Platinum Metallacycles

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High-Yield Synthesis of Medium and Large Platinacycloalkanes from Bis(alkenyl) Precursors**

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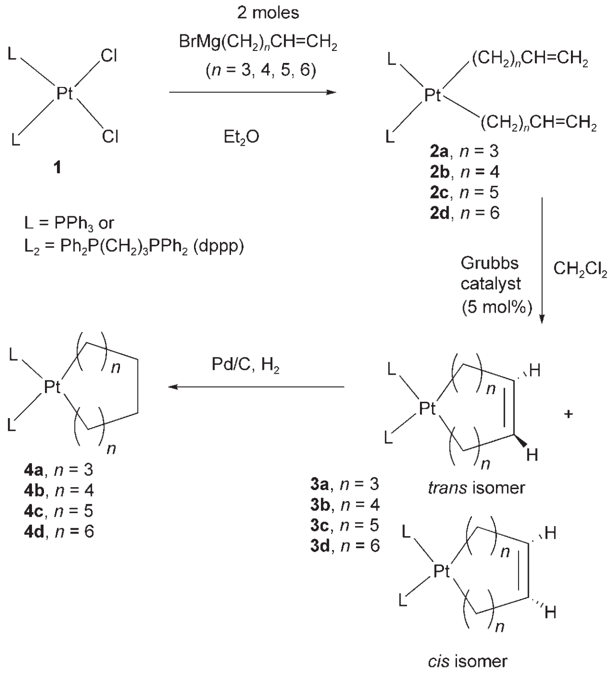
Metallacycloalkanes are an important class of compounds which have been known for many years to be key intermediates in useful catalytic reactions.[1] For example, metallacyclobutanes are known to be present in the alkene metathesis reaction.[2] More recently, metallacycloheptanes were first implicated,[3] then proven[4] to be involved in ethylene trimerization. There has been interesting discussion[5–7] and a belief that the formation of nine-membered and other larger metallacycloalkane rings is unlikely.

In 2005, selective tetramerization of ethylene was discovered, which implicated metallacyclononanes as intermediates,[8] and Gibson and co-workers showed that larger metallacycloalkanes were involved in the catalytic formation of higher ethylene oligomers.[9] In spite of the demonstrated importance of medium to large metallacycloalkanes as intermediates, very little is known about such compounds.[10] The elegant synthesis of "molecular gyroscopes" through intramolecular alkene metathesis reactions using the Grubbs catalyst has been described by Gladysz and co-workers.[11] Recently, we introduced a new approach for the synthesis of small metallacycloalkane complexes using ring-closing metathesis (RCM) with the Grubbs catalyst.[12] Herein, we use this route to synthesize new medium to large ring metallacycloalkanes (Scheme 1), that is, exactly the ones that appear difficult to make by conventional methods.



Scheme 1. Preparation of platinacycloalkanes.

The bis(alkenyl)platinum(II) complexes **2a–d** were obtained by the transmetalation reaction of 1-alkenyl Grignard reagents with the corresponding dichloroplatinum(II) precursors **1**. Complexes **2** were then readily converted into the platinacycloalkenes **3** using the RCM reaction with the Grubbs catalyst in CH_2Cl_2, and were obtained as colorless solids in high yield after recrystallization from CH_2Cl_2/diethyl ether. The hydrogenation of these compounds yielded the platinacycloalkanes **4** in high yield. The $^{31}P\{^1H\}$ NMR spectra of **4** in C_6D_6 displayed a singlet at $\delta = 3.4$ ppm with Pt satellites ($^1J_{Pt\text{-}P} = 1620$ Hz), which is quite similar to the precursor compounds **2** and **3**.[13] These and all new compounds described in Scheme 1 were fully characterized. Crystals of **2c** and **3d** (L_2 = dppp = 1,3-bis(diphenylphosphino)propane) suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/hexane at T = 0 °C. To our knowledge, this is the first example of a structurally characterized larger metallacycloalkene compound reported in the literature.

The molecular structures of **2c** and **3d** are illustrated in Figures 1 and 2, respectively. The structural analysis confirms that **3d** is the RCM product. The most striking structural features of complexes **2c** and **3d** are the differences in some of the bond angles and bond lengths. The Pt–C and Pt–P bond lengths in the two compounds are almost identical and comparable to the literature values[14] (2.118(3)–2.110(3) Å and 2.263(9)–2.293(7) Å, respectively), while the C=C distances range from 1.229(7) to 1.341(7) Å. The C=C distance in **3d** is comparatively long. The P-Pt-P, P-Pt-C, and C-Pt-C bond angles in **2c** and **3d** vary from 92.53(3) to 96.72(3), 92.52(8) to 89.49(8), and 85.44(11) to 84.45(11)° respectively. These differences may indicate that the variance in the structural features depends on the degree of strain on the bridging C=C bonds, which is necessary to stabilize the ring.

The above RCM reactions were found to depend on the concentration, temperature, solvent, length of alkenyl chains, tertiary phosphine ligand, and catalyst used. The concentration of **2** had a noticeable effect on the RCM rate, thus at high

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

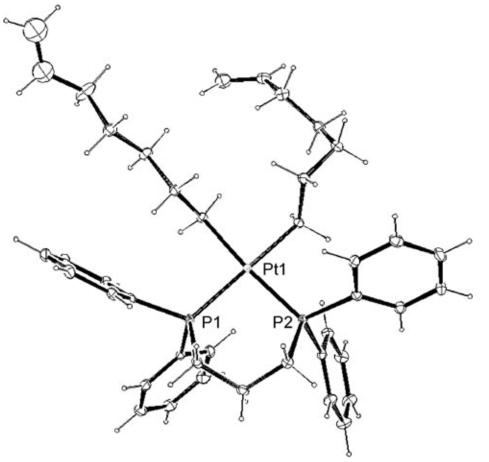


Figure 1. ORTEP diagram of the molecular structure of **2c** (L_2 = dppp); thermal ellipsoids set at 30%.

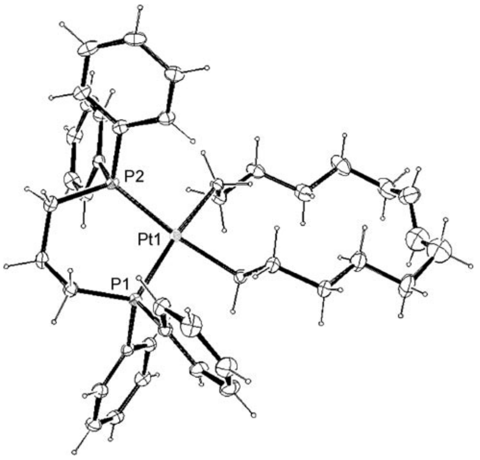
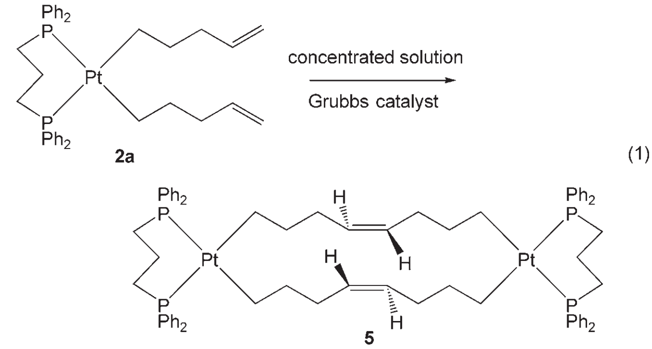


Figure 2. ORTEP diagram of the molecular structure of **3d** (L_2 = dppp); thermal ellipsoids set at 30%.

concentrations dimeric products such as **5** were observed [Eq. (1)].

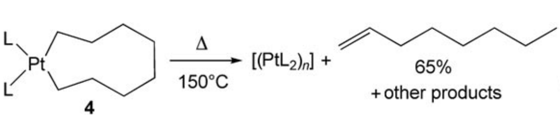


(1)

The mass spectrum of compound **5** also displayed a peak corresponding to the molecular ion of monomeric platinacycle **3**. This peak could be a result of interconversion of monomer to dimer, or it could be due to one of the fragments of the dimeric species. The same trends were obtained when the RCM was carried out with **2d** in a concentrated solution; the mass spectra showed a mixture of monomer **3d** and its corresponding dimeric species. Owing to the steric, electronic, and chelating effects of ligands, the donor-ligand system in **2** plays an important role in the RCM reactions. PPh_3 enhances the rate of reaction with the Grubbs catalyst compared to the diphosphine ligands. There was no RCM observed with the first-generation Grubbs catalyst when $PtBu_3$ was used as ligand. However, the reaction proceeds smoothly with the second-generation Grubbs catalyst. The thermal stability of **2** increases along the series: $PPh_3 < PtBu_3 <$ diphosphine. Using 10 mol% rather than 5 mol% of the Grubbs catalyst causes a dramatic enhancement (ca. 10-fold) of the rate of conversion **2**→**3** (Scheme 1). It is interesting to note that the length of alkenyl chain also has a substantial effect on the rate of the RCM reaction. When the bis(butenyl) complex with PPh_3 was used, the catalyzed reaction was completed in 90 minutes. The same reaction with the bis(heptenyl) complex **2c**, however, took 9 h to go to completion.

The RCM reaction discussed here is not general for all metal systems, since the terminal alkenyl groups in metal–alkenyl complexes are reactive and may undergo a variety of reactions, depending on the nature of metal center, such as conversion to η^1,η^2-alkenyl complexes. ^{31}P NMR examination of products derived from RCM reactions to form **3** indicates the presence of different conformations of platinacycloalkenes in solution. Each spectrum shows a multiplet, which displays only one coupling constant ($^1J_{Pt\text{-}P} = 1620$ Hz). It was found that the ^{31}P NMR spectra of solutions of platinacycloalkenes **3** changed after aging and showed sharp singlets. This aging could be due to the conversion of possible isomers to the most stable conformation. The aging also indicates that such structural changes are sensitive to light and temperature. The alkene protons in **3d** were observed to be mutually *trans*. The same results were observed with the other platinacycloalkene compounds (**3a**–**c**).

Thermal decomposition of the platinacycloalkanes in the solid state generated a mixture of alkenes, which consisted mainly of 1-alkene derived from the metallacyclic moiety through β-hydride elimination [Eq. (2)], which is consistent with the literature data for small ring compounds.[15] This result suggests that these compounds can be useful models for metallacyclic intermediates in ethylene oligomerization reactions.



(2)

In conclusion, we have demonstrated that it is possible, at least with platinum, to prepare medium to large ring metallacycloalkanes in high yield through a ring-closing metathesis reaction, and that such compounds are quite thermally stable. Currently, we are exploring the interesting properties and reactivity of these compounds to determine the reaction pathways that are available to metallacycloalkanes. We are also investigating similar compounds with other metals as well as even-membered ring metallacycloalkanes and cross ring-closing metathesis reactions to prepare larger metallacycloalkanes.

Experimental Section

2 c (L_2 = dppp): A solution of 1-heptenyl Grignard reagent (2.3 mL, 1.22 M, 2.806 mmol) in diethyl ether was added to a solution of [(cod)$PtCl_2$] (296 mg, 0.791 mmol, cod = 1,5-cyclooctadiene) in diethyl ether (25 mL) cooled to −78 °C. The solution was brought to 0 °C and stirred until the solution became clear. Solid dppp (327 mg, 0.793 mmol) was added and the resulting mixture was stirred for 36 h until a clear solution was formed. The excess Grignard reagent was removed by hydrolyzing the reaction mixture with saturated aqueous NH_4Cl (5 mL) at −78 °C. The aqueous layer was washed with dichloromethane (2 × 5 mL) and the organic layer was separated. The solvent was removed under reduced pressure, and the residue was recrystallized from a CH_2Cl_2/hexane mixture (3 mL:5 mL) at −10 °C for 48 h. The colorless crystalline solid was isolated by decanting the mother liquor and dried under vacuum. Yield: 95 %; m.p. 80–82 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.61$–7.23 (m, 20 H; Ph), 5.77–5.57 (m, 2 H; =CH), 4.91–4.69 (m, 4 H; =CH_2), 2.66–2.41 (m, 6 H; P−CH_2), 2.12–0.84 ppm (m, 20 H; −CH_2); $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): $\delta =$ 3.32 ppm (s, $J_{\text{Pt-P}} =$ 1612 Hz). Elemental analysis (%) calcd for $C_{41}H_{52}P_2Pt$: C 61.41, H 6.54; found: C 61.53, H 6.58.

3 d (L = dppp): Compound **2 d** (L = dppp; 366 mg, 0.441 mmol) and the first generation Grubbs catalyst (9 mg, 0.0109 mmol, 2.5 mol %) were added to dichloromethane (30 mL). The solution was heated at reflux at 50 °C. After 3 h, additional catalyst (9 mg, 0.0109 mmol, 2.5 mol %) was added. After another 3 h, the solvent was removed in vacuo. The residue was recrystallized from a CH_2Cl_2/hexane mixture (3 mL:5 mL) to give **3 d** (L = dppp) as a white solid. Yield: 91 %; m.p. 163–166 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.81$–7.28 (m, 20 H; Ph), 5.40–5.21 (m, 2 H; =CH), 2.64–2.34 (m, 6 H; P−CH_2), 2.12–0.70 ppm (m, 12 H; −CH_2); $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): $\delta = 3.08$ (m, $J_{\text{Pt-P}} = 1610$ Hz; a mixture of isomers). Elemental analysis (%) calcd for $C_{41}H_{52}P_2Pt$: C 61.41, H 6.54; found: C 61.23, H 6.69. MS: $m/z = 802.1$ $[M]^+$, 606.8 $[(\text{dppp})\text{Pt}]^+$. The experimental procedures as well as the characterization data of the remaining compounds **2 a,b,d**, **3 a–c**, **4 a–d**, and **5** are given in the Supporting Information.

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Keywords: metallacycles · metathesis · platinum · structure elucidation · thermal decomposition

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[1] J. P. Collman, J. R. Norton, L. S. Hegedus, R. G. Finke, *Principles and Applications of Organotransitionmetal Chemistry*, University Science Books, Mill Valley, California, **1976**, pp. 459–522.

[2] R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117–7140.

[3] R. Emrich, O. Heinemann, P. W. Jolly, C. Kruger, G. P. J. Verhovnik, *Organometallics* **1997**, *16*, 1511–1513.

[4] T. Agapie, S. J. Schofer, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2004**, *126*, 1304–1305.

[5] Z.-X. Yu, K. N. Houk, *Angew. Chem.* **2003**, *115*, 832–835; *Angew. Chem. Int. Ed.* **2003**, *42*, 808–811.

[6] A. N. J. Blok, P. H. M. Budzelaar, A. W. Gal, *Organometallics* **2003**, *22*, 2564–2570.

[7] 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, S. Kuhlmann, *J. Am. Chem. Soc.* **2004**, *126*, 14712–14713.

[8] M. J. Overett, K. Blann, A. Bollmann, J. T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D. S. McGuinness, D. H. Morgan, *J. Am. Chem. Soc.* **2005**, *127*, 10723–10724.

[9] A. K. Tomov, J. J. Chirinos, D. J. Jones, R. J. Long, V. C. Gibson, *J. Am. Chem. Soc.* **2005**, *127*, 10166–10167.

[10] B. Blom, H. Clayton, M. Kilkenny, J. R. Moss, *Adv. Organomet. Chem.* **2006**, *54*, 149–205.

[11] A. J. Nawara, T. Shima, F. Hampel, J. A. Gladysz, *J. Am. Chem. Soc.* **2006**, *128*, 4962–4963, and references therein.

[12] K. Dralle, N. L. Jaffa, T. L. Roex, J. R. Moss, S. Travis, N. D. Watermayer, A. Sivaramakrishna, *Chem. Commun.* **2005**, 3865–3866.

[13] a) Structure determination and crystallographic data for **2 c**: crystals were obtained by slow diffusion of *n*-hexane into a solution of **2 c** in dichoromethane. $C_{41}H_{52}P_2Pt_1$, $M_r = 801.86\ \text{g mol}^{-1}$, triclinic, space group $P\bar{1}$, $a = 12.1550(1)$, $b = 12.3649(1)$, $c = 14.4431(2)$ Å, $\alpha = 108.061(1)$, $\beta = 95.214(1)$, $\gamma = 114.631(1)°$, $V = 1814.14(3)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.468\ \text{g cm}^{-3}$, $T = 113(2)$ K, $\mu = 3.982\ \text{mm}^{-1}$, $F(000) = 812$, $3.37° < 2\theta < 26.37°$, $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å, crystal size $0.15 \times 0.17 \times 0.21\ \text{mm}^3$. Intensity data were collected with a Nonius KappaCCD diffractometer. 34532 reflections, 7379 independent ($R_{\text{int}} = 0.0309$), empirical absorption correction (SADABS), structure solution using direct methods (SHELXS-97), structure refinement on F^2 using full-matrix least-squares procedures (SHELXL-97), $R_1 = 0.0229$ $[I > 2\sigma(I)]$, $wR_2 = 0.0498$ (all data), GOF = 1.043, max/min residual electron density = 1.899/−0.977 e Å^{-3}; b) Structure determination and crystallographic data for **3 d**: crystals were obtained by slow diffusion of *n*-hexane into a solution of **3 d** in dichoromethane. $C_{41}H_{52}P_2Pt_1$, $M_r = 801.86\ \text{g mol}^{-1}$, monoclinic, space group $P2_1/c$, $a = 17.0142(2)$, $b = 14.4679(1)$, $c = 15.9256(1)$ Å, $\beta = 111.499(1)°$, $V = 3647.49(5)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.460\ \text{g cm}^{-3}$, $T = 113(2)$ K, $\mu = 3.962\ \text{mm}^{-1}$, $F(000) = 1624$, $3.09° < 2\theta < 25.69°$, $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å, crystal size $0.06 \times 0.10 \times 0.12\ \text{mm}^3$. Intensity data were collected with a Nonius KappaCCD diffractometer. 103989 reflections, 6891 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), $R_1 = 0.0258$ $[I > 2\sigma(I)]$, $wR_2 = 0.0547$ (all data), GOF = 1.066, max/min residual electron density = 1.512/−0.861 e Å^{-3}. CCDC-629152 (**2 c**) and CCDC-629153 (**3 d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

[14] F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *International Tables for Crystallography*, *Vol. C* (Ed. A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, **1992**.

[15] 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, E. M. Staudt, *Organometallics* **1985**, *4*, 1819–1830; b) J. X. McDermott, J. F. White, G. M. Whitesides, *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.