Facile Deprotonation of Coordinated Bis(diphenylphosphino)methane by an Acetylacetonate Anion

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The first homoleptic bis(diphenylphosphino)-methanido complexes of the type $[M(Ph_2PCHPPh_2)_2]$ (M = Ni, Pd, Pt) were prepared from $[MCl_2(PMe_3)_2]$, using $Li(Ph_2PCHPPh_2)$ as a reactant [1]. These complexes were taken as polymeric because of their insolubilities in common organic solvents. A subsequent paper reported that the complex (M = Pt) was also prepared from $K_2[PtCl_4]$, dppm (Ph_2PCH_2-PPh_2) and KOH in an aqueous ethanolic solution, and the crystals obtained from a benzene solution were shown to be monomeric by an X-ray analysis [2]. Some complexes containing the $[Ph_2PCHPPh_2]^-$ ion as a chelating ligand together with other coexisting ligands have also been prepared [3–7]. These were only obtained by deprotonation of the coordinated dppm in complexes if $Li(Ph_2PCHPPh_2)$ was not used as a reactant. It required invariably a strong base, such as NaH, MeLi or BuLi. We investigated the reactions of acetylacetonato complexes of the type $[M(acac)_2]$ (M = Pt (**1a**), Pd (**1b**)) with dppm and found unexpected formation of complexes containing the $[Ph_2PCHPPh_2]^-$ ion as a ligand.

Results and Discussion

When **1a** was allowed to react with two equivalents of dppm in CH_2Cl_2 for 2–3 h under reflux, a yellow precipitate which was insoluble in common organic solvents was obtained. The IR spectrum of this compound showed no absorption bands assignable to ν(C=O), but exhibited new bands (1113, 889, 853, 557 cm^{-1}) which had not appeared for free dppm, suggesting that the compound was the same as that described above, *i.e.*, a polymeric solid of $[Pt(Ph_2PCHPPh_2)_2]$ (**3a**). The fact was demonstrated by elemental analysis and by protonation with an acid HX (X = Cl, BF_4 or NO_3) in ethanol to give a cationic complex $[Pt(dppm)_2]X_2$, the IR spectrum of which coincided with that of the authentic sample [8]. A reverse reaction, *i.e.*, deprotonation of $[Pt(dppm)_2]X_2$ to give **3a**, readily occurred by Tl(acac), as well as some other bases like NEt_3, NaOMe and Na_2CO_3, suggesting that the acetylacetonate ion was working as a base to deprotonate.

The more labile palladium complex **1b** reacted at room temperature in a similar manner as above, but after stirring the mixture for a few minutes prompt isolation of the product gave an organic soluble monomeric complex $[Pd(Ph_2PCHPPh_2)_2]$ (**3b**) as a yellowish orange powder in an 85% yield. Complex **3b** showed an IR spectrum similar to that of **3a** and gave satisfactory elemental analysis and molecular weight data. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ showed a single resonance line (δ(P) +24.6 ppm downfield from 85% H_3PO_4), disclosing the existence of four magnetically equivalent phosphorus atoms. No useful data were obtained by the ^1H NMR spectrum because of its low solubility in any appropriate solvent. However, $[Pd(Ph_2PC(Me)PPh_2)_2]$ prepared similarly using $Ph_2PCH(Me)PPh_2$ instead of dppm, showed the methyl proton resonance as a quintet due to virtual coupling with four phosphorus atoms.

In an equimolar reaction we succeeded in isolating the intermediate of this reaction $[Pd(acac)(Ph_2PCHPPh_2)]$ (**2**) as an orange powder in a 93% yield, which was fully characterized by elemental analysis, IR spectroscopy and particularly by ^1H, ^{13}C and ^{31}P NMR spectroscopy. The reaction of $[PdCl_2(dppm)]$ with two equivalents of Tl(acac) also afforded **2**.

On the basis of these results we propose the processes represented in Scheme 1 as the likely mechanism for formation of $[M(acac)(Ph_2PCHPPh_2)]$ and $[M(Ph_2PCHPPh_2)_2]$ by the reaction of $[M(acac)_2]$ with dppm. Although no intermediates of **A** to **C** were detected in the present case, complexes of these types including **D** and **E** have been obtained by the reactions of $[M(\beta\text{-dik})_2]$ (M = Pt, Pd) containing various β-diketonato ligands with unidentate tertiary phosphines [9–12]. Isolation of **2** (M = Pd) is especially noteworthy since the reactions of **1a** and **1b** with $P(C_6H_{11})_3$ and PPh_3, respectively, in the 1:2 mole ratios in aprotic solvents afforded complexes of the type **E**, alone [9, 11], although in MeOH, the almost quantitative formation of $[Pd(acac)(PPh_3)_2](acac)$ was recognized *in situ* by an NMR probe [13]. Furthermore, change of intermediate **C** to the product **2** or **3a–b** is particularly interesting from the viewpoint of the relative acidity of acacH and dppm, whose pK_a values are 9.0 [14] and 29.9 [15], respectively. These results are probably due to the electronic effect on coordination of dppm to the metal atom.

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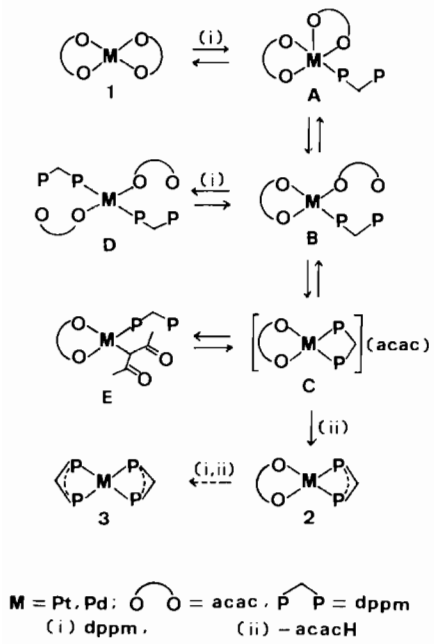

Scheme 1.

It may be relevant to note here that the equimolar reaction between **1a** and dppm afforded **3a**, exclusively, leaving a half-molar amount of **1a** as unreactive. When the reaction in CD_2Cl_2 was followed by ^{31}P NMR spectroscopy, two kinds of intermediates were detected. One of them appeared as **AB** quartet flanked by the ^{195}Pt satellites [$\delta(P_A)$ −5.4 ppm, $\delta(P_B)$ −29.2 ppm, $^1J(Pt-P_A)$ 4457 Hz, $^3J(Pt-P_B)$ 53 Hz, $^2J|(P_A-P_B)|$ 73 Hz], and the other as a broad resonance line [$\delta(P)$ −42.3 ppm, $^1J(Pt-P)$ 1912 Hz]. The signal pattern of the former intermediate and its $^1J(Pt-P_A)$ value similar to that of [Pt(tfac)(tfac-O)-(P(o-tolyl)$_3$] (tfac = $CH_3COCHCOCF_3^-$) [$^1J(Pt-P)$ 4410 Hz for *cis*(Me, P), 4380 Hz for *trans*(Me, P)] [10] or [Pt(acac)(acac-O)($P(C_6H_{11})_3$)] [$^1J(Pt-P)$ 4176 Hz] [13] suggest that the intermediate is of type **B**. The latter intermediate probably is that in the second reaction step, *i.e.*, [$Pt(Ph_2PCHPPh_2)$(dppm)]-(acac) analogous to the authentic sample [$Pt(Ph_2PCHPPh_2)$(dppm)](PF_6) [$\delta(P)$ −42.2 ppm, $^1J(Pt-P)$ 1916 Hz] [13]. Details of different reactivities of **1a** and **1b** described above will be discussed in a full paper.

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