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Preliminary communication

A THREE-MEMBERED RING FORMED THROUGH INTERNAL METALLATION IN A DIPHENYLMETHYLPHOSPHINE—PLATINUM(II) COMPLEX

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Summary

Prolonged treatment of *cis*-$(MePh_2P)_2PtCl_2$ with a large excess of 1-Li-2-C_6H_5-1,2-$B_{10}C_2H_{10}$ in ether gives the internally metallated complex *cis*-1-[$(MePh_2P)$-$Pt(PCH_2Ph_2)$]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$) in which a methyl group of one coordinated phosphine is involved in the ring formation.

In previous papers [1, 2] we reported that the reaction of *trans*-L_2PtCl_2 (L = $P(C_2H_5)_3$, $P(n\text{-}C_3H_7)_3$) with lithium-carborane derivatives yields internally metallated complexes of platinum(II) containing 1,2- or 1,7-dicarba-*closo*-dodecaborane(12) bonded through metal—carbon σ bonds. These complexes were the first well established examples of intramolecular metallation involving a C—H bond of an alkyl group in trialkylphosphine metal complexes. Structural X-ray analysis showed the platinum to be coordinated via σ bond by the carboranyl group through its C(1) atom and the other three coordination positions to be occupied by two mutually *cis* P atoms of phosphine ligands and by the first carbon atom of one alkyl side group of the phosphines [3]*. These results indicate that the internal metallation gives a three-membered Pt—P—C ring rather than a four-membered ring, as we first suggested [2]. Recently, an intramolecular C—H addition in a trimethylphosphine complex of iron(0) with formation of a three-membered Fe—P—C ring has also been reported [5]. In order to extend our researches on the intramolecular metallation reactions we have investigated the chemistry of the carborane complexes of platinum(II) containing diphenylmethylphosphine ligands.

A solution of 4.5 mmol of 1-Li-2-C_6H_5-1,2-$B_{10}C_2H_{10}$ in 10 ml of diethyl ether was added dropwise to a stirred suspension of 1.5 mmol of *cis*-$(Ph_2MeP)_2$-

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*The X-ray data on the triethylphosphineplatinum(II) complex are in course of publication [4].

$PtCl_2$ in 10 ml of diethyl ether under argon at room temperature. After being stirred for 16 h, the mixture was washed with H_2O. The organic layer was separated, dried (Na_2SO_4), filtered and rotary evaporated. The pale yellow product was purified by repeated recrystallization from CH_2Cl_2/n-hexane to give white pure crystals of 1-[$(Ph_2MeP)\underline{Pt(PC}H_2Ph_2)$]-2-$C_6H_5$-1,2-($\sigma$-$B_{10}C_2H_{10}$), I, (15% yield based on *cis*-$(Ph_2MeP)_2PtCl_2$), m.p. 180—181°C. Anal. Found: C, 50.55; H, 4.86. $PtP_2B_{10}C_{34}H_{40}$ calcd.: C, 50.17; H, 4.95%. Mol. wt. Found: 810 (osmometric in 1,2-dichloroethane); calcd.: 814.

This complex react with dry HCl in benzene at room temperature to give *cis*-1-[$(Ph_2MeP)_2PtCl$]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$)*. Collectively, these results and the IR and NMR** spectroscopic data allow us to assign the structure shown in Fig. 1. Thus, the infrared spectrum (Nujol mull) exhibits, in addition to the absorption bands due to the phosphine ligands, the strong absorptions in the region 2580—2610 cm^{-1} assigned to ν(B—H) of the dicarba-*closo*-dodecaborane(12) ligand. Since no bands characteristic of *ortho*-disubstituted phenyl rings [6] are observed, internal metallation through an *ortho*-C—H bond of one phenyl side group can be ruled out.

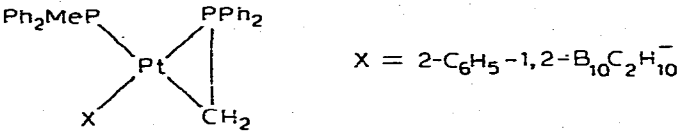

Fig. 1.

The ^1H NMR spectrum of I at 60 MHz in $CDCl_3$ (TMS internal) shows two doublets of relative total intensities 3/2 centred at τ 7.92 ppm (J(PH) 8.5 Hz) and τ 9.20 ppm (J(PH) 9.5 Hz) which are assigned to the CH_3 protons of one phosphine ligand and to the CH_2 protons of the other "metallated" phosphine, respectively. These signals are flanked by their corresponding satellites due to coupling with the platinum-195 isotope, with J(Pt—H) values of 26.0 and 45.1 Hz at low and high field, respectively***. The ^{31}P NMR spectrum at 24.28 MHz in $CDCl_3$ exhibits two doublets of relative total intensities 1/1 centred at δ −7.9 and δ +17.7 ppm (shifts relative to external 85% H_3PO_4) with J(P—P) 31 Hz, indicating that the phosphine ligands are in mutual *cis* positions. Each main peak of the ^{31}P resonances show coupling to platinum with J(Pt—P) values of 3298 and 1641 Hz at low and high field, respectively. These phosphorus resonances can be compared with those exhibited by the corresponding and structurally well-defined complex *cis*-$(n\text{-}Pr_3P)\underline{Pt[P(C}HCH_2CH_3)(n\text{-}Pr)_2]$($\sigma$-carb), II [3]. The ^{31}P NMR spectrum of II ($CDCl_3$ solution) shows two doublets of relative total intensities 1/1 centred at δ −8.1 and δ +28.0 ppm (J(PP) 29 Hz) with their corresponding pairs of satellites due to the ^{195}Pt splitting with J(Pt—P) values of 3073 and 1686 Hz at low and high field, respectively.

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[*] The chlorocarborane derivative was identified by comparison with an authentic sample prepared otherwise: unpublished data.

[**] The NMR spectra were obtained with WP-60 FTNMR and HFX-90 Bruker spectrometers. ^1H chemical shifts vs. TMS are ± 0.01 ppm; J(Pt—H) and J(P—H) are ± 0.2 Hz. ^{31}P chemical shifts vs. H_3PO_4 are ± 0.1 ppm; J(P—P) and J(Pt—P) are ± 1 Hz.

[***] At 90 MHz in CH_2Cl_2 an identical ^1H NMR pattern was obtained.

Our results show that a bulky ligand such as the carborane promotes internal metal—carbon bond formation in platinum(II)—tertiary phosphine complexes and confirm that the formation of a three-membered Pt—P—C ring is much favoured.

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