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# A new route to metallacycloalkanes

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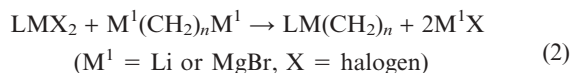
Reaction of the bis-alkenyl complex cis-[Pt(PPh$_3$)$_2$-(CH$_2$CH$_2$CH=CH$_2$)$_2$] with Grubbs 1st generation catalyst gives, in high yield, the metallacycloalkene cis-[Pt(PPh$_3$)$_2$(CH$_2$CH$_2$CH=CHCH$_2$CH$_2$)], which can be hydrogenated to the metallacycloalkane cis-[Pt(PPh$_3$)$_2$(CH$_2$)$_6$].

Metallacycloalkane compounds are well known[1] and many have been prepared by the following two routes:[2–4]

$$LM^{2-} + Y(CH_2)_nY \rightarrow LM(CH_2)_n + 2Y^- \quad (Y = triflate) \quad (1)$$

$$LMX_2 + M^1(CH_2)_nM^1 \rightarrow LM(CH_2)_n + 2M^1X$$
$$(M^1 = Li\ or\ MgBr,\ X = halogen) \quad (2)$$

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 implicated[6] and recently shown[7] 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 Na$_2$Os(CO)$_4$ with Y(CH$_2$)$_n$Y (Y = triflate).[2] They found that, whereas the 5-, 6- and 7-membered ring compounds (CO)$_4$Os(CH$_2$)$_n$ (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–(CH$_2$)$_m$CH=CH$_2$. Few compounds of this class have been prepared although the compounds ($\eta^5$-C$_5$R$_5$)Fe(CO)$_2$(CH$_2$)$_m$CH=CH$_2$ (R = H or Me

and m = 2,3)[12] and Cp*$_2$HfH(CH$_2$)$_m$CH=CH$_2$ (m = 4 or 5) have been described.[13]

We now find that reaction of Pt(COD)Cl$_2$ with the Grignard reagent BrMgCH$_2$CH$_2$CH=CH$_2$, followed by PPh$_3$ leads to the bis-alkenyl compound cis-[Pt(PPh$_3$)$_2$(CH$_2$CH$_2$CH=CH$_2$)$_2$] 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 CH$_2$Cl$_2$–hexane and the structure with two pendant alkene groups was confirmed (see Fig. 1).‡

Reaction of 1 with Grubbs 1st generation catalyst, RuCl$_2$(PCy$_3$)$_2$(=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 =CH$_2$ signal of 1 in the $^1$H 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
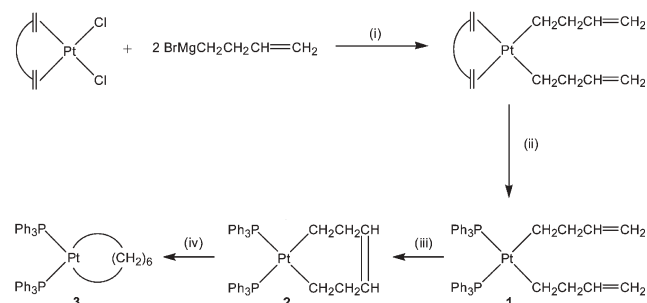


**Scheme 1** (i) Et$_2$O, −78 °C; (ii) PPh$_3$; (iii) Grubbs catalyst generation 1, CH$_2$Cl$_2$, reflux 1 h; (iv) Pd/C, H$_2$, MeOH–CH$_2$Cl$_2$.

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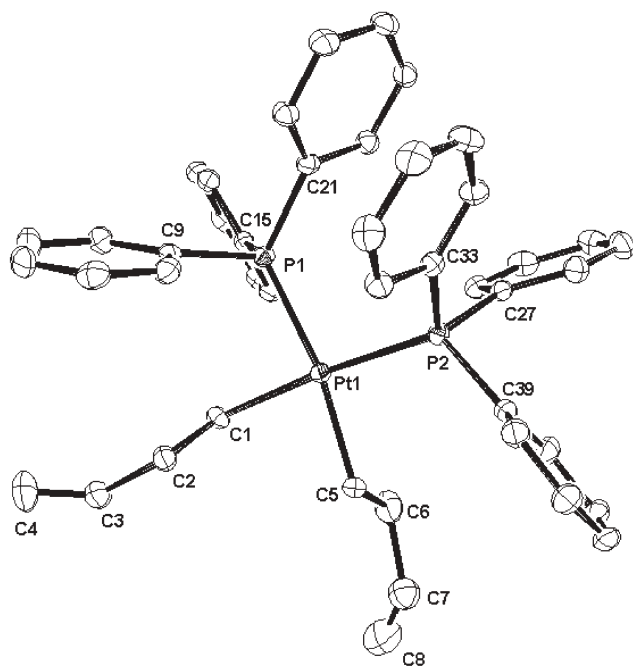
**Fig. 1** Molecular structure of the major component of compound **1**. Selected bond lengths (Å): Pt(1)–P(1) 2.300; Pt(1)–P(2) 2.304; Pt(1)–C(1) 2.127(2); Pt(1)–C(5) 2.095(3); C(3)–C(4) 1.304(4); C(1)–C(2) 1.535(4); C(7)–C(8) 1.247(6); C(5)–C(6) 1.533(4). Selected bond angles (°): P(1)–Pt(1)–P(2) 99.65(2);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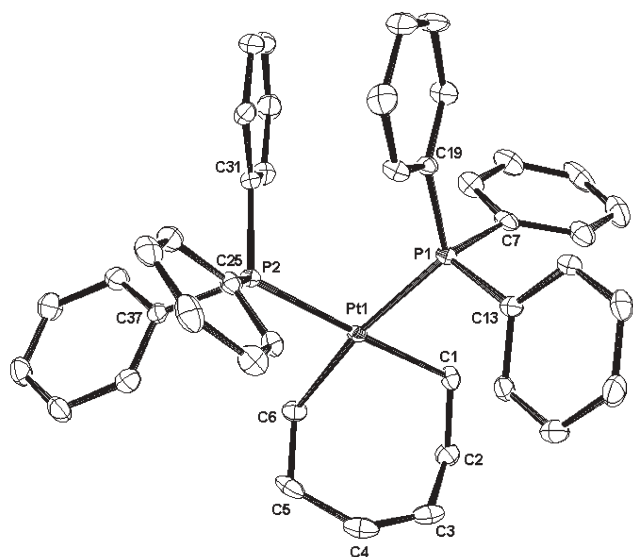


**Fig. 2** Molecular structure of compound **2**. Selected bond lengths (Å): Pt(1)–P(1) 2.290; Pt(1)–P(2) 2.317; Pt(1)–C(1) 2.136(3); Pt(1)–C(6) 2.115(3); C(2)–C(3) 1.507(5); C(3)–C(4) 1.328 (6); C(4)–C(5) 1.497 (6). Selected bond angles (°): P(1)–Pt(1)–P(2) 97.34(3); C(1)–Pt(1)–C(6) 87.15(14).

to show for example that the bis-pentenyl complex, *cis*-[Pt(PPh$_3$)$_2$(CH$_2$CH$_2$CH$_2$CH=CH$_2$)$_2$], also undergoes RCM to give, after hydrogenation, the corresponding platinacyclononane **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]

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