Journal of Organometallic Chemistry, 269 (1984) 285–293
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

NEOPENTYL COMPLEXES OF PALLADIUM

P. DIVERSI *, D. FASCE and R. SANTINI

Istituto di Chimica Organica Industriale, Università di Pisa, Via Risorgimento 35, 56100 Pisa (Italy)

(Received March 8th, 1984)

Summary

New dineopentyl complexes of palladium, with the formula $[Pd(CH_2CMe_3)_2L_2]$ (L_2 = dppe, bipy; L = PMe_2Ph) have been prepared by the alkylation of the corresponding dichlorides with $Mg(CH_2CMe_3)Br$ or $LiCH_2CMe_3$. Thermal decomposition of these complexes in solution yields 2,2,5,5-tetramethylhexane. The reactions of these compounds with CO and with some electrophiles (Ph_3C^+, $PhCH_2Br$, HCl) have been investigated. The reaction with CO produces dineopentyl ketone (when L_2 = dppe; L = PMe_2Ph) or promotes rapid decomposition to 2,2,5,5-tetramethylhexane (when L_2 = bipy). The electrophiles (E^+) attack the neopentyl ligand to eliminate ECH_2CMe_3. In the reaction of $[Pd(CH_2CMe_3)_2(bipy)]$ with $PhCH_2Br$, $[PdBr(CH_2CMe_3)(bip)]$ has been isolated.

A palladacyclic analogue of these systems, $[Pd(CH_2CMe_2CMe_2CH_2)(dppe)]$, has been prepared by the alkylation of $[PdCl_2(dppe)]$ with $Li(CH_2CMe_2CMe_2CH_2)Li$.

Introduction

Recently, interest has been shown in the reactions of transition metals with neopentyl systems. This is partly because transition metal neopentyl complexes have exhibited unusual chemical transformations, such as α- or γ-hydrogen elimination reactions, to yield alkylidene complexes [1] or metallacyclobutane derivatives [2], respectively.

Following our studies on palladacycle chemistry [3], and being attracted by the possibility of preparing palladacyclobutane derivatives via a cyclometallation reaction of the corresponding bis-neopentyl metal complexes, we became involved in the study of palladium dineopentyls. So far the only reports on these systems are an unsuccessful attempt to prepare $[Pd(CH_2CMe_3)_2(PEt_3)_2]$ [4] and some reactions between $PdCl_2$ and neopentyl Grignard reagents [5]. This paper gives details of the synthesis and some reactions of a series of neopentyl palladium complexes, and of a palladacyclopentane analogue.

* To whom correspondence should be addressed.

0022-328X/84/$03.00

Results

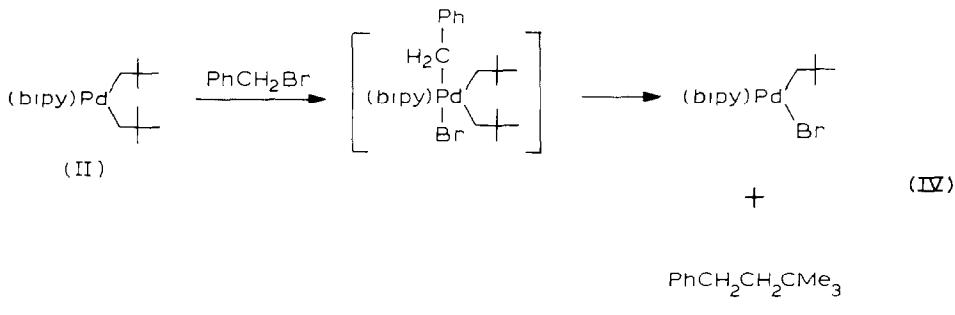
Preparation of neopentyl derivatives

By reaction of the dichlorides $[PdCl_2L_2]$ (L_2 = dppe, bipy; L = PMe_2Ph) with an excess of neopentylmagnesium bromide or neopentyllithium in ether, the new dineopentylpalladium derivatives $L_2Pd(CH_2CMe_3)_2$ (I, L_2 = dppe; II, L_2 = bipy; III, L = PMe_2Ph) are obtained in good yields as crystalline solids.

Compound III is much more unstable in solution than I and II, and care must be used during its preparation to carry out the alkylation and the subsequent work-up at temperatures lower than $-10\,^{\circ}C$ and to add a little free phosphine in order to avoid fast decomposition. The ^1H NMR spectrum of III, even at low temperatures, does not exhibit well-resolved signals as in the case of I and II, and a positive assignment of its configuration is precluded. In fact the NMR pattern of all of the methyl groups consists of a single broad peak with no evidence of fine structure. This may be because the phosphine ligands may be undergoing rapid exchange and both the methyl groups of the phosphine and of the alkyl ligand resonate at very similar frequencies. However the fact that the alkylation of bis(tertiary phosphine)palladium dihalides with an excess of an alkyllithium is known to give *cis*-dialkylpalladium complexes [6], makes it most likely to have a *cis*-configuration.

We were also interested to see whether mono-alkylated products could be prepared from palladium dichlorides $[PdCl_2L_2]$ by treatment with strictly stoicheiometric amounts (1/1) of the alkylating agent. Under these conditions, or even by using a lower mol ratio of alkylating agent to palladium (0.5/1), we have isolated the dineopentyl derivative, along with much unconverted starting material. Only in the case of the alkylation of $[PdCl_2(bipy)]$ have traces of the monoalkylated compound been observed spectroscopically. A possible explanation for these findings could be the fact that the compounds $[PdCl_2L_2]$ are all virtually insoluble in diethyl ether. Consequently, the alkylating reagent is always in excess in solution during the alkylation. The preparation of mononeopentylpalladium derivatives was also attempted by cleavage reactions of the dialkyls: reaction of I in solution with one equivalent of hydrochloric acid or bromine failed to afford the expected alkylhalo derivative, but gave the corresponding palladium dihalide in slightly less than 50% yield and unchanged I.

We have finally found that a way to circumvent this difficulty is to treat the dineopentyl system with benzyl bromide. Indeed, reaction of II with a slight excess of benzyl bromide resulted in the slow formation of $[PdBr(CH_2CMe_3)(bipy)]$ (IV). The reaction has been studied by ^1H NMR spectroscopy by following the disappearance of the methyl signals of II as the reaction progresses. After 30 h at room



temperature the dialkyl II was almost quantitatively converted into IV. This reaction may be explained by oxidative addition of benzyl bromide to the electron-rich palladium(II) dialkyl, giving an unstable palladium(IV) intermediate, which reductively eliminates $PhCH_2CH_2CMe_3$. A similar mechanism has been postulated for other oxidatively-induced reductive elimination reactions from dialkylpalladium complexes [7].

The analogous reaction between I and benzyl bromide did not yield the expected monoalkyl derivative.

Chemical studies

(a) Thermal decomposition. Solutions of compounds I–III in aromatic solvents are not very stable : I and II decompose slowly at room temperature, while III decomposes rapidly even at 0 °C. The thermolysis has been studied by ^1H NMR spectroscopy in benzene solutions and in all cases the main product is 2,2,5,5-tetramethylhexane. No signal attributable to the formation of a palladacyclobutane derivative has been detected.

(b) Reaction with trityl tetrafluoroborate. Compound I reacts rapidly with one or two equivalents of trityl tetrafluoroborate to give a yellow solution from which, by the addition of ether, a brown-yellow solid is precipitated. This compound contains the BF_4^- group and the dppe ligand and has not been further investigated. From the ethereal solution, white crystals of $Ph_3CCH_2CMe_3$ have been isolated. Thus the reaction of I with Ph_3C^+ results in electrophilic cleavage of the neopentyl group rather than abstraction of hydride. The unidentified inorganic species is probably a dicationic species in which the vacant coordination sites, created by reaction with Ph_3C^+, become occupied by solvent molecules. A few examples of the attack by Ph_3C^+ on the carbon atom of metal-bonded alkyl groups are reported in the literature [8–10].

(c) Reaction with carbon monoxide. $[Pd(CH_2CMe_3)_2(dppe)]$ reacts smoothly with CO in benzene or pentane under mild conditions (room temperature, 1 atm) to give a golden-yellow solution. Monitoring the reaction in C_6D_6 by means of ^1H NMR spectroscopy shows the formation of dineopentyl ketone [11] (δ 1.99 (singlet, CH_2, 2 H) and 0.97 ppm (singlet, CH_3, 9 H)), which is complete in ca. 20 h; no dineopentyl diketone has been observed. The golden-yellow solution is unstable in the absence of carbon monoxide, but can be evaporated under a stream of CO to leave a solid residue (IR (KBr disc): 1840, 1825 cm^{-1}). By comparison with $[Pd_3(CO)_3(PPh_3)_4]$ [12] which shows very similar IR bands, the structure $[Pd_3(CO)_3(dppe)_2]$ can be tentatively assigned. However, purification and full characterization of the complex was unsuccessful.

$[Pd(CH_2CMe_3)_2(PMe_2Ph)_2]$ reacts quickly with carbon monoxide (1 atm, −20 °C) to yield, quantitatively, dineopentyl ketone (80%) and 2,2,5,5-tetramethylhexane (20%) after 2 h. The latter compound could arise from the thermal decomposition of some unreacted III, which occurs when the temperature is raised.

It is interesting to note that in the reaction of complexes of the formula $[PdR_2(dppe)]$ with CO only thermal decomposition products are obtained when R = Me, Et; but in the case where R = n-Pr some ketone is formed, together with propane [13]. The palladacyclopentane $[Pd(CH_2CH_2CH_2CH_2)(dppe)]$ also does not insert CO, and gives butenes as the only products [3]. The influence on the carbonylation reaction of the nature of the migrating group has already been

reported in the literature and, as Hoffman has pointed out, the trend toward greater ease of migration with increasing chain length seems to reflect both electronegativity effects and decreasing bond strength in the initial reactants [14].

$[Pd(CH_2CMe_3)_2(bipy)]$ behaves quite differently on reaction with CO. Indeed II at room temperature (1 h), or even at $-40\,^{\circ}C$ (3 h), under 1 atm of CO decomposes completely to 2,2,5,5-tetramethylhexane and palladium metal. This is a remarkable acceleration of the rate of thermal decomposition of II, if one considers that a benzene solution of II remains almost unchanged after 2 days at $60\,^{\circ}C$.

A similar effect has been observed in a study of the reductive elimination of R–R from $[NiR_2(bipy)]$ in the presence of π-acid ligands [15], and it has been related to the removal of electronic charge from the metal on coordination. This should be reflected in a less polar metal–carbon bond and in a lower energy barrier for the reductive elimination reaction.

Preparation of a β,β'-tetramethylpalladacyclopentane

We have prepared a cyclic analogue of the dineopentylpalladium compound I, in order to compare some of its properties with those of I and of $[Pd(CH_2CH_2CH_2CH_2)(dppe)]$. By treatment of $[PdCl_2(dppe)]$ with an excess of $Li(CH_2CMe_2CMe_2CH_2)Li$ in diethyl ether, $[Pd(CH_2CMe_2CMe_2CH_2)(dppe)]$ (V) has been isolated in 34% yield. V is the first isolated metallacyclopentane derivative in which both of the α-carbon atoms are of the neopentyl type: a similar reaction between WCl_6 and $XMg(CH_2CMe_2CMe_2CH_2)MgX$ has been reported in the literature but no products have been isolated [16]. V is considerably more robust with respect to thermolysis than either the dineopentyl derivative I or the unsubstituted palladacyclopentane analogue. The major organic product of the thermal decomposition in solution is 1,1,2,2-tetramethylcyclobutane. The reaction has been monitored by ^1H NMR spectroscopy, by following the disappearance of the signals of the methyl groups of V, and it is complete after 200 h at $20\,^{\circ}C$ or after 22 h at $50\,^{\circ}C$. As in the case of the thermolysis of I, the reductive elimination reaction is the predominant decomposition process. It is interesting to note that, on treatment with trityl tetrafluoroborate at room temperature, V decomposes almost immediately to give 1,1,2,2-tetramethylcyclobutane. The acceleration of the rate of reductive elimination is not unusual in the case of the addition of reagents such as benzyl bromide or methyl iodide, which can add oxidatively to palladium(II) dialkyls, but has no precedent in the case of the trityl cation.

Discussion

It is generally accepted that although palladium in its dialkyl complexes is formally in the 2+ oxidation state, it can be considered electron-rich due to the presence of two alkyl groups and the absence of strong acceptor ligands [7]. This should be particularly true for the dialkyls I–III, and of V, where the highly electron-releasing neopentyl ligands are present, and this accounts for the facile reductive elimination reaction we have observed in these systems: as has been pointed out for d^8 systems by Whitesides [17] and Hoffmann [18], the more strongly electron-donating is the leaving group R, the more rapid is the reductive elimination of R–R. This tendency to decompose via a reductive elimination reaction, in the case of the dineopentylpalladiums, is high enough to prevail over other modes of

decomposition: indeed no γ-hydrogen elimination reaction to give palladacyclobutanes has been observed. This is not in contrast with the formation of platinacyclobutanes via γ-hydrogen elimination from dineopentylplatinums, because dialkylplatinum(II) compounds apparently do not eliminate R–R readily and therefore a hydrogen elimination, where feasible, can be observed [18]. Another consequence of the high electron charge on palladium in these systems is the easy carbonylation, to give dineopentyl ketone. We have already compared the reactivity of I with the inertness observed in the carbonylation of the analogue, $[PdMe_2(dppe)]$. This may be because the more electron-rich palladium atom in I should coordinate CO more strongly in the postulated first step, and because the labilization of the palladium–carbon bond in the alkyl migration step should become easier [14].

Finally, it is interesting to examine the behaviour of I and of the cyclic analogue V in the reaction with the trityl cation. It is known that oxidizing electrophiles E^+ can promote, in addition to the formation of R–E, reductive elimination reactions to give R–R [19]. Such observations have been made, for instance, in the case of the decomposition of diarylnickel(II) compounds [20], and, more recently, also in the case of rhodium(IV) derivatives [19].

By analogy, one could think of an electron transfer from I and V to Ph_3C^+, followed by the loss of the neopentyl group as a radical and capture by $Ph_3C^{\cdot}$, to give $Ph_3CCH_2CMe_3$ in the case of I, or by a reductive elimination reaction of R–R in the case of V. The different course of the reaction in the two cases could be related to the different ability of the alkyl ligands to give intermolecular or intramolecular C–C bond formation.

Experimental

All manipulations and reactions were carried out under an atmosphere of dinitrogen or argon. Solvents were dried in the usual manner, and distilled and stored under an inert atmosphere. Neopentyllithium [21] and neopentylmagnesium bromide [5] were prepared as described. $[PdCl_2(dppe)]$ [22], $[PdCl_2(bipy)]$ [23] and $[PdCl_2(PMe_2Ph)_2]$ [24] were prepared according to literature procedures. ^1H NMR spectra were recorded using a Varian T60 or a Varian XL100 spectrometer, and ^{13}C NMR spectra using the Varian XL100 instrument. Microanalyses were by the Laboratorio di Microanalisi of Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. IR spectra were obtained on a Perkin–Elmer 225 instrument, and the mass spectra with a Varian MAT-CH7 spectrometer.

Preparation of $[Pd(CH_2CMe_3)_2(dppe)]$ (I)

A mixture of $[PdCl_2(dppe)]$ (0.478 g, 0.83 mmol) and Et_2O (30 ml) at 0 °C was treated dropwise over 1 h with 9.22 ml (4.15 mmol) of an ethereal solution of neopentylmagnesium bromide. The mixture was then stirred at room temperature for 3 h, and hydrolyzed at 0 °C with water (1 ml). The ethereal solution and the combined ethereal extracts were dried over anhydrous sodium sulphate, and the solvent was removed under vacuum. The solid residue was extracted with pentane (40 ml) and after filtration, the pentane solution was cooled at −78 °C overnight to give white crystals of $[Pd(CH_2CMe_3)_2(dppe)]$ (0.275 g, 51% yield), m.p. 117–118 °C(dec.). Anal. Found: C, 67.95; H, 7.61. $C_{36}H_{46}P_2Pd$ calcd.: C, 66.82; H, 7.16%. ^1H NMR (δ, ppm, C_6D_6): 1.53 (s, 18, CH_3), 2.14 (d, J(P–H) 16 Hz, 4,

P-CH_2), 2.64 (dd, J(P-H) 11.25 and 6 Hz, 4, Pd-CH_2), 6.81-7.35 (m, 20, C_6H_5). ^{13}C NMR (δ, ppm, C_6D_6): 24.31 (t, J(P-C) 17.6 Hz, Pd-CH_2), 35.72 (d, J(P-C) 8.5 Hz, CH_3), 34.53 (d, J(P-C) 133.2 Hz, P-CH_2), 128.17, 128.52, 129.62, 133.3, 133.76 (aromatic carbons); C(β) not observed.

Preparation of [Pd(CH_2CMe_3)$_2$(bipy)] (II)

To a suspension of 0.333 g (1 mmol) of [$PdCl_2$(bipy)] in 10 ml of ether, a solution of $LiCH_2CMe_3$ (0.199 g, 2.55 mmol) in diethyl ether (18 ml) was added dropwise (1 h, −78 °C). The mixture was stirred for 1 h, and was then allowed to warm to room temperature. Stirring was continued for 1 h at this temperature. The deep-red mixture was hydrolyzed at 0 °C with water (5 ml) and the organic layer separated and dried over anhydrous sodium sulphate. The red solution was evaporated under vacuum and the solid residue extracted with pentane (40 ml). The extracts were filtered and concentrated, then cooled to −40 °C to give red-orange crystals (0.180 g, 45% yield), m.p. 115 °C. Anal. Found: C, 58.97; H, 7.22. $C_{20}H_{30}N_2Pd$ calcd.: C, 59.33; H, 7.46%. ^1H NMR (δ, ppm, C_6D_6): 1.64 (s, 18, CH_3), 2.25 (s, 4, CH_2), 6.59, 6.97, 9.0 (m, 8, bip).

Preparation of [Pd(CH_2CMe_3)$_2$(PMe_2Ph)$_2$] (III)

[$PdCl_2$(PMe_2Ph)$_2$] (0.35 g, 0.77 mmol) in diethyl ether (7 ml), containing a few drops of PMe_2Ph, was reacted at −70 °C with 0.163 g (1.75 mmol) of $LiCH_2CMe_3$. The mixture was then stirred at −70 °C for 5 h. The solvent was removed at −10 °C under reduced pressure. The solid residue was extracted with 40 ml of cold pentane at −10 °C, and the solution quickly filtered and concentrated to 10 ml, and maintained at −25 °C overnight to give white crystals (0.2 g, 50% yield). Anal. Found: C, 59.23; H, 8.49. $C_{26}H_{44}P_2Pd$ calcd.: C, 59.50; H, 8.39%. ^1H NMR (δ, ppm, CD_3COCD_3, −20 °C): 1.05 (bs, 30, CH_3), 1.5 (m, 4, CH_2), 7.4 (m, 10, C_6H_5).

Preparation of [PdBr(CH_2CMe_3)(bipy)] (IV)

To [Pd(CH_2CMe_3)$_2$(bip)] (0.106 g, 0.26 mmol) in benzene (6 ml) a solution of benzyl bromide (0.044 g, 0.27 mmol) in benzene (3 ml) was added, and the resulting solution was kept at 40 °C for 4 days. The solvent was removed under reduced pressure and the resulting solid was extracted several times with pentane to leave a yellow-orange solid (0.095 g, 90%). Anal. Found: C, 44.20; H, 4.33, N, 6.41. $C_{15}H_{18}BrN_2Pd$ calcd.: C, 43.66; H, 4.39; N, 6.78%. ^1H NMR (δ, ppm, $CDCl_3$): 1.16 (s, 9, CH_3), 2.23 (s, 2, CH_2), 7.16-9.66 (m, 8, bipy).

Thermal decomposition of the dineopentylpalladiums

A solution of the freshly crystallized dineopentylpalladium derivative in C_6D_6 was heated at the desired temperature in an NMR tube until decomposition occurred and the solution turned black. The solution was analyzed by ^1H NMR: δ 0.87 and 1.17 (2,2,5,5-tetramethylhexane).

Reaction of I with trityl tetrafluoroborate

A solution of 0.088 g (0.135 mmol) of I in 3 ml of CH_2Cl_2 was treated dropwise with 0.089 g (0.27 mmol) of [Ph_3C][BF_4] in 6 ml of CH_2Cl_2. After 5 min stirring, the yellow solution was added to diethyl ether, and a brown-yellow solid precipitated out. The solid was filtered off, and the solvent was removed from the filtrate under

vacuum. The residue was dissolved in a small amount of CH_2Cl_2 and applied to a preparative silica gel TLC plate, which was then eluted with hexane. A band was developed, which was isolated and extracted with CH_2Cl_2. After removal of the solvent, white crystals of $Ph_3CCH_2CMe_3$ were obtained. ^1H NMR (δ, ppm, $CDCl_3$): 0.7 (s, 9, CH_3), 2.93 (s, 2, CH_2), 7.15–7.8 (m, 15, C_6H_5). MS: m/e 314 (M^+), 243 ($M^+ - C_5H_{11}$).

Reaction of dineopentylpalladium complexes with carbon monoxide

To a pre-evacuated Schlenk tube containing 0.1 g (0.15 mmol) of I in pentane (30 ml), frozen at −70 °C, carbon monoxide was introduced. The temperature was raised and the solution was stirred at room temperature for 14 h, the colour changing from pale yellow to golden yellow. The volatile products were distilled under vacuum and collected: after slow evaporation under a stream of nitrogen an oily residue remained, which was identified by ^1H NMR and IR spectroscopy as dineopentyl ketone. ^1H NMR (δ, ppm, $CDCl_3$): 2.3 (s, 4, CH_2), 1.0 (s, 18, Me). IR (pentane): ν(C=O) 1715 cm^{-1}. The residue of the distillation was extracted with ether under CO and the filtered solution was evaporated to dryness under a stream of CO. IR (Nujol): ν(C=O) 1840, 1825 cm^{-1}.

The similar reactions of II with CO yielded 2,2,5,5-tetramethylhexane, and the reaction of III yielded a mixture of dineopentyl ketone (80%) and 2,2,5,5-tetramethylhexane (20%).

Preparation of $Li(CH_2CMe_2CMe_2CH_2)Li$

$HOCH_2CMe_2CMe_2CH_2OH$ was prepared by reduction of the corresponding diacid (9.8 g) [25] in THF (70 ml) with $LiAlH_4$ (20 g) in THF (50 ml) (with refluxing for 25 h, then stirring at room temperature for 15 h), followed by hydrolysis with H_2O (10 ml), 15% NaOH (10 ml) and H_2O (30 ml), extraction with ether of the solid formed, and evaporation of the solvent to dryness. 6.4 g of the dialcohol (70% yield) were obtained. ^1H NMR (δ, ppm, $CDCl_3$): 0.9 (s, 12, CH_3), 3.42 (s, 4, CH_2), 4.8 (m, 2, OH).

$CH_3S(O)_2OCH_2CMe_2CMe_2O(O)_2SCH_3$ was prepared by reacting the dialcohol (3.14 g, 21.5 mmol) in pyridine (10 ml) with $CH_3S(O)_2Cl$ (4 ml, 43 mmol) in pyridine (20 ml) at 0 °C. The mixture was stirred at 0 °C for 12 h, then at room temperature overnight. The mixture was extracted with chloroform, and the extracts were washed with diluted hydrochloric acid and water. The organic layer was dried over Na_2SO_4, and then the solvent was removed at reduced pressure, to give 4.9 g (75.4% yield) of the product. ^1H NMR (δ, ppm, $CDCl_3$): 1.1 (s, 12, CH_3), 3.1 (s, 6, $CH_3S(O)_2$), 4.12 (s, 4, CH_2).

$ClCH_2CMe_2CMe_2CH_2Cl$ was prepared [16] by heating the dimesylate (2.45 g, 8.1 mmol) and LiCl (3.12 g, 73.7 mmol) in hexamethylphosphoric triamide (36 ml) at 130 °C for 24 h. The solution was poured into water (80 ml), and extracted with pentane (40 ml). The pentane extracts were washed with water and dried over Mg_2SO_4. After removal of the solvent, the dichloride, 1.36 g (92% yield), was obtained. ^1H NMR (δ, ppm, CCl_4): 1.08 (s, 12, CH_3), 3.58 (s, 4, CH_2).

$Li(CH_2CMe_2CMe_2CH_2)Li$ was prepared by reacting at 0 °C under argon for 24 h, lithium chips (0.8 g, 115 mmol) with the dichloride (0.548 g, 2.99 mmol) in diethyl ether (18 ml). The mixture was filtered, to give a solution containing 1.1 mmol of the dilithio derivative (37% yield).

Preparation of [Pd(CH$_2$CMe$_2$CMe$_2$CH$_2$)(dppe)] (V)

To a suspension of [PdCl$_2$(dppe)] (0.23 g, 0.4 mmol) in diethyl ether (20 ml), a solution of Li(CH$_2$CMe$_2$CMe$_2$CH$_2$)Li (1.2 mmol, 0.055 *M*) in ether (21.8 ml) was added dropwise (−70 °C, 30 min). The mixture was stirred at this temperature for 1 h, and was then warmed to room temperature and stirred for 1 h. The mixture was hydrolyzed at 0 °C, and the ethereal layer and the combined ether extracts were separated, dried over anhydrous Na_2SO_4, and evaporated to dryness under vacuum. The residue was extracted with toluene and filtered. To the filtrate, pentane (20 ml) was added, and the solution cooled to −30 °C; the resulting white crystals were separated off, washed with pentane and dried (0.074 g, 34% yield). Anal. Found: C, 66.87; H, 6.64. $C_{34}H_{40}P_2Pd$ calcd.: C, 66.23; H, 6.49%. ^{1}H NMR (δ, ppm, C_6D_6): 1.52 (s, 12, CH_3), 1.97 (d, *J*(P–H) 18 Hz, 4, (P–CH_2), 2.7 (t, *J*(P–H) 6 Hz, 4, Pd–CH_2), 7–7.9 (m, 20, C_6H_5). ^{13}C NMR (δ, ppm, C_6D_6): 27.16 (t, *J*(P–C) 21 Hz, Pd–C), 29.02 (s, CH_3), 46.92, 50.47 (dd, *J*(P–C) 89 Hz, *J*(P–C) 7 Hz, P–CH_2, 48.02 (m, *J*(P–C) 3 Hz, CMe_2), 126.82–135.51 (m, C_6H_5).

Thermal decomposition of V

An NMR tube was charged with V (0.030 g) and C_6D_6 (0.5 ml), and thermostatted at the desired temperature. ^{1}H NMR (δ, ppm): 0.97 (s, 12, CH_3), 1.62 (s, 4, CH_2); these absorptions coinciding with those reported in the literature for 1,1,2,2-tetramethylcyclobutane [26].

Reaction of V with trityl tetrafluoroborate

An NMR tube was charged with V in $CDCl_3$. One equivalent of [Ph_3C][BF_4] was added. After a shaking, the tube was quickly transferred to an NMR probe. The ^{1}H NMR spectrum showed the formation of 1,1,2,2-tetramethylcyclobutane. The content of the tube was applied to a silica gel preparative TLC plate. Elution with pentane gave a band, from which 1,1,2,2-tetramethylcyclobutane was isolated, m.p. 40 °C [26].

Acknowledgement

The authors wish to thank the Ministero della Pubblica Istruzione (Rome) for financial support.

References

1 R.R. Schrock, Acc. Chem. Res., 12 (1979) 98.
2 P. Foley, R. DiCosimo and G.M Whitesides, J Am. Chem. Soc., 102 (1980) 6713.
3 P. Diversi, G. Ingrosso, A. Lucherini and S. Murtas, J. Chem. Soc., Dalton Trans., (1980) 1633
4 B. Wozniak, J.D. Ruddick and G. Wilkinson, J. Chem. Soc A, (1971) 3116
5 M. Tamura and J.K. Kochi, Bull. Chem. Soc. Jpn., 44 (1971) 3063.
6 H. Nakazawa, F. Ozawa and A. Yamamoto, Organometallics, 2 (1983) 241.
7 D. Milstein and J.K. Stille, J. Am. Chem. Soc., 101 (1979) 4981; A. Gillie and J.K. Stille, J. Am Chem. Soc., 102 (1980) 4933; A. Moravskiy and J.K Stille, J Am Chem. Soc., 103 (1981) 4182.
8 R.R. Schrock and P.R. Sharp, J. Am. Chem. Soc., 100 (1978) 2389.
9 P.J. Harris, S.A.R. Knox, R.J. McKinney and F G.A. Stone, J. Chem. Soc. Dalton Trans., (1978) 1009.
10 A. Sanders, T. Bauch, C.V Magatti, C Lorenc and W.P. Giering, J. Organomet. Chem., 107 (1976) 359
11 J. Ciabattoni and E.C Nathan III, J. Am. Chem. Soc., 91 (1969) 4766.

12 K. Kudo, M. Hidai and Y. Uchida, J. Organomet. Chem., 33 (1971) 393.
13 T. Ito, H. Tsuchiya and A. Yamamoto, Bull. Chem. Soc. Jpn., 50 (1977) 1319.
14 H. Berke and R Hoffmann, J. Am. Chem Soc., 100 (1978) 7224.
15 B. Akermark, H. Johansen, B. Roos and U. Wahlgren, J. Am. Chem. Soc., 101 (1979) 5876.
16 J. Levisalles, H. Rudler and D. Villemin, J. Organomet. Chem., 193 (1980) 69.
17 A.C. Balazs, K.H. Johnson and G.M. Whitesides, Inorg. Chem., 21 (1982) 2162.
18 K. Tatsumi, R. Hoffmann, A. Yamamoto and J.K. Stille, Bull. Chem. Soc. Jpn., 54 (1981) 1857.
19 A. Nutton, A.V. de Miguel, K. Isobe and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1983) 166, and refs. therein.
20 D.R. Fahey, Organomet. Chem. Rev., Sect. A, 7 (1972) 245.
21 R.R. Schrock and J.D. Fellmann, J. Am. Chem. Soc., 100 (1978) 3359.
22 A.D. Westland, J. Chem. Soc., (1965) 3060.
23 M.D. Rausch and F.E. Tibbetts, J. Organomet. Chem., 21 (1970) 492.
24 J.M. Jenkins and B.L. Shaw, J. Chem. Soc. (A), (1966) 770.
25 A.F. Bickel and W.A. Waters, Rec. Trav. Chim., 69 (1950) 1490.
26 A.J.L Beckwith and G. Mood, J. Chem. Soc., Perkin Trans. 2, (1980) 1083.