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Consecutive Methylation and Protonation of the Carbanions in $[Pt(Ph_2PCHPPh_2)_2]$ Giving Rise to Ligand Scrambling

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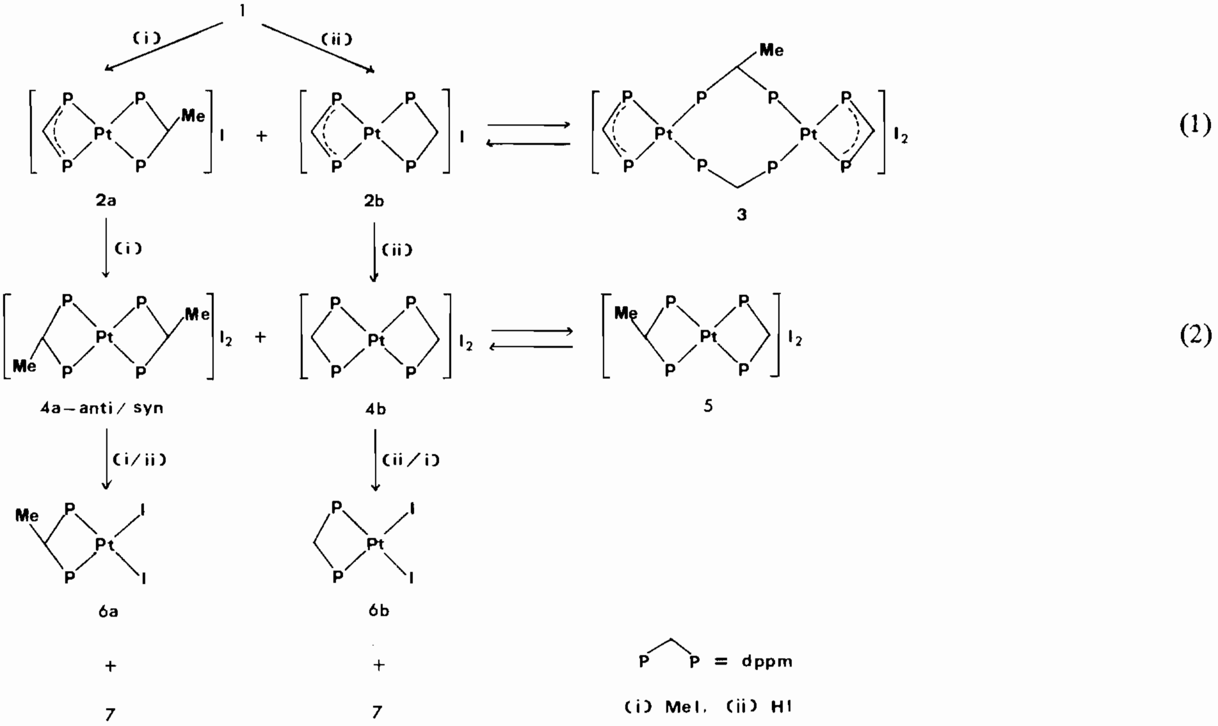
We have investigated the reactions of $[M(acac)_2]$ (M = Pt, Pd; acac = $CH_3COCHCOCH_3$) with dppm ($Ph_2PCH_2PPh_2$) and found that the reactions proceed via deprotonation of the coordinated dppm in the intermediary products, [M(acac)(dppm)](acac) and $[M(Ph_2PCHPPh_2)(dppm)](acac)$, by the acac anion to give $[M(Ph_2PCHPPh_2)_2]$, finally [1]. The complex with M = Pt, $[Pt(Ph_2PCHPPh_2)_2]$ (**1**), was insoluble in common organic solvents but was solubilized by protonation with an acid HX (X = Cl, BF_4 or NO_3), affording a cationic species $[Pt(dppm)_2]X_2$. Similarly, a clear solution was obtained by adding excess MeI to a suspension of **1** in CH_2Cl_2 under reflux, but isolation of the methylation products, syn- and anti-$[Pt(Ph_2PCH(Me)PPh_2]I_2$, was unsuccessful probably because side reactions made it difficult. When the same reaction was performed in tetrahydrofuran, $[PtI_2(Ph_2PCH(Me)PPh_2)]$ was isolated together with a small amount of contaminant $[PtI_2(dppm)]$. These strange results prompted our interest in elucidating the whole reaction scheme in the methylation of **1** with MeI. All results obtained are represented in advance in Scheme 1 with the notation of each compound.

Results and Discussion

Ten equivalents of MeI were added to a suspension of **1** in CH_2Cl_2 and the reaction was followed by ^{31}P NMR spectroscopy under reflux. The spectrum was recorded at 30, 70, 130 and finally ~10^4 (7 days) min after the beginning of the reaction. To analyze these spectral changes, the following complexes were



Scheme 1.

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synthesized as authentic samples: **4a**-syn and -anti*, **4b** [2], **5***, **6a*** and **6b** [3], and their $^{31}P\{^1H\}$ NMR spectra were recorded to utilize in the assignment of the observed signals (see Table I).

As can be seen in Table I, the final products were found to be **6a**, **6b** and phosphonium iodides (**7**), e.g., $[MePh_2PCH(Me)PPh_2Me]I_2$ and the like, in addition to the expected products **4a**-syn and -anti. The existence of **6b** suggests that protonation also occurred, probably by the reaction with HI, a small amount of contaminant in prepurified MeI. The spectral data at the reaction time 70 and 130 min included five more signals corresponding to **4b**, **5** and three unknowns A, B and C, which could not be assigned to any authentic sample. One of the unknowns, A, showed a broad resonance at δ −36.3 ppm [^1J(Pt–P) = 1943 Hz], while B and C had one and two resonances, each with a complex spin system at δ −43.7 ~ −40.0 ppm [^1J(Pt–P) = 1914 Hz] and, δ −25.2 [^1J(Pt–P) = 1963 Hz] and −29.7 [^1J(Pt–P) = 1947 Hz] ppm, respectively.

Hoping to elucidate the spectral assignment of these unknowns, we then treated **1** with two equivalents of Me_2SO_4 (1 mol Me_2SO_4 = 1 equiv.) in CH_2Cl_2 at room temperature. After stirring the mixture for 32 h, the products were isolated from the supernatant solution and subjected to $^{31}P\{^1H\}$ NMR measurement. The spectrum recorded in $CDCl_3$ was in accord with the first spectrum in the reaction with MeI. In this case, however, signals corresponding to the unknowns A and B resonated at δ −36.3 ppm [^1J(Pt–P) = 1942 Hz] and δ −41.9 ppm [^1J(Pt–P) = 1914 Hz] with the same spin system AA′BB′. Moreover, the latter resonance completely coincided in both chemical shift and spectral pattern with that in $[Pt(Ph_2PCHPPh_2)(dppm)](PF_6)$ [δ −42.2 ppm (CD_2Cl_2), ^1J(Pt–P) = 1916 Hz] [4], suggesting that B is $[Pt(Ph_2PCHPPh_2)(dppm)]I$ (**2b**) which was produced by the reaction with a contaminant HI. Based on the following experimental results, it is also unequivocally concluded that another unknown A contains the cation $[Pt(Ph_2PCHPPh_2)(Ph_2PCH(Me)PPh_2)]^+$ (**2a**: iodide): (1) the signal of the cation appears as the most intense one in the earlier stage of reaction, (2) the spin system is the same as in B and the ^1J(Pt–P) value is similar to that in B. As noted above, the $^{31}P\{^1H\}$ NMR spectrum of C showed two resonances, each with a complex spin system. We can now assign this spin system to AA′BB′ analogous to that in **2a** and **2b**, and hence a binuclear structure such as **3** in Scheme 1 was supposed for C.

The main conclusion drawn from these results is as follows: (1) the rates of methylation and protonation are very slow even in CH_2Cl_2 under reflux, thus retaining **2a** and **2b** in fairly high concentrations in solution during the reactions, (2) the monocationic species **2a** and 2b readily dissociate one of the phosphorus atoms in the neutral ligand and recombine to produce the scrambling product 3, (3) similarly, the dicationic species **4a** and **4b** are prone to dissociate one of the neutral ligands to form the mixed-ligand complex 5, (4) transient diphosphines freed from **4a** and **4b** partially react with MeI or HI to afford phosphonium iodides **7** [5], while the counterpart $[Pt(diphosphine)]I_2$ is stabilized as the diiodo complexes **6a** and **6b**. Inspection of equilibrium (1) and (2) also confirmed these experimental results and further details of these reactions will be reported in the full paper.

TABLE I. Intermediates and Products[a] Formed during the Reaction between 1 and 10 equivalents MeI in CH_2Cl_2 under Reflux and Their $^{31}P\{^1H\}$ NMR Data.[b]

Compound[c]	δ(P) [^1J(Pt–P)]	Reaction time[d]			
		30	70	130	~10^4
2a	−36.3 [1943]	—	—	—	
2b	−43.7 ~ −40.0 [1914]	—	—	—	
3	−25.2 [1963], −29.7 [1947]	—	—	—	
4a-syn	−40.7 [2240][e]		—	—	—
4a-anti	−36.6 [2240][e]		—	—	—
4b	−59.4 [2189][e]	—	—	—	
5	−42.9 [2234], −52.4 [2176][e]		—	—	
6a	−51.1 [2884][e]		—	—	—
6b	−70.2 [2778][e]		—	—	—
7[f]	+15.9	—	—	—	—

[a] The time-range of each compound existing in solution after the beginning of the reaction is represented by a solid line. [b] δ in ppm from 85% H_3PO_4 (up-field negative); J in Hz. [c] Refer to Scheme 1 for assignment to each compound. [d] In min. [e] In fair agreement with the data of authentic samples synthesized to confirm $^{31}P\{^1H\}$ NMR signal assignment. [f] Only the chemical shift of the most intense signal is given.

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*4a-syn and -anti, 5 and 6a were synthesized by the methods analogous to the preparations of 4b, 4b and 6b, respectively, using $Ph_2PCH(Me)PPh_2$ appropriately, instead of dppm.

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