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**Preliminary communication**

# A NEW ROUTE TO 1-PLATINA-3-SILACYCLOBUTANE

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## Summary

Treatment of chlorobis(trimethylsilyl)methylbis(dimethylphenylphosphine)platinum(II) (1) with t-butyllithium in toluene yields 1,1-bis(dimethylphenylphosphine)-2-trimethylsilyl-3,3-dimethyl-1-platina-3-silacyclobutane (2) via intramolecular nucleophilic attack of the Si-stabilized carbanion or the platinum(II) center.

During the past decade great effort has been devoted to the chemistry of metallacyclobutanes which are strongly suspected to be reactive intermediates in the olefin metathesis reaction [1] and the Ziegler—Natta polymerization of olefins [2]. Various synthetic routes which lead to the metallacyclobutane derivatives have been developed. These methods include oxidative addition of an olefin to a carbenemetal or a Lewis acid-stabilized carbene such as Tebbe's reagent [3], $\gamma$-hydrogen abstraction from a bulky alkyl ligand [4], and oxidative addition of cyclopropane derivatives [5]. Although the reaction of carbanion with metal halide is the most versatile and straightforward method which leads to the formation of metal—carbon bonds, the application of carbanions to the formation of metallacyclobutanes has been limited [6]. Here we wish to report a new and simple synthetic route giving 1-platina-3-silacyclobutane via intramolecular alkylation.

After addition of t-butyllithium (2 *M* in hexane) (0.48 ml, 0.95 mmol) to a solution of chlorobis(trimethylsilyl)methylbis(dimethylphenylphosphine)-platinum(II)* (1) (0.61 g, 0.95 mmol) in toluene (10 ml) at —78°C the reac-

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*Complex 1 was derived from dichloro(1,5-cyclooctadiene)platinum(II), (1,5-COD)$PtCl_2$, in 87% yield via alkylation with bis(trimethylsilyl)methyllithium followed by ligand exchange with dimethylphenylphosphine. 1: M.p. 150°C; IR (KBr): 1240 (Si—C), 857 $cm^{-1}$ (Si—C); $^1H$ NMR ($C_6D_5CD_3$/TMS): $\delta$ 0.61 (18H, s, Si—$CH_3$), 0.99—1.50 (12H, m, P—$CH_3$), and 6.94—7.44 ppm (10H, m, phenyl); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$/external $PPh_3$) $\delta$ —7.85 (1P, $J(^{195}Pt—P)$ 4251.0 Hz, $J(P—P)$ 15.6 Hz, *trans* to the Cl ligand), and —1.50 ppm (1P, $J(^{195}Pt—P)$ 1833.0 Hz, $J(P—P)$ 15.6 Hz, *cis* to the Cl ligand). Found: C, 42.37; H, 6.62; Cl, 5.72. $C_{23}H_{41}ClP_2Si_2Pt$ calcd.: C, 41.46; H, 6.21; Cl, 5.32%.

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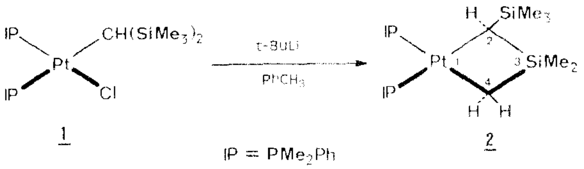
tion mixture was stirred for 4 h at ambient temperature. The mixture was then concentrated to dryness under reduced pressure, and the product was extracted with a mixed solvent of toluene and hexane. Evaporation of the solvent gave 1,1-bis(dimethylphenylphosphine)-2-trimethylsilyl-3,3-dimethyl-1-platina-3-silacyclobutane (2) (0.56 g, 92%) as a pale yellow semisolid substance (eq. 1).



Complex 2 was identified by elemental analysis, $^1$H (100 MHz), and $^{31}$P NMR (40.5 MHz) spectroscopy. 2: $^1$H NMR (CDCl$_3$/CHCl$_3$) $\delta$ −0.06 (s, 15H, Si—CH$_3$), 0.57 (m, 1H, $J(^{195}$Pt—H) 90.1 Hz, $J$(P—H) 12.9 Hz, $J$(P—H) 8.6 Hz), 0.78 (m, 2H, $J(^{195}$Pt—H) 41.3 Hz, $J$(P—H) 9.3 Hz, $J$(P—H) 2.0 Hz), 1.49—1.90 (m, 12H, P—CH$_3$), 7.14—7.63 (m, 10H, P—C$_6$H$_5$) ppm; $^{31}$P NMR (CDCl$_3$/external PPh$_3$) $\delta$ −32.6 (1P, $J(^{195}$Pt—P) 1269.5 Hz, $J$(P—P) 26.9 Hz), 0.82 (1P, $J(^{195}$Pt—P) 3198.2 Hz, $J$(P—P) 26.9 Hz). Found: C, 43.11; H, 6.58. $C_{23}H_{40}P_2Si_2Pt$ calcd.: C, 43.86; H, 6.58%.

The cyclic structure of complex 2 was confirmed on the basis of the $^1$H NMR spectrum recorded in CDCl$_3$ at 30°C (Fig. 1). The resonance peaks for the protons bound to the carbons C(2) and C(4) were observed at 0.57 and 0.78 ppm, respectively, as multiplets due to spin coupling with $^{195}$Pt and $^{31}$P nuclei.

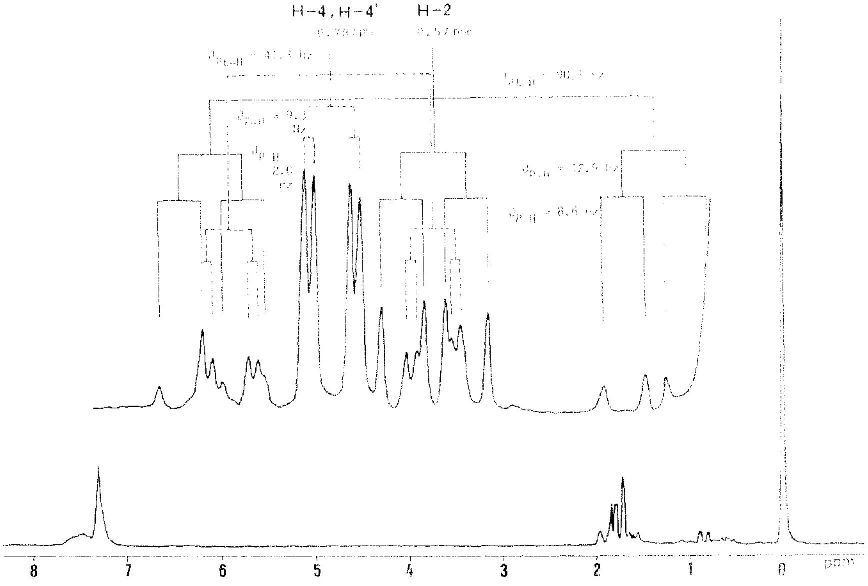
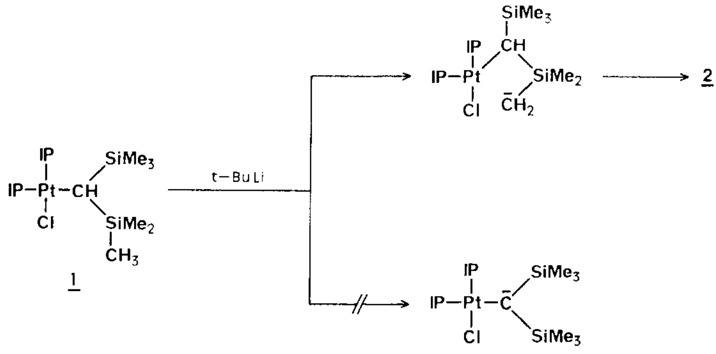


Fig. 1. $^1$H NMR spectrum of complex 2 in CDCl$_3$.

The formation of the platinacycle can be reasonably explained by intramolecular nucleophilic attack of an Si-stabilized carbanion generated at the less-hindered terminal methyl group on the platinum(II) center (Scheme 1). Because of the steric bulk of t-butyllithium, the abstraction of a proton from the $\alpha$-carbon, where thermodynamically a more stable carbanion should be generated, is prohibited.



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