well defined shapes and geometries.¹ The self assembly of diverse molecular squares with variable cavities using transition metals and the appropriate bidentate ligands as building blocks are elegant recent examples of the application of the above concept. To date all molecular squares have been constructed with the aid of either late-transition metals, like Pt and Pd,^{2,3} Re,⁴ or early-transition metals such as W and Cr,⁵ or the main group element iodine^{6,7} in its trivalent I^{III} form.⁸ Here, we report the formation *via* modular self assembly of the first examples of early–late transition-metal hybrid Ti–Pt heterobimetallic tetranuclear macrocycles.

Interaction of the known⁹ $\text{Ti}(\eta\text{-C}_5\text{H}_5)_2$ complex **3** with the *cis*-square-planar platinum bistriflate complexes **4**² in MeNO_2

(0.12 M) at room temp. for 5 h afforded the desired novel macrocycles **5** in excellent isolated yields *via* self assembly, as shown in Scheme 1.‡ Work-up proceeded by simply reducing the solvent to *ca.* 2 ml under vacuum and subsequently precipitating and washing the macrocycles with diethyl ether. Macrocycles **5a**, **5b** are stable, orange, microcrystalline solids, characterized by spectroscopic means and, in the case of **5a**, by liquid secondary ion mass spectrometry (LSIMS). All spectral data are consistent with the proposed structures. Particularly characteristic of **5** are the respective single, sharp singlets (with appropriate Pt satellites) in the ³¹P NMR spectrum and the downfield shift of the pyridine hydrogens of **3** upon complexing to Pt in **5**, in particular the α-H shift of *ca.* 0.5 ppm and the β-H of *ca.* 0.3 ppm downfield in **5a** relative to precursor **3**. Most importantly the LSIMS of **5a** shows an $(\text{M} - 2 \text{OSO}_2\text{CF}_3)^{2+}$ signal at $m/z = 1002.6$ whose experimental isotope pattern very closely matches the calculated value (Fig. 1), leaving little doubt about the tetranuclear nature and identity of this interesting metallomacrocyclic. Fig. 2 displays an MM-2 minimized ball-and-stick (a) and space-filling model (b) of **5a**, illustrating the shape and cavity of this unique heterobimetallic metallomacrocyclic with both square-planar Pt and distorted tetrahedral Ti as the shape-defining corner units.



Scheme 1 Synthesis of macrocycle **5**; dppp = 1,3 bis(diphenylphosphino)propane

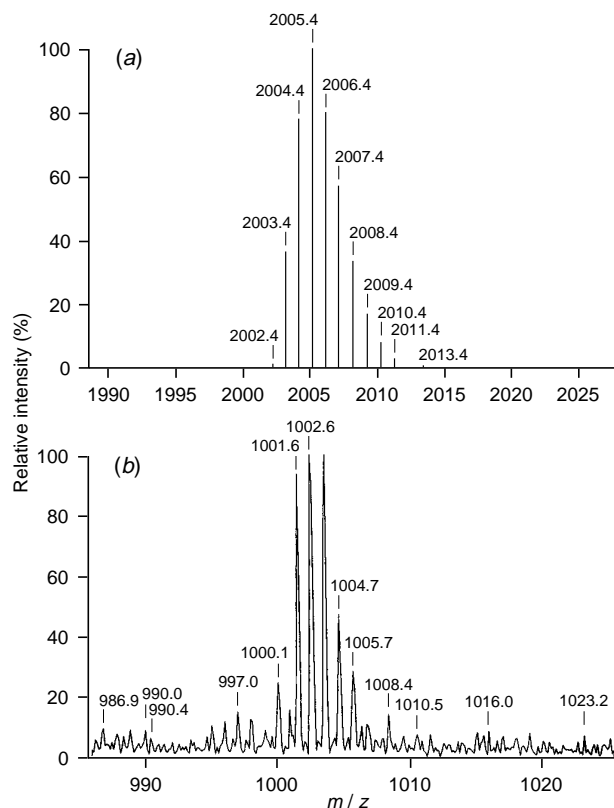


Fig. 1 Selected region of the calculated (a) and experimental (b) LSIMS of macrocycle **5a** showing an $(\text{M} - 2 \text{OSO}_2\text{CF}_3)^{2+}$ signal at m/z 1002.6

In summary, the first example of novel mixed Ti–Pt heterobimetallic tetranuclear metallomacrocycles are reported *via* self assembly from readily available precursors. LSIMS, along with spectral and physical data, are used to unambiguously characterize these new supramolecular species.

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Footnotes

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‡ For ³¹P{¹H} spectra, 85% H₃PO₄ was used as an external reference at δ 0.00, and for ¹⁹F{¹H} spectra CFCl₃ was used as an external reference at δ 0.00. *Selected spectroscopic data:* **3**, ¹H NMR (CDCl₃), δ 8.76 (d, 4 H, *J* 6.0 Hz), 7.80 (d, 4 H, *J* 6.0), 6.65 (s, 10H). ¹³C{¹H} NMR (CDCl₃), δ 170.2 (CO₂), 150.6 (C_α), 140.9 (C_γ), 123.4 (C_β), 119.2 (C₅H₅). **5a**, mp 198–200 °C (decomp.) (**5a**·H₂O Found: C, 36.7; H, 4.4; N, 2.8; S, 5.7. Requires C, 37.0; H, 4.3; N, 2.4; S, 5.5%). IR (CCl₄) ν_{Ar} 3091w, ν_{CH₂} 2972w, ν_{CO₂} 1652s, 1540s, ν_{OTf} 1258s, 1221s, 1145s, 1028s cm⁻¹. ¹H NMR (CD₃NO₂), δ 9.30 (d, 8 H), 8.08 (d, 8 H), 6.68 (s, 20 H), 1.94 (t, 24 H), 1.37 (m, 36 H). ¹³C{¹H} NMR (CD₃NO₂), δ 168.1 (CO₂), 152.6 (C_α), 146.7 (C_γ), 128.7 (C_β), 121.6 (C₅H₅), 16.0 (m, CH₂), 8.3 (CH₃). ³¹P{¹H} NMR (CD₃NO₂), δ 2.8 (*J*_{PtP} 3060 Hz). ¹⁹F{¹H} NMR (CD₃NO₂), δ -76. LSIMS, *m/z* 1002.6 (*M* - 2 OTf)²⁺. **5b**, mp 218–220 °C (decomp.). IR (CCl₄) ν_{Ar} 3106w, ν_{CH₂} 2920w, ν_{CO₂} 1655s, 1543s, ν_{OTf} 1253s, 1224s, 1150s, 1029s cm⁻¹. ¹H NMR (CD₃NO₂), δ 9.07 (8 H), 7.88–7.50 (m, 48 H), 6.59 (s, 20 H), 3.50–3.30 (m, 8 H), 2.65–2.35 (m, 4 H). ¹³C{¹H} NMR (CD₃NO₂), δ 167.8 (CO₂), 152.3 (C_α), 145.3 (C_γ), 134.5 (*o*-C), 134.0 (*p*-C), 130.9 (*m*-C), 127.6 (C_β), 125.9 (*ipso*-C), 122.7 (q, *J*_{CF} 321 Hz, OSO₂CF₃), 121.3 (C₅H₅), 23.0 (m, CH₂P), 18.8 (CH₂). ³¹P NMR (CD₃NO₂), δ -10.8 (*J*_{PtP} 3009 Hz). ¹⁹F{¹H} NMR (CD₃NO₂), δ -76.

References

- Reviews: D. Philip and J. F. Stoddart, *Angew. Chem.*, 1996, **108**, 1242; D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229; J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; P. Ball, *Designing the Molecular World*, Princeton Univ. Press, 1994.
- P. J. Stang and B. Olenyuk, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 732; P. J. Stang, B. Olenyuk, J. Fan and A. M. Arif, *Organometallics*, 1996, **15**, 904; P. J. Stang, D. H. Cao, S. Saito, and A. M. Arif, *J. Am. Chem. Soc.*, 1995, **117**, 6273; P. J. Stang and D. H. Cao, *J. Am. Chem. Soc.*, 1994, **116**, 4981; P. J. Stang and J. A. Whiteford, *Organometallics*, 1994, **13**, 3776.
- M. Fujita, F. Ibukuro, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 4175; M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645.
- R. V. Slone, D. I. Youn, R. M. Calhoun and J. T. Hupp, *J. Am. Chem. Soc.*, 1995, **117**, 11 588.
- P. M. Stricklen, E. J. Volcko and J. G. Verkade, *J. Am. Chem. Soc.*, 1983, **105**, 2494.
- P. J. Stang, K. Chen and A. M. Arif, *J. Am. Chem. Soc.*, 1995, **117**, 8793; P. J. Stang and K. Chen, *J. Am. Chem. Soc.*, 1995, **117**, 1667.
- P. J. Stang and V. V. Zhdankin, *J. Am. Chem. Soc.*, 1993, **115**, 9808.
- Review: P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123.
- S. C. Dixit, R. Sharon and R. N. Kapour, *Inorg. Chem. Acta*, 1989, **158**, 109.

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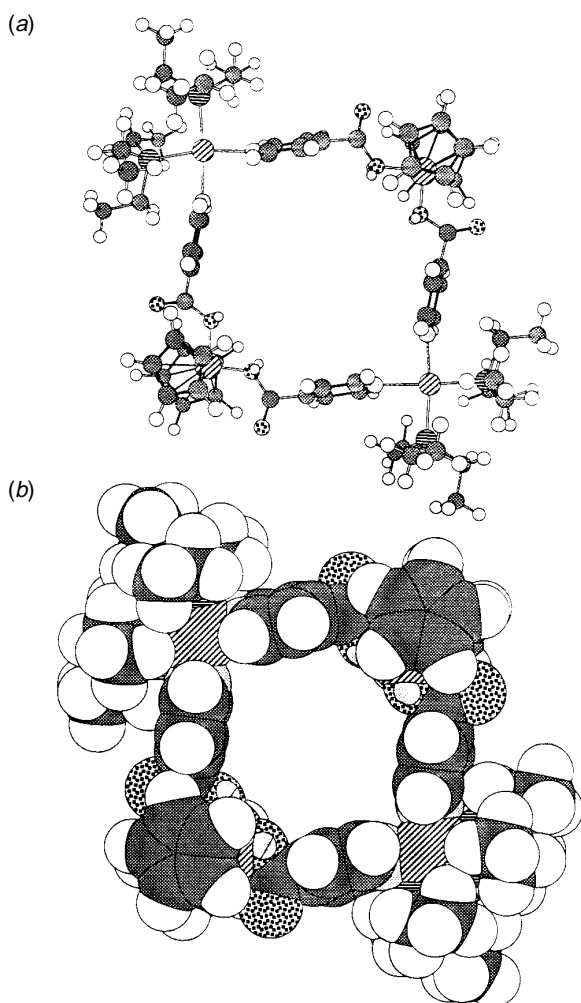


Fig. 2 Chem-3D MM-2 minimized ball-and-stick (a) and space-filling model (b) of **5a**