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Solvent Effects on the Metalation of Tri-*tert*-butylphosphine. Preparation and Characterization of $[\overline{\mathrm{PtPBu^t_2C(CH_3)_2CH_2}}\mathrm{Cl}]_2$ and $[\overline{\mathrm{PdPBu^t_2C(CH_3)_2CH_2}}\mathrm{Cl}]_2$

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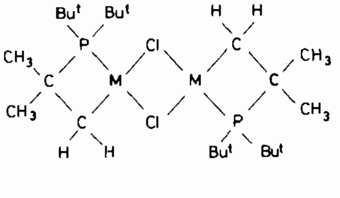
Although intramolecular metalation of *ortho*-carbon–hydrogen bonds of tertiary phosphines containing aryl substituents has been extensively studied [1], only a few examples of intramolecular metalation of purely aliphatic phosphines are known [2–5]. Recently, we reported [2] that tri-*tert*-butylphosphine undergoes facile metalation during its reaction with platinum(II) or palladium(II) chloride, forming the internally metalated complexes, *trans*-$\overline{\mathrm{M[PBu^t_2C(CH_3)_2CH_2}}\mathrm{]PBu^t_3Cl}$ (*1*, M = Pt; *2*, M = Pd). Further investigations have now shown that the course of the reaction of the phosphine and Pt(II) or Pd(II) is markedly affected by the nature of the solvent. As reported earlier, in benzene tri-*tert*-butylphosphine reacts with $\mathrm{PtCl_2(NCPh)_2}$ according to the following equation:

$$\mathrm{6PBu^t_3 + 3PtCl_2(NCPh)_2 \rightarrow 2\overline{Pt[PBu^t_2C(CH_3)_2CH_2}]PBu^t_3Cl + (Bu^t_3PH)_2PtCl_4} \qquad (1)$$

However, the hitherto unknown dimeric complex $[\overline{\mathrm{Pt(PBu^t_2C(CH_3)_2CH_2}}\mathrm{)Cl}]_2$, *3*, as well as *1* and $\mathrm{Bu^t_3PHCl}$ are obtained when the above reaction is carried out in dichloromethane.



3, M = Pt ; *4*, M = Pd

When $\mathrm{Bu^t_3P}$ and $\mathrm{PtCl_2(NCPh)_2}$ are allowed to react in equimolar amounts in dichloromethane, the complex $\mathrm{PtCl_2(PBu^t_3)(NCPh)}$, *5*, is obtained. Complex *5* is converted almost quantitatively into complex *3* when stirred in ethanol. In dichloromethane, complex *5* is converted very slowly into complex *3*, but in the presence of one mol equivalent of free $\mathrm{PBu^t_3}$, the reaction proceeds rapidly to give a mixture of *1*, *3*, and $\mathrm{Bu^t_3PHCl}$.

The following equations describe these reactions:

$$\mathrm{PBu^t_3 + PtCl_2(NCPh)_2 \rightarrow Pt(PBu^t_3)(NCPh)Cl_2 + NCPh} \qquad (2)$$

$$\mathrm{Pt(PBu^t_3)(NCPh)Cl_2 \rightarrow 1/2\,[\overline{Pt(PBu^t_2C(CH_3)_2CH_2}})Cl]_2 + HCl + NCPh} \qquad (3)$$

$$\mathrm{nPBu^t_3 + nHCl \rightarrow nBu^t_3PHCl} \qquad (4)$$

$$\mathrm{(1-n)PBu^t_3 + 1/2(1-n)[\overline{Pt(PBu^t_2C(CH_3)_2CH_2}})Cl]_2 \rightarrow (1-n)\overline{PtCl[PBu^t_2C(CH_3)_2CH_2}]PBu^t_3} \qquad (5)$$

It also appears, from the above results, that the steps represented by equations 3, 4 and 5 take place almost simultaneously. This is further supported by the fact that the ^{31}P NMR spectrum of the reaction solution of $\mathrm{Bu^t_3P}$ with $\mathrm{PtCl_2(NCPh)_2}$ in 2:1 molar ratio in $\mathrm{CH_2Cl_2}$ shows all of the signals for complexes *1*, *3* and $\mathrm{Bu^t_3PHCl}$. Also, when complex *3* is allowed to react with two mol equivalents of $\mathrm{PBu^t_3}$, complex *1* is formed (equation 6). However, when complex *1* is kept in benzene solution for several days, complex *3* is re-formed. Thus, complexes *1* and *3* are related through a solvent-dependent equilibrium.

$$\mathrm{[\overline{PtCl(PBu^t_2C(CH_3)_2CH_2}})]_2 + 2Pbu^t_3 \rightleftharpoons 2\overline{PtCl[PBu^t_2C(CH_3)_2CH_2}]PBu^t_3} \qquad (6)$$

Interestingly, when complex *1* is treated with $\mathrm{PtCl_2(NCPh)_2}$ in refluxing benzene, complex *3* is obtained within a few minutes.

The ^{1}H NMR spectrum of *3* in dichloromethane showed two sets of doublets at $\delta = 1.50$ ppm (J(P–C–C–H) = 13.8 Hz) and $\delta = 1.46$ ppm (J(P–C–C–H) = 14.4 Hz) in 3:1 intensity ratio due to the *tert*-butyl and methyl protons respectively, along with two weak and broad signals due to methylene protons at $\delta = 1.40$ ppm (J(P–C–C–H) = 6.5 Hz and J(^{195}Pt–H) = 128 Hz). The ^{31}P NMR spectrum of *3* showed a triplet consisting of a main peak ($\delta = -18.6$ ppm) and two satellite peaks due to ^{195}Pt–^{31}P spin–spin coupling (J(Pt–P) = 3757 Hz).

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When a solution of tri-*tert*-butylphosphine (2 mmol) and $PdCl_2(NCPh)_2$ (1 mmol), in dichloromethane, was left for a few hours the complex $[Pd(PBu^t_2C(CH_3)_2CH_2)Cl]_2$, *4*, was formed. Complex *4* was also obtained in almost quantitative yield from the reaction of tri-*tert*-butylphosphine and potassium tetrachloropalladate in N,N-dimethylformamide. The ^{31}P NMR spectrum of complex *4* in dichloromethane consists of a single peak at $\delta = -11.86$ ppm and its ^1H NMR spectrum in $CDCl_3$ shows of a set of three doublets (δ = 1.35, 1.46, and 1.56 ppm) in the intensity ratio of 9:1:3, with J(P–C–C–H) = 12.2, 13.8 and 14.0 Hz respectively.

Experimental

All reactions were carried out under an atmosphere of *oxygen-free* dry nitrogen.

Reactions of PBu^t_3 with $PtCl_2(PhCN)_2$ in Dichloromethane

(a) PBu^t_3 (4 mmol) was added dropwise to a well stirred solution of $PtCl_2(NCPh)_2$ (4 mmol) in CH_2Cl_2 (30 ml). After stirring the reaction mixture for 30 minutes the solvent was removed to give a pale yellow solid which was washed with n-hexane. *Anal.* Calcd. for $Pt(PBu^t_3)(NCPh)Cl_2$: C, 39.9; H, 5.6; Cl, 12.4. Found: C, 39.5; H, 5.7; Cl, 12.2. Upon stirring $Pt(PBu^t_3)(NCPh)Cl_2$ in ethanol for 15 minutes a white solid was formed which was filtered off and recrystallized from a benzene/n-hexane mixture to give colourless prism-shaped crystals. Yield 86%. *Anal.* Calcd. for $[Pt(PBu^t_2C(CH_3)_2CH_2)Cl]_2$: C, 33.40, H, 6.03; Cl, 8.23; mol. wt. 863. Found C, 33.30, H, 6.03; Cl, 8.22; mol. wt. 856 (in benzene). M.p. 212–215 °C (decomposition started at 212 °C and the decomposed product melted at 230 °C).

(b) A mixture of PBu^t_3 (4 mmol) and $PtCl_2(NCPh)_2$ (4 mmol) in CH_2Cl_2 (35 ml) was allowed to react for ~30 h, the solvent was removed, and the residue was extracted with benzene. After removal of benzene and washing the resulting solid with ethanol, a white crystalline solid was obtained. The analytical data, m.p. and proton NMR spectrum corresponding with complex *3*.

(c) A solution of $PtCl_2(NCPh)_2$ (3 mmol) and PBu^t_3 (6 mmol) in CH_2Cl_2 was stirred for an hour to give a clear pale yellow solution. After removing the solvent, the resulting pale yellow solid was treated with n-hexane. The hexane soluble fraction was concentrated to give a white crystalline solid. Yield 40%. *Anal.* Calcd. for $Pt[PBu^t_2C(CH_3)_2CH_2]PBu^t_3Cl$: C, 45.44; H, 8.43; Cl, 5.60. Found: C, 45.40; H, 8.41; Cl, 5.62. The hexane insoluble solid was washed with ethanol and the white insoluble solid was recrystallized from a benzene n-hexane mixture. Yield 36%. *Anal.* Calcd. for $[Pt(PBu^t_2C(CH_3)_2CH_2)Cl]_2$: C, 33.40; H, 6.03; Cl, 8.23; mol. wt. 863. Found: C, 33.30; H, 6.02; Cl, 8.23; mol. wt. 851 (in benzene). The ethanol soluble fraction was evaporated to give a white solid which was characterized to be BPu^t_3HCl by its infrared and ^1H and ^{31}P NMR spectra [2].

Reaction of PBu^t_3 with K_2PdCl_4 and $PdCl_2(NCPh)_2$

(a) PBu^t_3 (4 mmol) was added to a solution of K_2PdCl_4 (2 mmol) in N,N-dimethylformamide and the solution was stirred for 12 hours. Upon removing the solvent *in vacuo*, a viscous material was obtained which was diluted with ethanol (20 ml) to give a yellowish precipitate which was washed with ethanol and dried in vacuum. *Anal.* Calcd. for $[Pd(PBu^t_2C(CH_3)_2CH_2)Cl]_2$: C, 42.24; H, 7.59; Cl, 10.36, mol. wt. 685. Found: C, 42.17; H, 7.85; Cl, 9.98; mol. wt. 700 (in benzene). Yield: 72%, m.p. = 172–174 °C(dec).

(b) PBu^t_3 (4 mmol) was added dropwise to a solution of $PdCl_2(NCPh)_2$ (2 mmol) in dichloromethane (25 ml) and the reaction mixture was stirred at room temperature for ≈2 h. The solvent was removed and the residue was extracted with benzene. Hexane was added to the benzene extract and the mixture was kept at room temperature overnight to give a crystalline solid. *Anal.* Calcd. for $[Pd(PBu^t_2C(CH_3)_2CH_2)Cl]_2$: C, 42.24; H, 7.59; Cl, 10.36. Found: C, 42.14; H, 7.46; Cl, 10.60. Yield 70%; m.p. 172–174 °C(dec).

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