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Reactions of Bis(β-diketonato)platinum(II) and -palladium(II) with Diphosphines $Ph_2PCHRPPh_2$ (R=H, Me): Unexpected Formation of the Homoleptic Bis(diphenylphosphino)-methanido and Related Complexes

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The reactions of $[M(\beta\text{-dik})_2]$ (M=Pt(II), Pd(II); β-dik=acetylacetonate (acac), dipivaloylmethanate (dpm), hexafluoroacetylacetonate (hfac) ions) with dppm (dppm=$Ph_2PCH_2PPh_2$) and mdppm (mdppm=$Ph_2PCH(Me)PPh_2$) have been investigated. $[M(hfac)_2]$ complexes react with dppm to afford the stable cationic complexes, $[M(dppm)_2](hfac)_2$. By contrast, $[M(acac)_2]$ complexes react to give the homoleptic bis(diphenylphosphino)methanido complexes, $[M(Ph_2PCHPPh_2)_2]$, through deprotonation of dppm by the displaced acac anions. The analogous complexes, $[M(Ph_2PC(Me)PPh_2)_2]$, are obtained using mdppm, instead of dppm. A complete reaction scheme leading to these products is proposed, based on the IR and ^1H, ^{13}C, and ^{31}P NMR spectral data. Some consideration is given to the dependence of these reactions on the metals and the β-diketonate ligands, employed.

Bis(diphenylphosphino)methane, dppm, is known to act as a monodentate ligand, as a chelating bidentate ligand, or as a bridging ligand, and hence extensive studies have been made on structures and reactivities of complexes containing dppm as a ligand.[1] This ligand, when free, is readily deprotonated by a strong base to give $Ph_2PCHPPh_2^-$ and the resulting anion can also serve as a ligand towards transition metals with a variety of bonding modes, including P,P′-chelated,[2] P,P′- or P,C-bidentate bridged,[3,4] and P,P′,C-tridentate bridged[5] forms, thus constituting recent interesting chemistry. These hitherto isolated complexes are mostly obtained by deprotonation of a coordinated dppm with a strong base such as *n*-BuLi, if $Li(Ph_2PCHPPh_2)$ is not used as a reactant.

Here we describe the novel reactions of $[M(\beta\text{-dik})_2]$, especially $[M(acac)_2]$ (M=Pt(II) (**1a**), Pd(II) (**1b**)), with dppm, during which the coordinated dppm is readily deprotonated without strong bases. A preliminary report of this work was published in a short communication.[6]††

Experimental

Infrared spectra were obtained in Nujol mulls with a JASCO DS701G infrared spectrophotometer. Proton NMR spectra were recorded on a JEOL MH100 (100 MHz) or a GX400 (400 MHz) spectrophotometer. Carbon-13 and phosphorus-31 NMR spectra were recorded on a JEOL FX60Q instrument operating at 15 and 24 MHz, respectively. Chemical shifts are described in ppm relative to tetramethylsilane (for ^1H, ^{13}C) and 85% phosphoric acid (for ^{31}P).

†† In this paper, dppm−H and mdppm−H represent bis(diphenylphosphino)methanide ($Ph_2PCHPPh_2^-$) and 1,1-bis(diphenylphosphino)ethanide ($Ph_2PC(Me)PPh_2^-$) ions, respectively.

Preparation of Complexes. Bis(diphenylphosphino)-methane, dppm, was purchased from Strem Co. and used without further purification.· 1,1-Bis(diphenylphosphino)-ethane, mdppm,[7] was prepared according to the literature. The starting complexes, **1a**, **1b**, $[Pt(hfac)_2]$, $[Pd(hfac)_2]$, and $[Pd(dpm)_2]$, were prepared by the methods described in the previous papers.[8] Diphosphine complexes, $[PdCl_2(dppm)]$[9] and $[Pd(dppm)_2]X_2$ (X=Br, PF_6),[10] were prepared according to the literature. Solvents were dried over an appropriate drying agent and distilled under an atmosphere of argon before use.

Bis[bis(diphenylphosphino)methanido]platinum(II), [Pt(dppm−H)$_2$] (3a): When dppm (0.600 g, 1.56 mmol) was added to a solution of **1a** (0.305 g, 0.776 mmol) in dichloromethane (3 cm^3) at room temperature, a yellow precipitate began to deposit after a while. The mixture was stirred for 2—3 h under reflux and the precipitate was filtered, washed with acetone, and dried in vacuo (yield 0.70 g, 94%). The product was insoluble in common organic solvents such as benzene, acetone, diethyl ether, and haloalkanes.

Found: C, 62.12; H, 4.40%. Calcd for $C_{50}H_{42}P_4Pt$: C, 62.44; H, 4.37%.

Similarly, bis[1,1-bis(diphenylphosphino)ethanido]platinum(II), [Pt(mdppm−H)$_2$] (**3c**), was prepared as a yellow powder, using mdppm instead of dppm (yield 51%). The product was also insoluble in common organic solvents described above.

Found: C, 62.89; H, 4.59%. Calcd for $C_{52}H_{46}P_4Pt$: C, 63.09; H, 4.65%.

[Pd(dppm−H)$_2$] (3b): A solid dppm (0.602 g, 1.57 mmol) was added to a solution of **1b** (0.239 g, 0.785 mmol) in dichloromethane (5 cm^3) at room temperature. The resulting solution was stirred for a few minutes and petroleum ether was added to deposit a yellowish orange solid, which was filtered, washed with petroleum ether, and dried in vacuo (yield 0.58 g, 85%). The product was slightly soluble in chloroform but after a while equilibrated in the solvent with other species, as evidenced by ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ=−36.7 (s).

Found: C, 68.31; H, 4.91%. Calcd for $C_{50}H_{42}P_4Pd$: C, 68.78; H, 4.85%.

[Pd(mdppm−H)$_2$] (3d): A solid mdppm (0.379 g, 0.952 mmol) was added to a solution of **1b** (0.145 g, 0.476 mmol) in dichloromethane (5 cm^3), and the resulting solution was stirred for 10 min to separate out reddish orange crystals, which were filtered, washed with dichloromethane, and dried in vacuo (yield 0.30 g, 70%). The product was slightly soluble in common organic solvents such as benzene and haloalkanes. ^{1}H NMR (C_6D_6, 400 MHz)[11] δ=1.78 (quintet, J_B(PH)=7.8 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6) δ=−25.5 (s).

Found: C, 69.40; H, 5.07%. Calcd for $C_{52}H_{16}P_4Pd$: C, 69.30; H, 5.14%.

Acetylacetonato[bis(diphenylphosphino)methanido]palladium(II), [Pd(acac)(dppm−H)] (2b): Method A: After dissolving dppm (0.633 g, 1.65 mmol) in a solution of **1b** (0.500 g, 1.64 mmol) in dichloromethane (5 cm^3), the resulting solution was diluted with pentane (30 cm^3) and allowed to stand in a freezer (ca. −5 °C). The yellow orange plates which separated out were filtered, washed with diethyl ether, and dried in vacuo. During the filtration, the crystals changed to a yellow powder with devitrification (yield 0.438 g). On standing the washing in a freezer, another crop was separated out as a reddish orange crystalline solid including no solvent of crystallization. Total yield: 0.581 g (50%). The melting point and the NMR and analytical data for the reddish orange crystals were as follows: mp: 157—159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=5.27 (s, 1H, acac-CH), 2.56 (br, 1H, PCHP), and 1.94 (s, 6H, acac-CH_3). ^{13}C NMR (CD_2Cl_2)[11] δ=187.2 (t, J_A=1 Hz, CO), 99.4 (s, acac-CH), 28.1 (t, J_A=4.5 Hz, acac-CH_3), and 16.8 (t, J(PC)=65 Hz, ^1J(CH)=177 Hz, PCHP). ^{31}P{^{1}H} NMR ($CDCl_3$) δ=−55.7 (s).

Found: C, 61.27; H, 4.82%. Calcd for $C_{30}H_{28}O_2P_2Pd$: C, 61.19; H, 4.79%.

Method B: Thallium(I) acetylacetonate (0.243 g, 0.801 mmol) was added to a suspension of [$PdCl_2$(dppm)] (0.225 g, 0.401 mmol) in dichloromethane (50 cm^3). After being stirred for 20 min at room temperature, the mixture was filtered, the filtrate was concentrated to dryness, and then the residue was extracted with toluene. The solvent was evaporated to dryness and the product was washed with pentane, and dried in vacuo (yield 0.20 g, 85%).

[Pd(acac)(dppm)](PF$_6$): To a dichloromethane solution (8 cm^3) containing **2b** (0.050 g, 0.085 mmol) and *p*-toluenesulfonic acid monohydrate (TsOH·H_2O, 0.017 g, 0.089 mmol) was added a methanol solution (4 cm^3) of potassium hexafluorophosphate (0.016 g, 0.087 mmol). The resulting KOTs was removed by filtration, pentane was added to the filtrate, and then the solution was kept in a freezer to deposit yellowish orange needles, which were collected, washed with diethyl ether, and air-dried (yield 0.028 g, 45%). ^{1}H NMR ($CDCl_3$) δ=5.62 (s, 1H, acac-CH), 4.67 (t, J(PH)=12 Hz, 2H, PCH_2P), and 2.16 (s, 6H, acac-CH_3). ^{13}C NMR ($CDCl_3$)[11] δ=187.2 (t, J_A=1.5 Hz, CO), 100.2 (s, acac-CH), 33.7 (t, J(PC)=32 Hz, PCH_2P), and 27.7 (t, J_A=5 Hz, acac-CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ=−52.3 (s, dppm) and −144.0 (heptet, J(FP)=711 Hz, PF_6). The same compound was also obtained as an orange red precipitate on addition of pentane to an equimolar mixture of [Pd(acac)-(Et_2NH)$_2$](PF$_6$) (vide infra) and dppm in dichloromethane (yield 49%).

[Pt(dppm−H)(dppm)](PF$_6$): A solid dppm (0.138 g, 0.359 mmol) was added to a solution of [Pt(acac)(PPh_3)$_2$]-(PF$_6$) (vide infra) (0.157 g, 0.160 mmol) in dichloromethane (3 cm^3). The resulting solution was diluted with pentane and kept in a freezer to deposit yellow needles, which were filtered, washed with diethyl ether, and dried in vacuo (yield 0.120 g, 64%). Mp: 233—235 °C (decomp). Inclusion of one molecule of dichloromethane per platinum atom as solvent of crystallization was confirmed by the ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=5.33 (s, 2H, CH_2Cl_2), 5.07 (br, t, J(PH)=11 Hz; J(PtH)=indiscernible, 2H, PCH_2P), and 3.85 (br, t, J(PH)=7 Hz; J(PtH)=171 Hz, 1H, PCHP). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ=−144.2 (heptet, J(FP)=711 Hz, PF_6). The signal assigned to (dppm+dppm−H) appeared as a AA'BB' spin system, of which the center was located at δ=−42.2 (J(PtP)=ca. 1916 Hz.).

Found: C, 52,18; H, 3.82%. Calcd for $C_{50}H_{43}F_6P_5Pt\cdot CH_2Cl_2$: C, 51.35; H, 3.80%.

The corresponding BF_4 salt was obtained in a similar manner using [Pt(acac)(PPh_3)$_2$](BF$_4$) as a starting material, which was readily synthesized by the reactions of **1a** with triphenylphosphine and sodium tetrafluoroborate in methanol. In this case, chloroform was used as a solvent and the product included one molecule of chloroform per platinum atom as solvent of crystallization. Yellow fine needles (yield 83%). Mp: 152—154 °C (decomp). ^{1}H NMR ($CDCl_3$) δ=5.16 (br, t, J(PH)=8 Hz; J(PtH)=48 Hz, 2H, PCH_2P) and 3.86 (br, t, J(PH)=5 Hz; J(PtH)=171 Hz, 1H, PCHP). The ^{31}P{^{1}H} NMR spectrum in $CDCl_3$ showed a signal assignable to (dppm+dppm−H) with a AA'BB' spin system, of which the center was located at δ=−41.9 (J(PtP)=ca. 1916 Hz).

Found: C, 52.74; H, 3.83%. Calcd for $C_{50}H_{43}BF_4P_4Pt\cdot CHCl_3$: C, 52.39; H, 3.79%.

[Pt(acac)(PPh_3)$_2$](PF$_6$): Compound **1a** (0.222 g, 0.565 mmol) was dissolved in hot methanol (10 cm^3) and allowed to react with triphenylphosphine (0.296 g, 1.13 mmol) under continued heating for 30 min. After cooling to room temperature, ammonium hexafluorophosphate (0.276 g, 1.69 mmol) was added and the resulting solution was further stirred for 30 min. The solution was concentrated and diethyl ether was added to deposit a white solid, which was filtered, washed with water, and dried in vacuo (yield 0.40 g, 72%). Recrystallization from dichloromethane–pentane gave the product including one fourth of dichloromethane molecule per platinum atom as solvent of crystallization.

Found: C, 50.38; H, 3.85%. Calcd for $C_{41}H_{37}F_6O_2P_3Pt\cdot 1/4CH_2Cl_2$: C, 50.30; H, 3.84%.

[Pd(acac)(Et_2NH)$_2$](PF$_6$): The compound was prepared by adding [Pd(acac)(Et_2NH)$_2$](acac)[12] (0.177 g, 0.393 mmol) to an aqueous solution (2 cm^3) of potassium hexafluorophosphate (0.089 g, 0.48 mmol). The yellow precipitate which separated out of the chilled solution was filtered, washed with methanol and diethyl ether, successively, and air-dried (yield 0.16 g, 81%). Recrystallization from dichloromethane–diethyl ether gave yellow plates. ^{1}H NMR ($CDCl_3$) δ=5.45 (s, 1H, acac-CH), 3.53 (br, 2H, NH), 2.72 (m, 8H, Et_2NH-CH_2), 2.01 (s, 6H, acac-CH_3), and 1.55 (t, J(HH)=7 Hz, 12H, Et_2NH-CH_3). ^{13}C NMR ($CDCl_3$) δ=186.6 (s, CO), 101.2 (s, acac-CH), 47.2 (s, Et_2NH-CH_2), 26.0 (s, acac-CH_3), and 14.1 (s, Et_2NH-CH_3).

Found: C, 31.53; H, 5.92; N, 5.68%. Calcd for $C_{13}H_{29}F_6N_2O_2PPd$: C, 31.43; H, 5.88; N, 5.64%.

[M(dppm)$_2$](hfac)$_2$ (M=Pd(II), Pt(II)): A solid dppm (0.268 g, 0.697 mmol) was added to a solution of [Pd(hfac)$_2$] (0.179 g, 0.344 mmol) in dichloromethane (2 cm^3). The

resulting solution was diluted with pentane and kept in a freezer to deposit a white or colorless crystalline solid, $[Pd(dppm)_2](hfac)_2$,[13] which was filtered and washed with diethyl ether, and air-dried (yield 0.28 g, 63%). ^1H NMR (CD_3CN)[11] δ=5.40 (s, 2H, hfac-CH) and 5.16 (quintet, J_B=5 Hz, 4H, PCH_2P). ^{13}C NMR (CD_3CN)[11] δ=172.9 (quartet, J(FC)=28 Hz, CO), 119.4 (quartet, J(FC)=293 Hz, hfac-CF_3), 82.5 (s, hfac-CH), and 38.4 (quintet, J_B=13 Hz, ^1J(CH)=141 Hz, PCH_2P). $^{31}P\{^1H\}$ NMR (CD_3CN) δ=−33.6 (s).

Found: C, 55.47; H, 3.57%. Calcd for $C_{60}H_{46}F_{12}O_4P_4Pd$: C, 55.90; H, 3.60%.

Starting from $[Pt(hfac)_2]$, $[Pt(dppm)_2](hfac)_2$ was prepared, analogously (yield 88%).

Found: C, 51.84; H, 3.36%. Calcd for $C_{60}H_{46}F_{12}O_4P_4Pt$: C, 52.30; H, 3.36%.

$[M(dppm)_2](OTs)_2$ (M=Pd(II), Pt(II)): The Pd(II) salt was obtained by adding acetone solutions (1 cm^3) of $TsOH\cdot H_2O$ (0.072 g, 0.38 mmol) and dppm (0.12 g, 0.32 mmol), successively, to a solution of $[Pd(dpm)_2]$ (0.075 g, 0.16 mmol) in dichloromethane (1 cm^3). The white solid which separated out was filtered, washed with diethyl ether, and dried in vacuo (yield 0.11 g, 56%). Recrystallization from methanol–diethyl ether gave colorless cubes, which changed to a white powder on vacuum drying.

Found (for powder): C, 62.78; H, 4.73%. Calcd for $C_{64}H_{58}O_6P_4PdS_2$: C, 63.13; H, 4.80%.

Starting from **1a**, $[Pt(dppm)_2](OTs)_2$ was obtained as a white powder, analogously.

Formation of the Cationic Complexes, $[Pt(dppm)_2]X_2$ (X=Cl, BF_4, NO_3), by Protonation of 3a. $[Pt(dppm)_2]Cl_2$: To a suspension of **3a** in ethanol was added an excess of 6 M hydrochloric acid (1 M=1 mol dm^{-3}), and the mixture was stirred for 1 h prior to evaporation of the solvent. The dichloromethane-extract of the residue was concentrated and pentane was added to produce a white precipitate, which was filtered, washed with pentane, and dried in vacuo. The compound included one molecule of dichloromethane per platinum atom as solvent of crystallization.

Found: C, 54.35; H, 4.19%. Calcd for $C_{50}H_{44}Cl_2P_4Pt\cdot CH_2Cl_2$: C, 54.71; H, 4.14%.

$[Pt(dppm)_2](BF_4)_2$: An excess of 42% tetrafluoroboric acid was added to a suspension of **3a** in ethanol and the mixture was stirred for 1 h to produce a white precipitate, which was collected, washed with water, and dried in vacuo.

Found: C, 52.44; H, 3.88%. Calcd for $C_{50}H_{44}B_2F_8P_4Pt$: C, 52.80; H, 3.90%.

$[Pt(dppm)_2](NO_3)_2$: Similarly, a suspension of **3a** in ethanol was allowed to react with an excess of 16 M nitric acid for 1 h. The solvent was evaporated to produce a white precipitate, which was filtered, washed with water, and dried in vacuo.

Found: C, 54.83; H, 4.02; N, 2.60%. Calcd for $C_{50}H_{44}N_2O_6P_4Pt$: C, 55.20; H, 4.08; N, 2.58%.

Yields of all these products were almost quantitative.

Regeneration of 3a and 3b by the Reactions of $[M(dppm)_2]^{2+}$ (M=Pt(II), Pd(II)) with Tl(acac) and Some Aqueous Bases. With Tl(acac): When two equivalents of Tl(acac) were allowed to react with $[Pt(dppm)_2]Cl_2$ in dichloromethane, a yellow precipitate was produced immediately, together with that of TlCl. The IR spectrum of the product confirmed the formation of **3a** by the appearance of its characteristic bands (vide infra). Similarly, $[Pd(dppm)_2]Br_2$ reacted with two equivalents of Tl(acac). After removal of the precipitated TlBr, organic soluble **3b** was isolated from the filtrate by the addition of hexane. The formation of **3b** was also confirmed by the IR data.

With Aqueous Bases: To a suspension of $[Pt(dppm)_2](NO_3)_2$ in methanol was added an excess of 5% aqueous solution of sodium carbonate as a base, and the mixture was stirred for 35 min at room temperature. The solvent was evaporated completely and the residue was extracted with dichloromethane. The extract was concentrated to dryness to leave a yellow powder, which was collected, washed with water and pentane, successively, and dried in vacuo. The yield was almost quantitative and the IR spectrum was in accord with that of **3a**. The use of triethylamine and sodium methoxide as bases was also effective on deprotonation of the coordinated dppm to produce **3a**.

Equimolar Reaction between 1a and dppm. When a dichloromethane solution (2 cm^3) containing equimolar amounts of **1a** (0.156 g, 0.400 mmol) and dppm (0.154 g, 0.400 mmol) was stirred for 30 min, a yellow precipitate began to deposit. Stirring was further continued for 3.5 h until no further precipitation occurred. The yellow precipitate obtained was filtered, washed with dichloromethane, and dried in vacuo. This product was identified as **3a** by IR assay. The yield was 0.155 g (0.161 mmol). The filtrate was evaporated to dryness and the residue was washed with diethyl ether to leave a deep yellow solid (0.067 g). This crude product was placed on the column (silica gel, 200 mesh) and eluted with dichloromethane. The eluate was again evaporated to dryness to give a yellow crystalline solid. This solid was identified as **1a** by IR spectroscopy. The recovered **1a** was 0.055 g (0.140 mmol), 35% of **1a** employed.

Another experiment was performed to confirm the intermediate species in this reaction. Equimolar amounts of **1a** and dppm were dissolved in CD_2Cl_2 in an NMR tube and the reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature. Signal intensities were accumulated from 20 min after the initiation of the reaction over a 34-min period and from 60 min over a 90-min period, and those spectral data were recorded. These results are shown in Fig. 1.

Results and Discussion

Reactions of $[M(\beta\text{-dik})_2]$ (M=Pt(II), Pd(II)) with dppm and mdppm in the 1:2 Mole Ratio. In dichloromethane, $[M(hfac)_2]$ reacted with dppm to afford the stable cationic complexes, $[M(dppm)_2](hfac)_2$, by displacement of the coordinated hfac ligands (Eq. 1), whereas $[M(acac)_2]$ (M=Pt(II) (**1a**), Pd(II) (**1b**)) gave the homoleptic bis(diphenylphosphino)methanido complexes, $[M(dppm-H)_2]$ (M=Pt(II) (**3a**), Pd(II) (**3b**)) (Eq. 2), which were previously prepared from $[MCl_2(PMe_3)_2]$ and $Li(Ph_2PCHPPh_2)$[2d] or from $K_2[PtCl_4]$, dppm, and KOH.[2f]

$$[M(hfac)_2] + 2dppm \longrightarrow [M(dppm)_2](hfac)_2 \quad (1)$$

$$[M(acac)_2] + 2dppm \longrightarrow [M(dppm-H)_2] + 2acacH \quad (2)$$

Table 1. IR Bands (cm^{-1}) Characteristic of the Deprotonated dppm and mdppm Complexes[a)]

Complex	dppm−H/mdppm−H	ν(C=O)+ν(C=C)
[Pd(acac)(dppm−H)] (**2b**)	1007(s), 853(vs), 553(vs)	1578(vs), 1510(vs)
[Pt(dppm−H)$_2$] (**3a**)	1113(vs), 889(vs), 858(vs), 558(w)	
[Pd(dppm−H)$_2$] (**3b**)	1117(vs), 882(s), 866(vs), 546(vs)	
[Pt(mdppm−H)$_2$] (**3c**)	1110(s), 847(vs)	
[Pd(mdppm−H)$_2$] (**3d**)	1110(s), 851(vs)	

a) In Nujol; v=very, s=strong, w=weak.

The IR spectra of **3a** and **3b** showed no absorption bands assignable to ν(C=O), but exhibited new bands which had not appeared for free or coordinated dppm. Table 1 lists these IR bands, which are characteristic of deprotonated dppm complexes. Protonation of **3a** with an acid HX (X=Cl, BF_4, or NO_3) in ethanol led to the formation of a cationic complex [Pt(dppm)$_2$]X_2 (Eq. 3), of which the IR spectrum coincided with that of the authentic sample,[14)] demonstrating that the diphosphines in **3a** were certainly deprotonated.

$$[Pt(dppm-H)_2] + 2HX \longrightarrow [Pt(dppm)_2]X_2 \quad (3)$$

A reverse reaction, i.e., deprotonation of [Pt(dppm)$_2$]X_2 to give **3a**, readily occurred by Tl(acac) (Eq. 4), as well as some other bases like NEt_3, NaOMe, and Na_2CO_3, suggesting that the acac anion was working as a base to deprotonate.

$$[Pt(dppm)_2]Cl_2 + 2Tl(acac) \longrightarrow [Pt(dppm-H)_2] + 2acacH + 2TlCl \quad (4)$$

When mdppm instead of dppm was allowed to react with [M(acac)$_2$], analogous complexes [M(mdppm−H)$_2$] (M=Pt(II) (**3c**), Pd(II) (**3d**)) were obtained. The characteristic IR bands are also listed in Table 1.

Although the platinum complexes **3a** and **3c** were insoluble in common organic solvents probably because of their polymeric nature as reported previously,[2d)] the palladium complexes **3b** and **3d** prepared by us were organic soluble and the $^{31}P\{^1H\}$ NMR spectra of these complexes showed a single resonance line, disclosing the existence of four magnetically equivalent phosphorus atoms. No useful ^1H NMR data were obtained for **3b** because of its low solubility in any appropriate solvent. However, the methyl-substituted complex **3d** showed the methyl proton resonance as a quintet due to virtual coupling to the four phosphorus atoms, thus indicating that the complex is a symmetric bis-chelate.

As described in the Experimental section, the $^{31}P\{^1H\}$ NMR spectrum of **3b** in $CDCl_3$ gradually changed with time, although no appreciable change was observed for that of **3d** in C_6D_6. After about 45 min, the signal originally assigned to **3b** completely disappeared and many other weak signals appeared, instead. This spectral change was not elucidated further, but the reaction of the coordinated bis(diphenylphosphino)methanido carbanions with the haloalkane solvent employed to form the cationic species like [Pd(dppm−H)($Ph_2PCHRPPh_2$)]Cl and [Pd($Ph_2PCHRPPh_2$)$_2$]Cl_2 (R=$CDCl_2$) might be assumed, since the carbanions in **3a** are methylated by excess methyl iodide to give similar cationic species.[15)]

Characterization of Some Reaction Intermediates. Although the equimolar reaction between **1a** and dppm afforded **3a** exclusively, leaving about 35% of **1a** employed as unreacted, we succeeded, in the palladium case, in isolating the intermediate species, [Pd(acac)(dppm−H)] (**2b**), in high yield. This was fully characterized by elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectroscopy (see the Experimental section). When the dipivaloylmethanido complex, [Pd(dpm)$_2$], was allowed to react with an equimolar amount of dppm in $CDCl_3$, the same type of complex, [Pd(dpm)(dppm−H)], was also formed in solution as evidenced by its NMR data.[16)] The IR spectrum of **2b** exhibited the absorption bands characteristic of both the *O,O'*-chelated acac and deprotonated dppm ligands as represented in Table 1.

In order to elucidate what kind of platinum-containing intermediate is formed in solution, we followed the reaction of **1a** with dppm in the 1:1 mole ratio by $^{31}P\{^1H\}$ NMR spectroscopy as described in the Experimental section. A yellow precipitate of **3a** began to deposit within 10 min after mixing both reactants in CD_2Cl_2. Figure 1 shows two spectra recorded at an appropriate time (see the figure caption) after the initiation of the reaction. The first spectrum (Fig. 1A) exhibited a sharp and most intense resonance line at δ −22.8. This coincided with the chemical shift of free dppm, suggesting that significant amounts of dppm still remained unreacted in this stage of the reaction. The spectrum also revealed the existence of two kinds of intermediates. One of them appeared at δ −5.4 (P_A) and −29.2 (P_B) as two doublets coupled each other with $^2J(P_A\text{-}P_B)$=73 Hz, each being flanked by the ^{195}Pt satellites with $^1J(Pt\text{-}P_A)$=4457 and $^3J(Pt\text{-}P_B)$=53 Hz, whereas the other showed a broad resonance line, of which the center was located at δ −42.3, with $^1J(PtP)$=1912 Hz. In the second spectrum (Fig. 1B), the signals of the intermediates increased in their intensities, whereas the free dppm disappeared. Based on both the signal pattern described above and the similarity of the $^1J(Pt\text{-}P_A)$ value to that of [Pt(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}][17)] (tfac=trifluoroacetylaceton-

ate ion) or [Pt(acac)(acac-*O*){P(C_6H_{11}}$_3$)],[18] the former intermediate was supposed to be of the type **A-2** (see Scheme 1). It seems reasonable to assume that the latter intermediate will be formed in the course of reaction process from **2** to **3**. If this is true, the intermediate would be expected to be of the type **B-3** because the strong trans effect of a phosphorus atom makes the existence of the *O*-unidentate acac intermediate of the type **B-2** very unlikely (see Scheme 1). In fact, the signal of the latter intermediate coincided both in chemical shift and in coupling constant, ^1J (PtP), with that of [Pt(dppm−H)(dppm)](PF_6), which was isolated incidentally from the reaction mixture of [Pt(acac)(PPh_3)$_2$](PF_6) and dppm in the mole ratio of 1:2.24 in CH_2Cl_2.

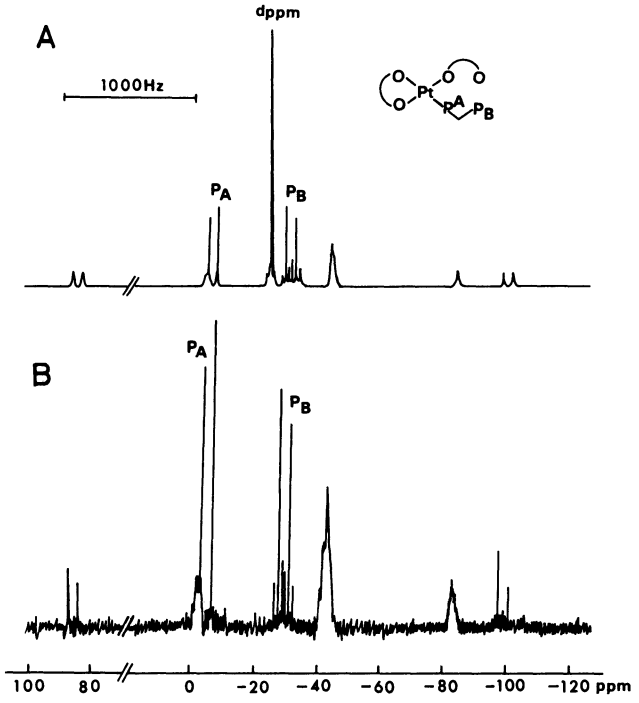
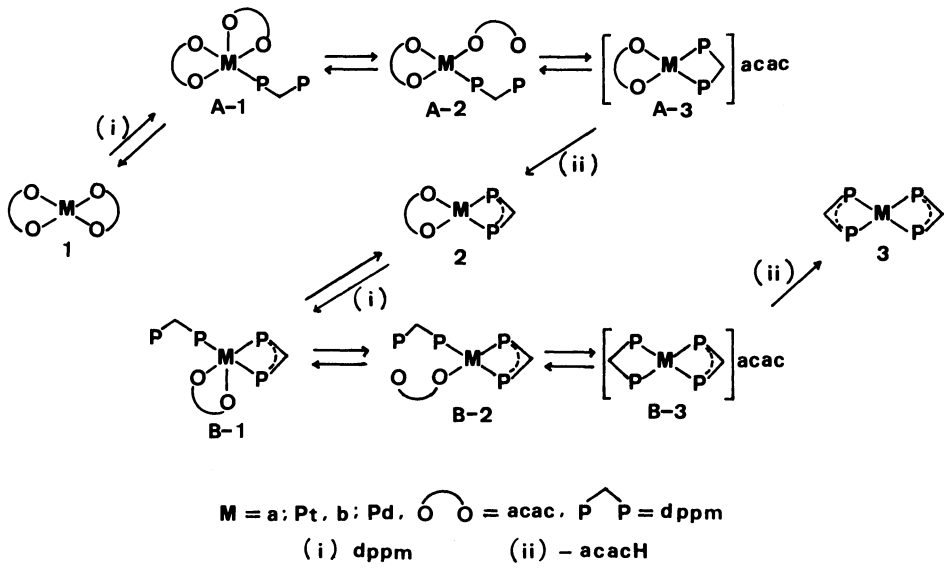


Fig. 1. ^{31}P NMR spectra obtained in the equimolar reaction between **1a** and dppm in CD_2Cl_2 at room temperature. The signal intensities accumulated from 20 min after the initiation of the reaction over a 34-min period (in A) and from 60 min over a 90-min period (in B) are shown. The signal for the final product, [Pt(dppm−H)$_2$] (**3a**), is not observed due to the insoluble character of the complex in CD_2Cl_2.

The Proposed Reaction Mechanism. On the basis of the results described above we can propose the processes represented in Scheme 1 as the likely mechanism for formation of [M(acac)(dppm−H)] and [M(dppm−H)$_2$] by the reactions of [M(acac)$_2$] (M=Pt(II), Pd(II)) with dppm. Although no intermediates of **A-1** to **A-3** were isolated in the present case, complexes of these types including the central-carbon-bonded β-diketonato complexes have been obtained by the reactions of [M(β-dik)$_2$] (M=Pt(II), Pd(II)) containing various β-dik ligands with unidentate tertiary phosphines.[17,19]

Isolation of the mixed ligand complex **2b** is especially noteworthy since the reactions of **1a** and **1b** with tricyclohexylphosphine and triphenylphosphine, respectively, in the 1:2 mole ratios in aprotic solvents such as benzene and diethyl ether afforded complexes of the type [M(acac)(acac-*O*)L] (L=unidentate tertiary phosphines), alone.[19b,c] However, when **1a** and **1b** were allowed to react with two equivalents of triphenylphosphine in methanol, the almost quantitative formation of [M(acac)(PPh_3)$_2$](acac) (M=Pt(II), Pd(II)) was recognized in situ by NMR probe.[20] Although we failed in isolating the acac salts, the PF_6 salt with M=Pt(II) was isolated from the reaction mixture and utilized as a starting complex for the preparation of [Pt(dppm−H)(dppm)](PF_6) (see the Experimental section). The formation of the latter com-



Scheme 1.

plex was also recognized in situ when $[Pt_2(PPh_3)_2(\mu\text{-dppm})_2](PF_6)_2$ was treated with **3a**, but its isolation was not attempted.[4]

The most important step to form the bis(diphenylphosphino)methanido complexes **2** and **3** is the deprotonation process from intermediate **A-3** to **2** or from **B-3** to **3**. This key step will be discussed in a succeeding paragraph.

Ligand and Metal Control in the Key Step. Deprotonation of the coordinated dppm by the acac anion is particularly interesting from the view point of the relative acidity of acacH and free dppm, whose pK_a values are 9.0[21] and 29.9,[22] respectively. Therefore, the above-mentioned chemical change is probably due to the electronic effect caused by coordination of dppm to the metal atom (vide infra).

In order to examine how the stability of intermediates of the type **A-3** varies with different β-dik ligands and with different metals, we conducted equimolar reactions of $[M(\beta\text{-dik})_2]$ with dppm in $CDCl_3$ and determined the species produced in solution by NMR spectroscopy. The effect of the β-dik ligand on the key step appeared as follows. When $[M(hfac)_2]$ was a starting complex, deprotonation of the coordinated dppm never occurred and either the stable product, [Pd(hfac)(dppm)](hfac)[23] or $[Pt(dppm)_2](hfac)_2$, was obtained, whereas for $[M(acac)_2]$, the deprotonation was effected, giving **2b** or **3a**, unless some strong acids were present. These results are clearly attributable to the difference in pK_a between hfacH (pK_a=4.3) and acacH (pK_a=9.0).[21] The reaction forming **2b** from $[PdCl_2(dppm)]$ and two equivalents of Tl(acac) also seems to take place via the precursor complex, [Pd(acac)(dppm)](acac) (Eq. 5).

$$[PdCl_2(dppm)] + 2Tl(acac) \xrightarrow{-2TlCl} [Pd(acac)(dppm)](acac) \xrightarrow{-acacH} \mathbf{2b} \qquad (5)$$

The relative thermodynamic stability of the intermediates depends on the metal. As noted above, a treatment of $[Pd(hfac)_2]$ with dppm in $CDCl_3$ resulted in the quantitative formation of [Pd(hfac)(dppm)](hfac) in an NMR tube,[23] while $[Pt(hfac)_2]$ did not afford [Pt(hfac)(dppm)](hfac) but $[Pt(dppm)_2](hfac)_2$ in a 50% yield. In the case of platinum(II), it is conceivable that the intermediate of type **A-3** is thermodynamically unstable, and hence the reaction proceeds ultimately to give the bis(dppm)-chelate. A similar situation was encountered in the reactions of **1a** and **1b** with dppm. Thus **1b** reacted with dppm to form **2b**, while **1a** afforded **3a** via intermediates of types **A-2** and **B-3**. In this case, the partially produced **2a** may be attacked by the second dppm to result in the formation of **3a**. In any event, it is certain that in contrast with the strong M–O bonds of **1**, those of the type-**A-3** intermediate and **2** are destabilized by the trans phosphorus donor atoms.

We may note here that, although complexes of the type **A-3** were never isolated, protonation of **2b** with a strong acid $TsOH\cdot H_2O$ led to the quantitative formation of [Pd(acac)(dppm)](OTs) in situ as evidenced by the NMR data.[24] The PF_6 salt was also readily isolated in the presence of potassium hexafluorophosphate.

Relationship between Diphosphine Coordination Modes and NMR Spectra. Mono(chelating dppm) Complexes: The PCH_2P protons in complexes of the type $[Pd(\beta\text{-dik})(dppm)]X$ resonated at δ 4.7—5.0 as a triplet with $J(PH)$=12 Hz and the corresponding carbon did at δ 32—34 as a triplet with $J(PC)$=32—33 Hz. For the ^1H-nondecoupled ^{13}C spectra of these complexes, the $^1J(CH)$ coupling constant was found to be 146 Hz, reflecting the situation of sp^3 carbon.

Bis(chelating dppm) Complexes: For complexes of the type $[M(dppm)_2]X_2$, the PCH_2P proton signal appeared at δ 4.9—5.7 as a quintet with J_B=5 Hz[11] and the corresponding carbon signal at δ 38—43 as a quintet with J_B=13—17 Hz. The $^1J(CH)$ of ca. 140 Hz, observed for these complexes, is also appropriate to sp^3 carbon. The quintet pattern comes from the virtual coupling with the second dppm-phosphorus-31 atoms. If $^4J(PH)$ and $^3J(PC)$ are considered negligibly small compared with $^2J(PH)$ and $^1J(PC)$, respectively, the latter coupling constants are evaluated to be ca. 10 and 28 Hz, respectively, according to the equation defined in Ref. 11. The values are comparable to those for the mono(chelating dppm) complexes, indicating that the M–P bonding characters of both types of complexes resemble each other.

Mono(chelating dppm−H) Complexes: In the case of $[Pd(\beta\text{-dik})(dppm-H)]$, we could not observe a well-resolved signal for the PCHP proton, but the corresponding carbon signal appeared at δ 15—17 as a clear triplet with $J(PC)$=65 Hz. The $^1J(CH)$ was found to be ca. 176 Hz. The signal is largely shifted to the higher-field compared with that of the above-mentioned PCH_2P carbon. This upfield shift reflects an increase in net electron density on the carbon atom caused by deprotonation. The coupling constant $J(PC)$ becomes twice in the value and the $^1J(CH)$ is also increased by ca. 30 Hz. These results reflect an increase in double-bond character of the P–C bonds, as well as increased sp^2 character of the carbon atom.

Complexes Bearing Both Chelating dppm and dppm−H: The PCH_2P protons in complexes of the type $[Pt(dppm-H)(dppm)]X$ resonated at δ 5.1—5.2 as a triplet with $J(PH)$=8—11 Hz, both the chemical shift and the coupling constant being close to those for the dppm complexes described above. In contrast with the case of $[Pd(\beta\text{-dik})(dppm-H)]$, the PCHP proton of the $[Pt(dppm-H)(dppm)]X$ complexes resonated at δ 3.86 as a well-resolved triplet with $J(PH)$=5—7 Hz. It is interesting to note that three bond coupling ($^3J(PtH)$=171 Hz) of the PCHP proton

Table 2. The CH_2-Proton Chemical Shifts of the Various dppm Complexes with Palladium in the Different Oxiation Numbers[a)]

Complex	Solvent	$\delta(CH_2)$	Lit
dppm	c)	2.80	g)
	Oxidation Number 0		
$[Pd_2(dppm)_3]$	d)	3.00	h)
	Oxidation Number 1		
$[Pd_2Br_2(dppm)_2]$	d)	4.22	h)
	Oxidation Number 2		
$[PdBr_2(dppm)]$	d)	4.33	h)
$[Pd(acac)(dppm)](PF_6)$	c)	4.67	g)
$[Pd(acac)(dppm)](OTs)$[b)]	c)	5.13	g)
$[Pd(hfac)(dppm)](hfac)$[b)]	c)	5.60	g)
$[Pd(dppm)_2]Br_2$	c)	4.26	g)
$[Pd(dppm)_2](PF_6)_2$	e)	4.92	g)
$[Pd(dppm)_2](hfac)_2$	e)	5.16	g)
$[Pf(dppm)_2](OTs)_2$	f)	ca. 5.3	g)

a) δ in ppm from internal TMS. b) Not isolated. c) $CDCl_3$. d) CD_2Cl_2. e) CD_3CN. f) CD_3OD. g) This work. h) H. C. Hunt and A. L. Balch, *Inorg. Chem.*, **20**, 2267 (1981).

to the platinum atom is more than three times as large as that ($^3J(PtH)$=48 Hz for X=BF_4) of the PCH_2P protons. It seems reasonable to assume that the bis(diphenylphosphino)methanido ligand coordinates more strongly to the central metal atom than does the neutral dppm.

Estimation of the Coordination Effect on Deprotonation of dppm. In order to estimate to what extent the C–H bond in dppm is activated when the diphosphine is coordinated to a metal, we examined the CH_2-proton chemical shifts of the various dppm complexes with palladium in the different oxidation states and compared those with that of free dppm. As shown in Table 2, the chemical shifts move to lower field on coordination of dppm to the metal and with increasing oxidation number of the metal, especially for the cationic complexes. These results imply that the CH_2 protons are largely deshielded in the cationic complexes with palladium(II), thus facilitating deprotonation of the dppm ligand. Although the counteranion dependence of the CH_2-proton chemical shift does not appear so clearly because the chemical interaction between the cation and the anion may be conceivable,[25] the CH_2 signal of the $[Pd(dppm)_2]X_2$ complexes tends to cause a downfield shift with decreasing acidity of the conjugate acid HX.

We can not compare the CH_2 chemical shift data for complexes with X=hfac and acac since even if $[Pd(dppm)_2](acac)_2$ is formed in solution, it will be deprotonated immediately to give **3b**. Although the behavior of $[Pd(tfac)_2]$ towards dppm is particularly interesting for pK_a of tfacH is intermediate between those of hfacH and acacH, the reaction profile is not so simple and the details will be reported separately.

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17) For [Pt(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}], the observed coupling constants were as follows; ^1J(PtP)=4410 Hz for cis(Me, P), 4380 Hz for trans(Me, P). See, S. Okeya, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 3396 (1981).

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24) ^{1}H NMR ($CDCl_3$) δ=5.60 (s, 1H, acac-CH), 5.13 (t, J(PH)=12 Hz, 2H, PCH_2P), and 2.16 (s, 6H, acac-CH_3). ^{13}C NMR ($CDCl_3$)[11] δ=187.1 (t, J_A=1.7 Hz, CO), 100.1 (s, acac-CH), 33.9 (t, J(PC)=32 Hz, PCH_2P), and 27.8 (t, J_A=5 Hz, acac-CH_3). ^{31}P NMR ($CDCl_3$) δ=−53.6 (s).

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