# Synthesis and characterization of the first metallacyclooctane†

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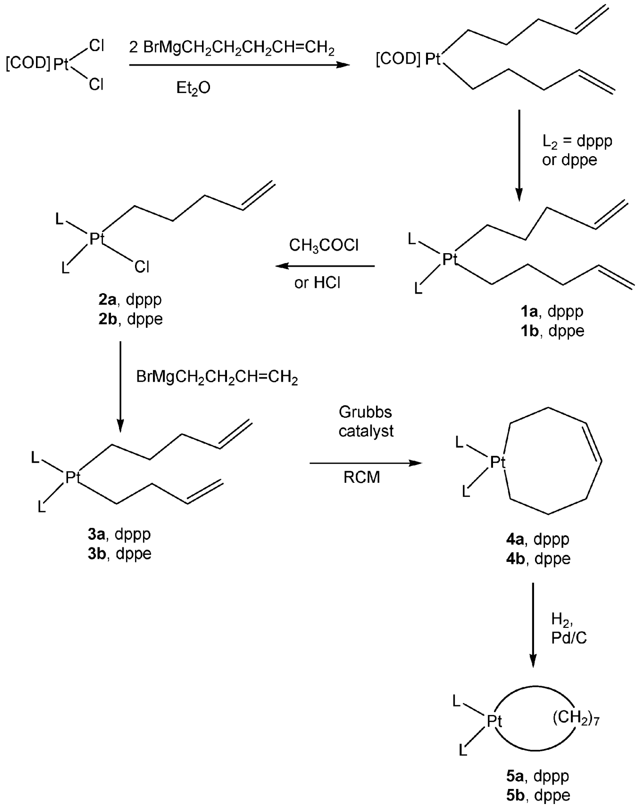
**Ring closing metathesis (RCM) using Grubbs' 1st generation catalyst with *cis*-[$L_2Pt(CH_2CH_2CH{=}CH_2)(CH_2CH_2CH_2CH{=}CH_2)$] yields a platinacyclooctene which can be hydrogenated to the platinacyclooctane, $L_2Pt(CH_2)_7$ [$L_2$ = $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp) or $Ph_2PCH_2CH_2PPh_2$ (dppe)] in high yield.**

Although many metallacycloalkanes have been prepared[1] and such compounds are important intermediates in catalytic reactions including metathesis[2] and ethylene oligomerization[3], no 8-membered ring metallacyclooctane $L_mM(CH_2)_7$ appears to have been previously reported.[1] Recently we have described a new method to prepare metallacycloalkanes of the type $L_mM(CH_2)_n$ (where $n$ = 6 or 8) from their bis(1-alkenyl) precursors.[4] This method can also be extended to larger rings[5] as well as other metal ligand systems.[6] However, because the metallacycle is derived from two equal length alkenyl groups, the method is therefore restricted to the preparation of odd numbered metallacycloalkanes.

We now describe the first synthesis of a metallacyclooctane namely $L_2Pt(CH_2)_7$, using a ring closing metathesis (RCM) step, followed by hydrogenation of the resulting metallacycloalkene. The use of RCM has recently been shown to be an effective method to prepare other types of new organometallic systems including "molecular gyroscopes".[7]

Reaction of $Pt(COD)Cl_2$ with the Grignard reagent $BrMgCH_2CH_2\ CH_2CH{=}CH_2$ by the transmetalation reaction yielded the known[5] bis(1-pentenyl) intermediate which can be converted in good yield to the diphosphine derivative **1** (Scheme 1). Careful reaction of **1** with acetyl chloride or dilute HCl solution in diethyl ether yielded the new mono-pentenyl compound **2**. The reaction of **2** with the 1-butenyl Grignard reagent gave compound **3**, which now contains two alkenyl groups of different lengths, *viz*. $C_4$ and $C_5$ (Scheme 1). The asymmetry in this molecule is clearly seen in the $^{31}P$ NMR spectrum which shows two doublets, each with platinum satellites.

These intermediate compounds, **3** were then readily converted into the platinacyclooctenes **4** in high yields (78–80%) using the RCM reaction with Grubbs' catalyst in $CH_2Cl_2$, and obtained as colorless solids after recrystallization from $CH_2Cl_2$–diethyl ether. The $^{31}P$ NMR spectrum of **4** indicated the presence of two singlets close together [(for **4a**, $\delta$ 3.23 and 3.51 ($J_{Pt-P}$ = 1574 and 1631 Hz) and for **4b**, $\delta$ 45.05, 45.5 ($J_{Pt-P}$ = 1619 and 1617 Hz)] and this is may be due to either the slightly different environments of the two phosphorus atoms or to the presence of *cis* and *trans* alkene isomers or both. This is in agreement with the stereochemistry of other platinacycloalkene compounds described earlier.[5] Hydrogenation of **4** with $H_2$ on Pd/C yields the platinacyclooctanes, **5**. All of these new compounds **1–5** were characterized by analytical and spectroscopic methods.‡ Crystals of **1a** and **3b**§ suitable for X-raydiffraction were obtained by recrystallization from $CH_2Cl_2$–hexane at $T$ = 0 °C. The structural analysis confirms that **1a** contains alkenyl chains of equal length. In contrast, the molecular structure of **3b** confirms the presence of two different alkenyl chains.



**Scheme 1** Preparation of the first platinacyclooctane.

The molecular structures of **1a** and **3b** are illustrated in Fig. 1 and 2 respectively. The Pt–C and Pt–P bonds are similar in both compounds and comparable with the literature reports[8] (2.106(4)–2.142(6) Å and 2.2748(14)–2.2855(7) Å respectively), while the C=C distances range from 1.2501(10)–1.283(7) Å. The P–Pt–P, P–Pt–C and C–Pt–C bond angles in **1a** and **3b** vary from 86.01(5) to 93.43(3), 90.23(11) to 94.22(18) and 84.66(15) to 85.7(2)° respectively. Clearly, the compound with two different alkenyl

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Electronic supplementary information (ESI) available: $^{31}P$ NMR, $^{13}C$ NMR and mass spectra of compounds **5a** and **5b**. See DOI: 10.1039/b800843b

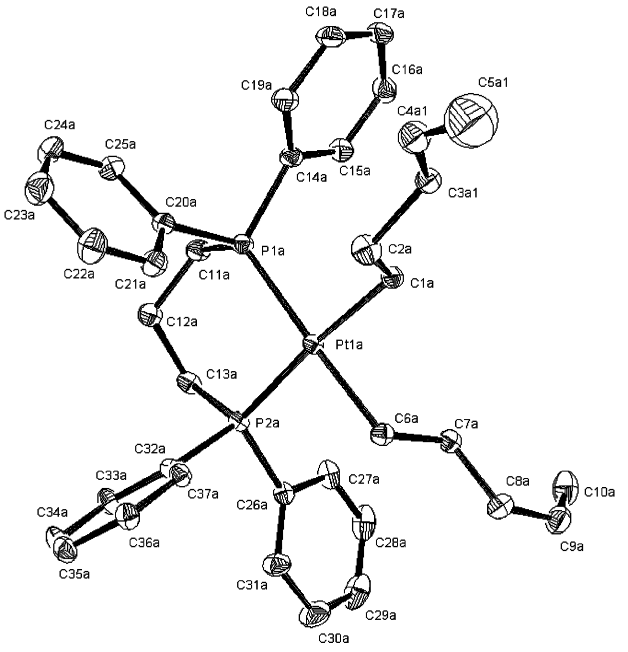


**Fig. 1** Molecular structure of (dppp)bis(1-pentenyl)platinum(II) (**1a**) (ORTEP diagram; 30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt(1a)–P(1a) 2.2824(10); Pt(1a)–P(2a) 2.2819(9); Pt(1a)–C(1a) 2.118(3); Pt(1a)–C(6a) 2.106(4); C(9a)–C(10a) 1.273(7); C(4a1)–C(5a1) 1.302(10). Selected bond angles (°): P(1a)–Pt(1a)–P(2a) 93.43(3); C(1a)–Pt(1a)–C(6a) 84.66(15). There are two crystallographically independent molecules (A and B) in the asymmetric unit. Carbon atoms around the C=C regions are disordered due to high thermal motion and they are modelled over two positions with refined site occupancy factors.

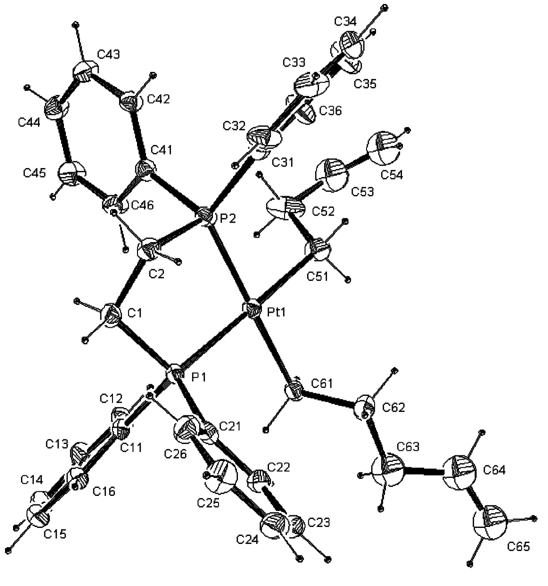


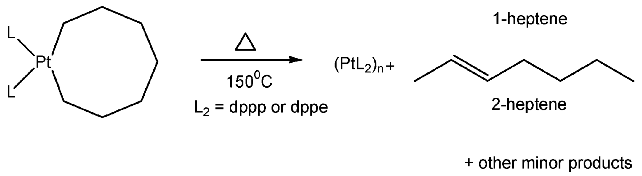
**Fig. 2** Molecular structure of (dppe)(1-butenyl) (1-pentenyl)platinum(II) (**3b**) (ORTEP diagram; 30% probability ellipsoids). Selected bond lengths (Å): Pt(1)–P(1) 2.2748(14); Pt(1)–P(2) 2.2855(15); Pt(1)–C(51) 2.133(6); Pt(1)–C(61) 2.142(6); C(53)–C(54) 1.2501(10); C(64)–C(65) 1.2501(10). Selected bond angles (°): P(1)–Pt(1)–P(2) 86.01(5); C(51)–Pt(1)–C(61) 85.7(2).

chains shows a different geometry with significant changes in the bond angles, consistent with the $^{31}$P NMR spectra.

The platinacyclooctane compounds **5a** and **5b** were characterized by $^{1}$H, $^{13}$C and $^{31}$P NMR, and mass spectral data.† In contrast to the $^{31}$P NMR spectra of the larger platinacycloalkane compounds, **5a** and **5b** showed sharp singlets at $\delta$ 3.35 and 45.46 ($J_{\mathrm{Pt-P}}$ = 1601 and 1623 Hz) respectively, indicating that in these cases the presence of conformers, if they are present, did not have any effect on the $^{31}$P NMR. The coupling constants, $J(^{195}\mathrm{Pt}–^{1}\mathrm{H})$ for the adjacent methylene group was found to be in the range 76 to 80 Hz. It was difficult to assign the coupling constants for the rest of the methylene hydrogens as the signals were seen as a broad multiplet in the $^{1}$H NMR. In a similar way, the $^{13}$C NMR spectra also showed coupling constants in the range 638 to 646 Hz for the $^{1}J(^{195}\mathrm{Pt}–^{13}\mathrm{C})$ for the compounds **5a** and **5b**.

Mass spectral data obtained[9] by FAB with low resolution indicated the presence of the molecular ion, M$^{+}$ = 705.7 (**5a**) and 691.7 (**5b**), but also some higher mass peaks as well as other expected mass fragments. The fragmentation patterns of the complexes also show peaks corresponding to the loss of the ligands as well as the hydrocarbon fragments. It is interesting to note that the higher molecular masses, *i.e.*, beyond the molecular ion peaks, were observed in **5a** and **5b**, which correspond to the masses with the inclusion of ethylene molecules. The highest peaks obtained at 803.2 (for **5a**) and 848.1 (for **5b**) were presumed to be due to the formation of 15-membered and 19-membered platinacycloalkane species. This kind of behaviour was also noticed in many other metallacycloalkane compounds during the FAB process.[6c] This could be due to either the formation of various products under the experimental conditions with FAB, or the presence of dimeric species.

The thermal decomposition of these platinacyclooctane compounds yielded as expected 1-heptene (70%), 2-heptene (15%) and other products including *n*-heptane, 1,6-heptadiene and 3-heptene in trace amounts (Scheme 2), through β-hydride elimination reactions at 150 °C in the solid state for 30 min. At high temperatures (≥180 °C), the results clearly indicated a significant increase in the formation of *n*-heptane and a decrease in the formation of 1-heptene (Table 1). The product distributions were not much affected by the decomposition mode whether it is in the solid state or in solution under reduced pressure. These observations were consistent with reported studies on other platinacycloalkanes.[6,10,11]



**Scheme 2** Thermal decomposition of platinacyclooctane complexes.

We have also demonstrated that this new methodology can be extended to the synthesis of other even membered ring compounds including the new 10- and 12-membered platinacycloalkanes, which have not been prepared by conventional routes.

**Table 1** Products for the thermal decomposition of the platinacyclooctane compounds **5a** and **5b** at 180 °C for 2 h

| | | Products observed[a] (%) | | | | |
|---|---|---|---|---|---|---|
| Complex | Medium | 1-Heptene | 2-Heptene | 1,6-Heptadiene | *n*-Heptane | Cycloheptane |
| **5a** | Solid | 45 | 14 | 9 | 32 | — |
| | Toluene | 43 | 22 | $<1$ | 35 | — |
| **5b** | Solid | 50 | 20 | 2 | 28 | — |
| | Toluene | 43 | 13 | 3 | 40 | — |

[a] Products were analysed by GC and GC-MS.

In conclusion, we have shown that it is possible, at least with platinum, to prepare even membered ring metallacycloalkane compounds in good yields through a ring closing metathesis reaction, and that such compounds are quite thermally stable. Currently, we are exploring the interesting chemical properties of these compounds to determine reaction pathways that are available to metallacycloalkanes. We are also investigating similar compounds with other metals as well as larger membered ring metallacycloalkanes.

## Acknowledgements

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## Notes and references

‡ Spectroscopic data (all at 298 K, $CDCl_3$): **1a** (dppp): This compound was prepared according to the reported procedure.[6] **1b** (dppe): yield 96%; mp 84–85 °C (decomp.). $^1$H NMR: $\delta$ 7.35–7.92 (m, 20H, Ph), 5.52–5.71 (m, 2H, =CH), 4.68–4.86 (m, 4H, $=CH_2$), 2.01–2.23 (m, 4H, P–$CH_2$), 1.17–1.89 (m, 12H, $CH_2$); $^{31}$P NMR: $\delta$ 45.7 (s) ($J_{\text{Pt-P}} = 1639$ Hz). Anal. calcd for $C_{36}H_{42}P_2Pt$: C, 59.09; H, 5.79. Found: C, 58.98; H, 5.69%. $m/z$ : 731.7, 662.6, 593.5. **2a** (dppp): yield 70%; mp 154–157 °C (decomp.). $^1$H NMR: $\delta$ 7.22–7.84 (m, 20H, Ph), 5.68–5.90 (m, 1H, =CH), 4.67–5.05 (m, 2H, $=CH_2$), 2.65–3.12 (m, 6H, P–$CH_2$), 0.62–1.33 (m, 6H, $CH_2$); $^{31}$P NMR: $\delta$ $-1.6$ (s) ($J_{\text{Pt-P}} = 3845$ Hz). Anal. calcd for $C_{31}H_{33}P_2PtCl$: C, 53.97; H, 4.95. Found: C, 54.04; H, 4.92. $m/z = M^+$, 712.1; $[M - Cl]^+$, 676.6; $[(dppp)Pt]^+$, 607.1. **2b** (dppe): yield 45%; mp 205–208 °C (decomp.). $^1$H NMR: $\delta$ 6.96–8.02 (m, 20H, Ph), 5.42–5.58 (m, 1H, =CH), 4.50–4.77 (m, 2H, $=CH_2$), 1.89–2.25 (m, 4H, P-$CH_2$), 0.69–1.81 (m, 6H, $CH_2$); $^{31}$P NMR: $\delta$ 42.40 (d), 43.33 (d) ($J_{\text{Pt-P}} = 4442$ and 1595 Hz). Anal. calcd for $C_{31}H_{33}P_2PtCl$: C, 53.34; H, 4.76. Found: C,53.46; H, 4.72%. **3a** (dppp): yield 76%; mp 95–104 °C (decomp.). $^1$H NMR: $\delta$ 6.93–7.78 (m, 20H, Ph), 5.68–6.27 (m, 2H, =CH), 4.74–5.26 (m, 4H, $=CH_2$), 1.82–2.22 (m, 6H, P-$CH_2$), 0.61–1.79 (m, 10H, $CH_2$); $^{31}$P NMR: $\delta$ 2.57, 2.68 (d), 4.25, 4.13 (d) ($J_{\text{Pt-P}} = 1674$ and 1689 Hz). $m/z$ : 731.6 ($M^+$), 676.7, 662.6, 607.5. **3b** (dppe): yield 79%; mp 162–166 °C (decomp.). $^1$H NMR: $\delta$ 7.24–7.95 (m, 20H, Ph), 5.54–5.83 (m, 2H, =CH), 4.46–5.15 (m, 4H, $=CH_2$), 2.25–2.46 (m, 4H, P-$CH_2$), 0.81–2.19 (m, 10H, $CH_2$); $^{31}$P NMR: $\delta$ 45.98, 45.91 (d), 45.76, 45.70 (d) ($J_{\text{Pt-P}} =$ 1685 and 1635 Hz). Anal. calcd for $C_{35}H_{40}P_2Pt$: C, 58.57; H, 5.62. Found: C, 58.92; H, 5.57%. $m/z$ : 717.72 ($M^+$), 662.6, 648.6, 593.5. **4a** (dppp): yield 70%; mp 164–168 °C (decomp.). $^1$H NMR: $\delta$ 7.14–7.81 (m, 20H, Ph), 5.27–5.47 (m, 2H, =CH), 0.84–2.17 (m, 6H, P-$CH_2$), 0.37–1.77 (m, 10H, $CH_2$); $^{31}$P NMR: $\delta$ 3.23 and 3.51 ($J_{\text{Pt-P}} = 1574$ and 1631 Hz). Anal. calcd for $C_{34}H_{38}P_2Pt$: C, 58.03; H, 5.44. Found: C, 58.16; H, 5.88%. $m/z$ : 703.7 ($M^+$), 607.5. **4b** (dppe): yield 64%; mp 138–142 °C (decomp.). $^1$H NMR: $\delta$ 7.18–8.02 (m, 20H, Ph), 5.12–5.29 (m, 2H, =CH), 2.28–2.47 (m, 4H, P–$CH_2$), 0.48–1.92 (m, 10H, $CH_2$); $^{31}$P NMR: $\delta$ 45.05, 45.5 ($J_{\text{Pt-P}} =$ 1619 and 1617 Hz). Anal. calcd for $C_{33}H_{36}P_2Pt$: C, 57.47; H, 5.26. Found: C, 57.68; H, 5.34%. **5a** (dppp): yield 82%; mp 134–136 °C (decomp.). $^1$H NMR: $\delta$ 6.96–7.80 (m, 20H, Ph), 2.34–3.43 (m, 6H, P–$CH_2$), 0.88–2.35 (m, 14H, $CH_2$); $^{13}$C NMR: $\delta$ 14, 15, 20, 26, 27, 29, 30, 33, 36, 37, 128, 129, 133, 134; $^{31}$P NMR: $\delta$ 3.35 (s) ($J_{\text{Pt-P}} = 1601$ Hz). Anal. calcd for $C_{34}H_{40}P_2Pt$: C, 57.87; H, 5.71. Found: C, 58.16; H, 5.89%. $m/z$ : 705.7 ($M^+$), 607.5 ($M - C_7H_{14}$). **5b** (dppe): yield 68%; mp 206–208 °C (decomp.). $^1$H NMR: $\delta$ 7.22–7.95 (m, 20H, Ph), 2.23–2.49 (m, 4H, P–$CH_2$), 0.61–2.16 (m, 14H, $CH_2$); $^{13}$C NMR: $\delta$ 14, 15, 29, 30, 32, 36, 128, 129, 130, 132, 133, 134; $^{31}$P NMR: $\delta$ 45.46 (s) ($J_{\text{Pt-P}} = 1623$ Hz). Anal. calcd for $C_{33}H_{38}P_2Pt$: C, 57.30; H, 5.54. Found: C, 57.56; H, 5.79%. $m/z$ : 691.7 ($M^+$), 593.5 ($M - C_7H_{14}$).

§ Crystallographic data for **1a** (CCDC number 630919): $C_{37}H_{44}P_2Pt$, $M =$ 745.75 g mol$^{-1}$, triclinic, space group $P\bar{1}$, $a = 13.3653(1)$ Å, $b = 13.9950(1)$ Å, $c = 18.3542(1)$ Å, $\alpha = 88.302(1)°$, $\beta = 75.629(1)°$, $\gamma = 89.361(1)°$, $V = 3324.19(4)$ Å$^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.490$ g cm$^{-3}$, $T = 213(2)$ K, $\mu =$ 4.341 mm$^{-1}$, $F(000) = 1496$, $1.15° < 2\theta < 26.02°$, $\lambda(\text{Mo-K}_\alpha) = 0.71073$ Å, crystal size 0.18 × 0.18 × 0.15 mm. Intensity data were collected with a Nonius KappaCCD diffractometer. 80402 reflections, 13036 independent ($R_{\text{int}} = 0.0380$, empirical absorption correction (SADABS),[12] structure solution using direct methods (SHELXS-97),[12] structure refinement on $F^2$ using full-matrix least-squares procedures (SHELXL-97),[12] $R_1 = 0.0265$ $[I > 2\sigma(I)]$, $wR_2 = 0.0586$ (all data), GOF = 1.087, max./min. residual electron density = 1.212/$-0.720$ e Å$^{-3}$. Crystallographic data for **3b** (CCDC number 630920): $C_{35}H_{40}P_2Pt$, $M = 717.70$ g mol$^{-1}$, triclinic, space group $P\bar{1}$, $a = 10.2728(2)$ Å, $b = 10.9231(2)$ Å, $c = 13.9720(2)$ Å, $\alpha =$ $82.127(1)°$, $\beta = 77.640(1)°$, $\gamma = 85.733(1)°$, $V = 1515.39(5)$ Å$^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.573$ g cm$^{-3}$, $T = 113(2)$ K, $\mu = 4.758$ mm$^{-1}$, $F(000) = 716$, $2.71° < 2\theta < 25.67°$, $\lambda(\text{Mo-K}_\alpha) = 0.71073$ Å, crystal size 0.06 × 0.07 × 0.07 mm. Intensity data were collected with a Nonius KappaCCD diffractometer. 32938 reflections, 5693 independent ($R_{\text{int}} = 0.0670$), empirical absorption correction (SADABS), structure solution using direct methods (SHELXS-97), structure refinement on $F^2$ using full-matrix least-squares procedures (SHELXL-97), $R_1 = 0.0360$ $[I > 2\sigma(I)]$, $wR_2 = 0.0960$ (all data), GOF = 1.092, max./min. residual electron density = 1.508/$-2.513$ e Å$^{-3}$.

1 B. Blom, H. Clayton, M. Kilkenny and J. R. Moss, *Adv. Organomet. Chem.*, 2006, **54**, 149.

2 R. H. Grubbs, *Tetrahedron*, 2004, **60**, 7177 and references therein.

3 (*a*) T. Agapie, S. J. Schofer, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2004, **125**, 1304; (*b*) 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; (*c*) M. J. Overett, K. Blann, A. Bollmann, J. T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D. S. McGuinness and D. H. Morgan, *J. Am. Chem. Soc.*, 2005, **127**, 10723; (*d*) A. K. Tomov, J. J. Chirinos, D. J. Jones, R. J. Long and V. C. Gibson, *J. Am. Chem. Soc.*, 2005, **127**, 10166.

4 (*a*) K. Dralle, N. L. Jaffa, T. L. Roex, J. R. Moss, S. Travis, N. D. Watermayer and A. Sivaramakrishna, *Chem. Commun.*, 2005, 3865; (*b*) A. Sivaramakrishna, H. Clayton, C. Kauschula and J. R. Moss, *Coord. Chem. Rev.*, 2007, **251**, 1294.

5 A. Sivaramakrishna, Hong Su and J. R. Moss, *Angew. Chem., Int. Ed.*, 2007, **46**, 3541.

6 (*a*) T. Mahamo, F. Zheng, A. Sivaramakrishna, G. S. Smith and J. R. Moss, *J. Organomet. Chem.*, 2008, **693**, 103; (*b*) A. Sivaramakrishna, B. L. Watson, F. Zheng and J. R. Moss, *Polyhedron*, 2008, accepted; (*c*) A. Sivaramakrishna, J. R. Moss, E. Hager, H. Clayton, T. Mahamo, F. Zheng, L. L. M. Mbatha and M. M. Mogorosi, unpublished results.

7 A. J. Nawara, T. Shima, F. Hampel and J. A. Gladysz, *J. Am. Chem. Soc.*, 2006, **128**, 4962 and references therein.

8 F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, vol. C.

9 Mass spectral data was obtained using VG70SE with 8kV acceleration and the FAB gun is an Iontech Saddlefield, using xenon gas and operating at 8 kV. All matrices were made with 3-nitrobenzyl alcohol.

10 (*a*) F. Zheng, A. Sivaramakrishna and J. R. Moss, *Coord. Chem. Rev.*, 2007, **251**, 2056; (*b*) F. Zheng, A. Sivaramakrishna and J. R. Moss, *J. Organomet. Chem.*, 2008, accepted.

11 (*a*) G. M. Whitesides, M. Hackett, R. L. Brainard, J. P. P. M. Lavalleye, A. F. Sowinski, A. N. Izumi, S. S. Moore, D. W. Brown and E. M. Staudt, *Organometallics*, 1985, **4**, 1819; (*b*) J. X. McDermott, J. F. White and G. aM. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

12 G. M. Sheldrick, *SADABS, SHELXS-97 and SHELXL-97*, University of Göttingen, Germany, 1997.