

A new route to metallacycloalkanes

Katja Dralle, Nastassia L. Jaffa, Tanya le Roex, John R. Moss,* Susan Travis, Nicholas D. Watermeyer and Akella Sivaramakrishna

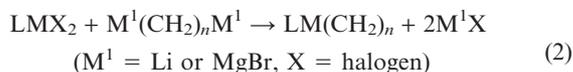
Received (in Cambridge, UK) 6th April 2005, Accepted 26th May 2005

First published as an Advance Article on the web 16th June 2005

DOI: 10.1039/b504747a

Reaction of the bis-alkenyl complex *cis*-[Pt(PPh₃)₂-(CH₂CH₂CH=CH₂)₂] with Grubbs 1st generation catalyst gives, in high yield, the metallacycloalkene *cis*-[Pt(PPh₃)₂(CH₂CH₂CH=CHCH₂CH₂)], which can be hydrogenated to the metallacycloalkane *cis*-[Pt(PPh₃)₂(CH₂)₆].

Metallacycloalkane compounds are well known¹ and many have been prepared by the following two routes:^{2–4}



Metallacycles are of particular importance since they are key intermediates in important catalytic reactions for example metallacyclobutanes in alkene metathesis.⁵

Although small metallacycles (with four- to six-membered rings) can be relatively easily prepared, medium ring compounds with seven to eleven members are difficult to make.¹ It is just these medium ring metallacycles that have been implicated⁶ and recently shown⁷ to occur as intermediates in catalytic trimerisation reactions of ethylene to give 1-hexene. More recently a process for tetramerisation of ethylene has been reported^{8,9} to give 1-octene, which might be expected to occur *via* a metallacyclononane.⁹

Lindner and co-workers made a systematic study of the synthesis of metallacycles by the reaction of Na₂Os(CO)₄ with Y(CH₂)_nY (Y = triflate).² They found that, whereas the 5-, 6- and 7-membered ring compounds (CO)₄Os(CH₂)_n (n = 4–6) could be synthesised, the yields of the 8-, 9-, and 10-membered ring analogs dropped to zero, and di- and trimetallacycles became the favoured and isolated products.²

The use of Grubbs catalysts for constructing medium and large rings in organic chemistry has found wide application and led to the efficient preparation of organic ring compounds that are otherwise very difficult to make.¹⁰

Recently the elegant synthesis of “molecular gyroscopes” was described by Gladysz *et al.* using Grubbs catalysts for ring closing metathesis (RCM) of alkene groups bonded to phosphorus.¹¹

We envisaged that new C–C bonds could be formed from complexes bearing pendant alkene groups, *i.e.* from metal alkenyl compounds containing the functionality M–(CH₂)_mCH=CH₂. Few compounds of this class have been prepared although the compounds (η⁵-C₅R₅)F₃(CO)₂(CH₂)_mCH=CH₂ (R = H or Me

and m = 2,3)¹² and Cp*₂HfH(CH₂)_mCH=CH₂ (m = 4 or 5) have been described.¹³

We now find that reaction of Pt(COD)Cl₂ with the Grignard reagent BrMgCH₂CH₂CH=CH₂, followed by PPh₃ leads to the bis-alkenyl compound *cis*-[Pt(PPh₃)₂(CH₂CH₂CH=CH₂)₂] **1** in good yield (see Scheme 1).

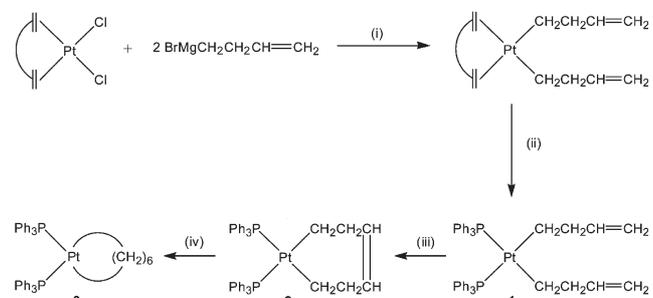
This compound was fully characterised by analytical and spectroscopic methods.† Crystals of **1** suitable for X-ray were grown from CH₂Cl₂–hexane and the structure with two pendant alkene groups was confirmed (see Fig. 1).‡

Reaction of **1** with Grubbs 1st generation catalyst, RuCl₂(PCy₃)₂(=CHPh), (5 mol%) results in ring closing metathesis (RCM) to yield the metallacycloheptene in high yield (see Scheme 1). This reaction can readily be followed by observation of the disappearance of the =CH₂ signal of **1** in the ¹H NMR spectrum and the appearance of a new =CH signal. Thus it is seen that the RCM is about 90% complete in the first 15 minutes. The organometallic product of this reaction, **2**, was isolated as colourless crystals in high yield and its composition was determined by analytical and spectroscopic methods.† Confirmation that the RCM had taken place to yield a metallacycloheptene was obtained from the X-ray crystal structure of **2** (see Fig. 2).‡

This structure appears to be the first example of a structurally characterised metallacycloheptene. The ring shows a twist-boat conformation.

Reaction of **2** with hydrogen in the presence of Pd/C (10%) results in saturation of the C=C double bond to yield the metallacycloheptane, **3**, in quantitative yield. This complex has been reported previously by Whitesides and co-workers, who prepared it using the dilithium route, but isolated it in only 3% yield.

The methodology described here can also be applied to metallacycles of larger size. Thus we have spectroscopic evidence



Scheme 1 (i) Et₂O, –78 °C; (ii) PPh₃; (iii) Grubbs catalyst generation 1, CH₂Cl₂, reflux 1 h; (iv) Pd/C, H₂, MeOH–CH₂Cl₂.

Department of Chemistry, University of Cape Town, Rondebosch, 7701, South Africa. E-mail: jrm@science.uct.ac.za; Fax: +27 21 689-7499; Tel: +27 21 650-2535

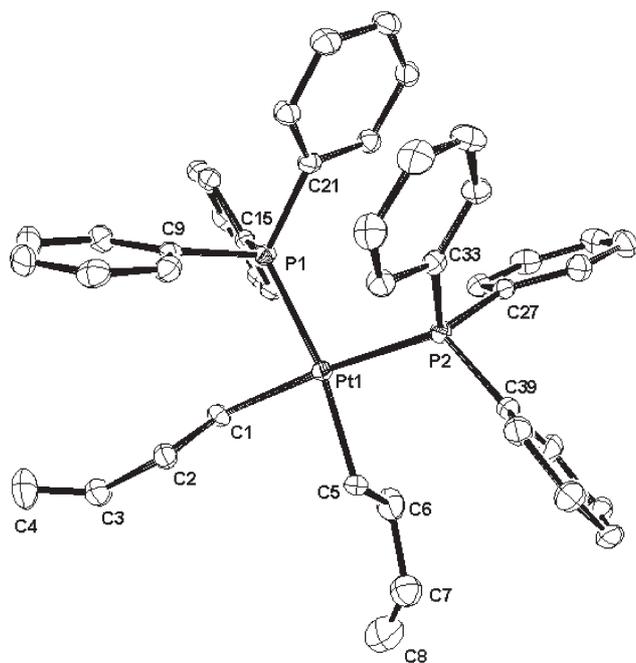


Fig. 1 Molecular structure of the major component of compound **1**. Selected bond lengths (Å): Pt(1)–P(1) 2.300; Pt(1)–P(2) 2.304; Pt(1)–C(1) 2.127(2); Pt(1)–C(5) 2.095(3); C(3)–C(4) 1.304(4); C(1)–C(2) 1.535(4); C(7)–C(8) 1.247(6); C(5)–C(6) 1.533(4). Selected bond angles (°): P(1)–Pt(1)–P(2) 99.65(2); C(1)–Pt(1)–C(5) 83.07(2).

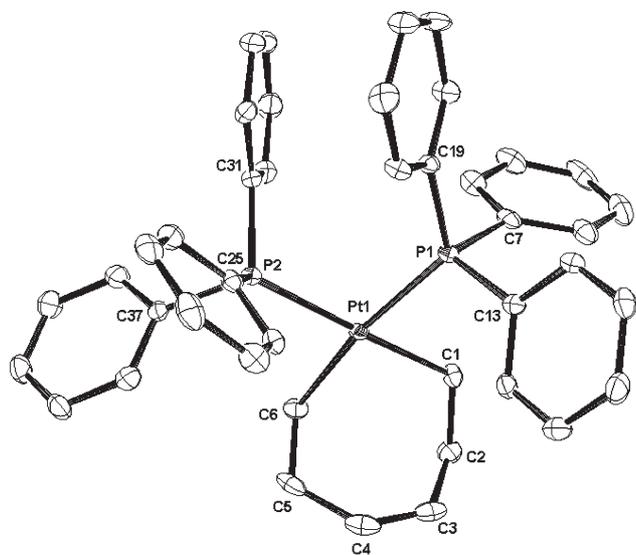


Fig. 2 Molecular structure of compound **2**. Selected bond lengths (Å): Pt(1)–P(1) 2.290; Pt(1)–P(2) 2.317; Pt(1)–C(1) 2.136(3); Pt(1)–C(6) 2.115(3); C(2)–C(3) 1.507(5); C(3)–C(4) 1.328 (6); C(4)–C(5) 1.497 (6). Selected bond angles (°): P(1)–Pt(1)–P(2) 97.34(3); C(1)–Pt(1)–C(6) 87.15(14).

to show for example that the bis-pentenyl complex, *cis*-[Pt(PPh₃)₂(CH₂CH₂CH₂CH=CH₂)₂], also undergoes RCM to give, after hydrogenation, the corresponding platinumacyclonane **4** in high yield and under mild conditions.¹⁴

In addition, we are also exploring the application of this route to other metal and ligand systems in order to prepare a range of previously unknown metallacycles with medium to large rings and thence to explore their chemistry.¹⁴

Notes and references

† *Spectroscopic data.* Compound **1** (all at 298 K, CDCl₃): δ¹H: 0.84–1.96 (m, 8H, CH₂), 4.38–4.68 (m, 4H, =CH₂), 5.35–5.55 (m, 2H, =CH), 7.08–7.83 (m, 30H, Ph). δ³¹P{¹H}: 27.01 (s) (¹J_{PtP} 1765). Yield = 67%; mp 105–120 °C (dec.). Compound **2**: δ¹H: 1.24–1.69 (m, 4H, CH₂), 2.23–2.55 (t, 4H, CH₂CH=), 5.67–5.74 (t, 2H, =CH), 7.07–7.52 (m, 30H, Ph). δ³¹P{¹H}: 27.4 (s) (¹J_{PtP} 1765). Yield = 80%; mp 167–169 °C (dec.). Compound **3**: δ¹H: 0.83–1.74 (m, 12H, CH₂), 7.11–7.80 (m, 30H, Ph). δ³¹P{¹H}: 28.6 (s) (¹J_{PtP} 3028). Yield = 98%; mp 138–146 °C (dec.). Compound **4**: δ¹H: 0.80–1.92 (m, 16H, CH₂), 6.7–7.94 (m, 30H, Ph). δ³¹P{¹H}: 29.3 (s) (¹J_{PtP} 2894). Yield = 62%; mp 140–141 °C (dec.).

‡ *Crystallographic data.* Intensity data were collected at 113 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). **1**: C₄₄H₄₄P₂Pt·0.5C₆H₁₄, *M* = 872.95, monoclinic, *P*₂/*n*, *a* = 17.2027(2), *b* = 10.3525(1), *c* = 23.4504(3) Å, α = 90.00, β = 108.608(1), γ = 90.00°, *V* = 3957.98(8) Å³, *Z* = 4, μ = 3.654 mm⁻¹, unique reflections = 9486 [*R*_{int} = 0.0471], *R*₁ = 0.0243, *wR*₂ = 0.0466 [*I* > 2σ(*I*)]. Atom C7 in one of the butenyl ligands was found to be disordered over two positions with site occupancy factors of 0.81 (C7A) and 0.19 (C7B). This disorder was treated by forcing the temperature factors of the two partial atoms to refine to the same value, then fixing this value and allowing the site occupancy factors to refine to give a total site occupancy of one. The refined site occupancy factors were then fixed and the isotropic temperature factors of the two partial atoms were allowed to refine independently. Hydrogen atoms were not placed on the two partial atoms. All non-hydrogen atoms were refined anisotropically, with the exception of the disordered atom C7 which was refined isotropically **2**: C₄₂H₄₀P₂Pt, *M* = 801.81, triclinic, *P* $\bar{1}$, *a* = 10.1405(1), *b* = 10.3988(2), *c* = 17.2796(3) Å, α = 94.001(1), β = 106.261(1), γ = 103.161(1)°, *V* = 1685.81(5) Å³, *Z* = 2, μ = 4.286 mm⁻¹, unique reflections = 8024 [*R*_{int} = 0.0612], *R*₁ = 0.0301, *wR*₂ = 0.0573 [*I* > 2σ(*I*)]. CCDC 270701–270702. See <http://dx.doi.org/10.1039/b504747a> for crystallographic data in CIF or other electronic format.

- B. Blom, H. Clayton, M. Kilkenny and J. R. Moss, *Adv. Organomet. Chem.*, 2005, accepted for publication.
- E. Lindner, R.-M. Jansen and H. A. Mayer, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1008; E. Lindner, R.-M. Jansen, W. Hiller and R. Fawzi, *Chem. Ber.*, 1989, **122**, 1403; E. Lindner, T. Liebfritz, R. Fawzi and M. Steinman, *Chem. Ber.*, 1996, **129**, 945.
- J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
- N. W. Alcock, K. H. Bryars and P. G. Pringle, *J. Organomet. Chem.*, 1990, **386**, 399.
- R. H. Grubbs, *Tetrahedron*, 2004, **60**, 7177 and references therein.
- D. S. McGuinness, P. Wasserscheid, W. Keim, J. T. Dixon, J. J. C. Grove, C. Hu and U. Englert, *Chem. Commun.*, 2003, 334 and references therein.
- T. Agapie, S. J. Schofer, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2004, **126**, 1304.
- A. Bollmann, K. Blann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. S. McGuinness, D. H. Morgan, A. Neveling, S. Otto, M. Overett, A. M. Z. Slawin, P. Wasserscheid and S. Kuhlmann, *J. Am. Chem. Soc.*, 2004, **126**, 14712.
- M. Overett, K. Blann, A. Bollmann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. H. Morgan, A. Neveling and S. Otto, *Chem. Commun.*, 2005, 622.
- M. P. Sibi and T. Subramian, *Synlett*, 2004, 1211 and references therein.
- T. Shima, F. Hampel and J. A. Gladysz, *Angew. Chem. Int. Ed.*, 2004, **43**, 2.
- L. Hermans and S. F. Mapolie, *Polyhedron*, 1997, **16**, 869 and references therein; G. Joorst, R. Karlie and S. F. Mapolie, *S. Afr. J. Chem.*, 1998, **51**, 132.
- J. E. Bercaw and J. R. Moss, *Organometallics*, 1992, **11**, 639.
- B. Blom, N. L. Jaffa, A. Sivaramakrishna, J. R. Moss, T. Mahamo, E. Hager, T. le Roex, H. Clayton and G. Smith, unpublished results.