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Preliminary communication

TRANSITION METAL—CARBON BONDS

XXXIX*. *Dihapto* {(8-METHYLENE)-1-NAPHTHYL}BIS(TRIPHENYLPHOSPHINE)PLATINUM(II)

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Summary

The preparation of *dihapto* {(8-methylene)-1-naphthyl}bis(triphenylphosphine)platinum(II), involving an internal metallation reaction, is described.

There are many examples of the internal C-metallation of neutral N-, P- or As-donor ligands to give chelates [2,3]. We have now investigated the possibility of the internal metallation of a C-donor radical (formally anionic) ligand and describe the synthesis of the title compound. We chose to metallate in the 8- or *peri*-position of a naphthyl group since this position has been shown to be readily metallated by platinum(II) or iridium(III) [3].

Chloro(1-naphthylmethyl)bis(triphenylphosphine)platinum(II) was synthesised by the oxidative addition of (1-chloromethyl)naphthalene to [Pt(stilbene)$(PPh_3)_2$]. The product had a second order methylene resonance pattern in the ^1H NMR spectrum probably indicative of a *cis*-stereochemistry for the two triphenylphosphine ligands [4—6]. We were unable to effect internal metallation at the *peri*-position by heating this complex: the decomposition temperature was high (> 210°) and mixtures were formed. However it has been shown that a methyl group directly bonded to platinum(II) promotes internal metallation and is itself lost as methane. We therefore converted the chloro complex to the methyl complex by treatment with methyllithium. On heating in toluene solution or on melting, the methyl complex was smoothly converted into the title compound (I) containing a metal—carbon bonded diradical (or dianionic ligand). The methyl complex showed a very low-field resonance at τ 1.45 characteristic of a *peri*-hydrogen and this was missing from the ^1H NMR pattern of the title compound. This showed that metallation had occurred at the 8- (or *peri*-)position and not at the 2- position.

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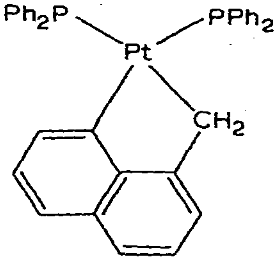
[*] For part XXXVIII see ref. 1.



(I)

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are corrected. Infrared spectra (500—200 cm^{-1}) were recorded on a Grubb—Parsons D.B.3/D.N.2. spectrophotometer. ^{1}H NMR spectra were recorded in deuteriochloroform at 60 MHz on a Perkin—Elmer R12A spectrometer.

Stilbenebis(triphenylphosphine)platinum(0) was prepared by a literature method.

Chloro(1-naphthylmethyl)bis(triphenylphosphine)platinum(II). Stilbenebis(triphenylphosphine)platinum(0) (0.681 g, 0.76 mmole) was warmed with a solution of (1-chloromethyl)naphthalene (0.176 g, 1.00 mmole) in benzene (5 ml) for 30 min. The resultant yellow solution was diluted with n-heptane (5 ml) to give the product as white prisms (0.673 g; 99% yield); m.p. 217—220° (decomp.) (Found: C, 63.1; H, 4.4; Cl, 3.5. $C_{47}H_{39}ClP_2Pt$ calcd. C, 62.95; H, 4.4; Cl, 3.7%). IR (Nujol mull) ν(Pt—Cl) 277s·cm^{-1}, τ (CH_2) 7.44, ^2J(Pt—H) 90 Hz.

Methyl(1-naphthylmethyl)bis(triphenylphosphine)platinum(II). A suspension of chloro(1-naphthylmethyl)bis(triphenylphosphine)platinum(II) (0.60 g, 0.67 mmol) in dry benzene (10 ml) was treated with methyllithium in ether (1 ml, 2.4 mmol) and the resultant yellow solution was stirred for 1 h. After hydrolysis with water the product was obtained as white needles from benzene/n-heptane (Yield 0.40 g, 69%); m.p. 146—156° (with evolution of gas). (Found C, 65.45, H, 5.0. $C_{48}H_{42}PtP_2$ calcd. C, 65.75, H, 4.8%). τ(CH_2) 7.16, ^2J(Pt—H) 99 Hz, τ(CH_3) 10.06, ^2J(Pt—H) 67 Hz.

Dihapto{(8-methylene)-1-naphthyl}bis(triphenylphosphine)platinum(II) (Benzene solvate). Methyl(1-naphthylmethyl)bis(triphenylphosphine)platinum(II) (0.244 g, 0.279 mmol) was heated under reflux in toluene (15 ml) for 1 h. The resultant orange solution was evaporated to dryness and the crude product recrystallised from benzene/n-heptane to give the product as needles (0.169 g, 67%); m.p. 238 — 240°. (Found C, 66.8, H, 4.65. $C_{47}H_{38}P_2Pt\cdot\frac{1}{2}C_6H_6$ calcd. C, 66.8, H, 4.6%) τ(CH_2) 6.97, ^2J(Pt—H) 67 Hz.

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