Articles

Cleavage of Metal−Carbon Bonds in Hydride-Bridged Platinum and Palladium A-Frame Complexes

Chongfu Xu and Gordon K. Anderson*

Department of Chemistry, University of Missouri−St. Louis, 8001 Natural Bridge Road, St. Louis, Missouri 63121

Received December 4, 1995[⊗]

The hydride-bridged A-frame complexes $[RPt(\mu\text{-}H)(\mu\text{-dppm})_2PtR']PF_6$ and $[RPt(\mu\text{-}H)(\mu\text{-dppm})_2PdR']PF_6$ react with HCl (generated by reaction of acetyl chloride with water) in acetone-d_6 solution by cleavage of one of the metal−carbon bonds. In the diplatinum systems the relative rates of Pt−C bond cleavage decrease in the order Me > Et > Ph, resulting in a single product in each case. For the heterometallic complexes reaction is faster at palladium, but mixtures of $[RPt(\mu\text{-}H)(\mu\text{-dppm})_2PdCl]PF_6$ and $[ClPt(\mu\text{-}H)(\mu\text{-dppm})_2PdR']PF_6$ result in several instances. Further reaction of these with HCl and/or CCl_4 generates the chloride-bridged species $[RPt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]PF_6$, formed, in some cases, by migration of the organic group from palladium to platinum. These complexes have been prepared also by reaction of [PtR(dppm-*PP*)(dppm-*P*)]PF_6 with $[PdCl_2(cod)]$. The $[RPt(\mu\text{-}Cl)(\mu\text{-dppm})_2\text{-}PdCl]PF_6$ complexes are fluxional at 298 K, although the motion may be arrested slightly below ambient temperature. A mechanism involving reversible bridge opening is proposed to account for the fluxional behavior.

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Published on April 2, 1996 on http://pubs.acs.org | doi: 10.1021/om950931x

Introduction

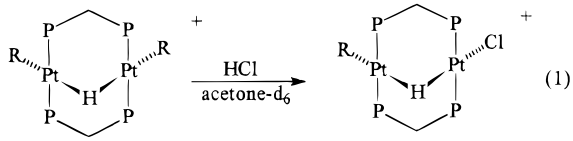
Several dppm-bridged A-frame complexes of platinum containing bridging hydride ligands have been reported,[1] and a number of their reactions have been described. These include reductive eliminations of H_2 from $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ or $[Pt_2HMe(\mu\text{-}H)(\mu\text{-dppm})_2]^+$[2,3] or CH_4 from $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$.[4] The analogous palladium complex $[Pd_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ has been reported to eliminate both CH_4 and C_2H_6.[5] The trihydridodiplatinum cation has also been reported to react with HCl or CCl_4 to produce first $[Pt_2H_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$, followed by $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$.[6]

We have reported recently the preparation of a series of unsymmetrical diplatinum or platinum−palladium A-frame complexes containing bridging hydride ligands, as well as their diplatinum and dipalladium counterparts.[7] Here we report on the reactions of these complexes of the type $[RM(\mu\text{-}H)(\mu\text{-dppm})_2M'R']PF_6$, with HCl or CCl_4, which proceed by cleavage of one of the metal−carbon bonds. In certain cases, the M−C bond cleavage is followed by migration of the remaining organic fragment between the metal centers or replacement of the bridging hydride by chloride.

Results and Discussion

The hydride-bridged complexes $[RM(\mu\text{-}H)(\mu\text{-dppm})_2M'R']PF_6$ exhibit poor solubility in dichloromethane, chloroform, or hydrocarbon solvents, but they are reasonably soluble in acetone. We have investigated their reactions in acetone-d_6 with excess HCl (formed from acetyl chloride by reaction with water in the acetone), with a stoichiometric amount of HCl (prepared similarly) dissolved in CCl_4, and with CCl_4 itself, using NMR spectroscopy.

The symmetrical diplatinum complexes $[Pt_2R_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$ (R = Me, Et, Ph) react with excess or 1 equiv of HCl in acetone-d_6 solution by substitution of one of the terminal organic moieties by chloride (eq 1).



R = Me, Et, Ph

The products, which are formed over several hours at ambient temperature, exhibit two ^{31}P NMR resonances (Table 1), which appear as complex multiplets. In each case, one resonance is located at a position very close to that found in the reactant, and with an almost identical $^1J_{PtP}$ coupling constant,[7] whereas the second appears at 12−13 ppm, with a one-bond coupling

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1996.

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Table 1. ^{1}H and ^{31}P{^{1}H} NMR Data for Complexes of the Type [RM(μ-H)(μ-dppm)$_2$M′Cl]PF$_6$

R	M	M′	δ(P)	$^1J_{PtP}$	J_{PP}	δ(H)	$^1J_{PtH}$
Me	Pt	Pt	19.1	2841	$^2J_{P_aP_c} = 51$, $^4J_{P_aP_d} = 17$	−13.90	960
			13.1	2458	$\lvert^2J_{P_aP_b} - {}^2J_{P_cP_d}\rvert = 22$		425
Et	Pt	Pt	18.6	3050	$^2J_{P_aP_c} = 46$, $^4J_{P_aP_d} = 19$	−14.29	965
			12.2	2494	$\lvert^2J_{P_aP_b} - {}^2J_{P_cP_d}\rvert = 12$		402
Ph	Pt	Pt	14.5	2845	$^2J_{P_aP_c} = 49$, $^4J_{P_aP_d} = 17$	−14.48	950
			12.4	2453	$\lvert^2J_{P_aP_b} - {}^2J_{P_cP_d}\rvert = 26$		415
Me	Pt	Pd	18.0	2802	$^2J_{P_aP_c} = 48$, $^4J_{P_aP_d} = 24$	−11.71	513
			13.5		$\lvert^2J_{P_aP_b} - {}^2J_{P_cP_d}\rvert = 13$		
Et	Pt	Pd	17.9	3021	$^2J_{P_aP_c} = 46$, $^4J_{P_aP_d} = 24$		
			13.7		$\lvert^2J_{P_aP_b} - {}^2J_{P_cP_d}\rvert = 16$		
Ph	Pt	Pd	13.8	2825	unresolved	−12.35	497
			13.6				
Me	Pd	Pt	16.7	2585	unresolved	−15.02	1205
			18.0				
Ph	Pd	Pt	16.0	2525	$^2J_{P_aP_c} = 44$, $^4J_{P_aP_d} = 21$	−15.12	1145
			12.8		$\lvert^2J_{P_aP_b} - {}^2J_{P_cP_d}\rvert = 2$		

[a] *J* values in Hz.

constant in the range 2450−2500 Hz. The first signal is assigned to the P atoms attached to the platinum still bearing the R group, and the second to the P atoms coordinated to the chloroplatinum moiety. As found for the reactants, the $^1J_{PtP}$ value is larger *cis* to an ethyl group (3050 Hz) than when the P atoms are bound to a methyl- (2841 Hz) or phenylplatinum (2845 Hz) moiety.[7] In each case a pseudoquintet (couplings to the two pairs of nonequivalent P atoms are similar) is observed in the ^{1}H NMR spectrum around −14 ppm, due to the bridging hydride. It exhibits two different couplings to ^{195}Pt, one of 950−965 Hz due to coupling to the chloroplatinum center and a smaller coupling in the range 402−425 Hz due to coupling to the organoplatinum moiety. The much greater *trans*-influence of the organic fragment accounts for the smaller $^1J_{PtH}$ value. The hydride resonance is shifted by 5−7 ppm to low frequency compared with that found for [Pt$_2$R$_2$(μ-H)(μ-dppm)$_2$]$^+$.[7] The ^{1}H NMR spectrum of [MePt(μ-H)(μ-dppm)$_2$PtCl]$^+$ also exhibits a triplet resonance at 0.2 ppm, with ^{195}Pt satellites, due to the remaining methyl group, and [EtPt(μ-H)(μ-dppm)$_2$PtCl]$^+$ gives rise to multiplets at −0.2 and 0.9 ppm (each with ^{195}Pt satellites) due to the CH$_2$ and CH$_3$ groups. In each complex a single multiplet due to the dppm methylene groups appears at *ca.* 5 ppm, and signals due to the phenyl hydrogens appear in the 7.0−8.0 ppm range.

The unsymmetrical diplatinum complexes [RPt(μ-H)(μ-dppm)$_2$PtR′]$^+$ (R = Ph, R′ = Me, Et; R = Et, R′ = Me) react in a similar manner, giving a single product in each case. In the phenyl-containing species, cleavage of the alkyl−platinum linkage occurs exclusively to generate [PhPt(μ-H)(μ-dppm)$_2$PtCl]$^+$, whereas in the mixed alkyl complex reaction at the methylplatinum center takes place preferentially to yield [EtPt(μ-H)(μ-dppm)$_2$PtCl]$^+$. Thus the relative rates of cleavage of the Pt−C bonds lie in the order Pt−Me > Pt−Et > Pt−Ph.

We and others have shown previously that [PtMeAr(cod)] complexes react with HCl by preferential cleavage of the aryl−platinum bond.[8,9] In contrast, treatment of bis(phosphine)platinum complexes of the type *cis*-[PtMeAr(PR$_3$)$_2$] with HCl results in Pt−Me bond cleavage.[9,10] To our knowledge, our results represent the first examples of such competitive cleavage reactions in a diplatinum system, and the selectivity for cleavage of the alkyl−platinum bond observed in mononuclear *cis*-bis(phosphine)platinum species is carried over to these diplatinum complexes which contain mutually *trans* phosphine ligands. We have no information at this point regarding the mechanism of the present cleavage reactions, but cleavage of alkylplatinum bonds by HCl in complexes containing bidentate nitrogen ligands has been shown recently to occur by an oxidative addition−reductive elimination sequence.[11,12]

The diplatinum complexes of the type [RPt(μ-H)(μ-dppm)$_2$PtCl]$^+$ have been characterized in solution only. On standing of samples in solution, further reaction occurs to give [PtCl$_2$(dppm)] (δ(P) −63.8, $^1J_{PtP}$ = 3084 Hz). In the case of [EtPt(μ-H)(μ-dppm)$_2$PtCl]$^+$, decomposition also takes place *via* [HPt(μ-Cl)(μ-dppm)$_2$PtH]$^+$ (δ(P) 17.4, $^1J_{PtP}$ = 2600 Hz; δ(H) −11.61, $^1J_{PtH}$ = 1140 Hz),[6] formed presumably by β-elimination of ethene.

As indicated above the [RPt(μ-H)(μ-dppm)$_2$PtCl]$^+$ cations react further to give [PtCl$_2$(dppm)] on standing in solution, but even with excess HCl, there is no evidence for cleavage of the second Pt−C bond to yield a species of the type [Pt$_2$Cl$_2$(μ-H)(μ-dppm)$_2$]$^+$. When complexes of the type [PtR$_2$L$_2$] (L = PR$_3$ or L$_2$ = cod) are treated with HCl, the first organic group is replaced rapidly by chloride but substitution of the second R group is much slower.[8−10] This permits isolation of species of the type [PtClRL$_2$]. In the present dimeric system only one metal−carbon bond is cleaved readily, although each metal center bears only one R group. It may be that the bridging hydride in [Pt$_2$R$_2$(μ-H)(μ-dppm)$_2$]$^+$ exerts a significant *trans*-influence on the Pt−C bonds, which promotes cleavage of one of them. In [RPt(μ-H)(μ-dppm)$_2$PtCl]$^+$, however, the hydride forms a stronger interaction with the chloroplatinum center, and its *trans*-influence on the remaining Pt−C bond is reduced. This is supported by the observation of a reduced $^1J_{PtH}$ coupling to the organoplatinum center compared with that found in [Pt$_2$R$_2$(μ-H)(μ-dppm)$_2$]$^+$. Thus, reaction at the second metal−carbon bond is slow.

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Published on April 2, 1996 on http://pubs.acs.org | doi: 10.1021/om950931x

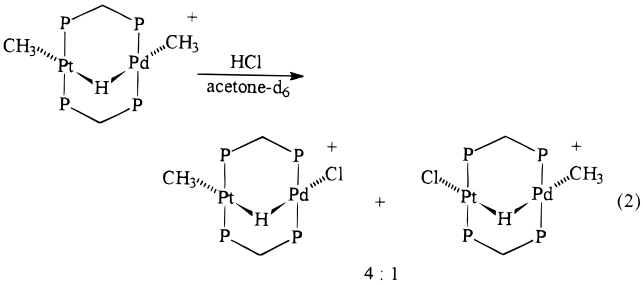
Table 2. $^{31}P\{^1H\}$ NMR Data for Complexes of the Type $[RM(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]PF_6$[a]

R	M	δ(P)	$^1J_{PtP}$	$^2J_{PP} + {}^4J_{PP}$
Me	Pt	14.1	2912	35
		8.3		
Et	Pt	14.3	3171	34
		7.8		
Ph	Pt	9.6	2933	33
		8.7		
Me	Pd	21.1		55
		17.9		
Ph	Pd	19.8		41
		12.8		

[a] *J* values in Hz.

Reactions of the dipalladium complexes $[Pd_2R_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$ (R = Me, Ph) with HCl proceed much more rapidly than those of their platinum counterparts. The reactions are accompanied by extensive decomposition to $[PdCl_2(dppm)]$ (δ(P) −54.6), but unsymmetrical species are observed at short reaction times. These intermediates do not contain hydride ligands and are proposed to be of the form $[RPd(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]^+$, by comparison of their $^{31}P\{^1H\}$ NMR spectra, which consist of two triplets (Table 2), with those of the mixed platinum−palladium species (*vide infra*).

Reactions of the mixed platinum−palladium complexes are somewhat more complicated. Treatment of the dimethyl species with excess HCl results in formation of two products (eq 2) in a 4:1 ratio, corresponding

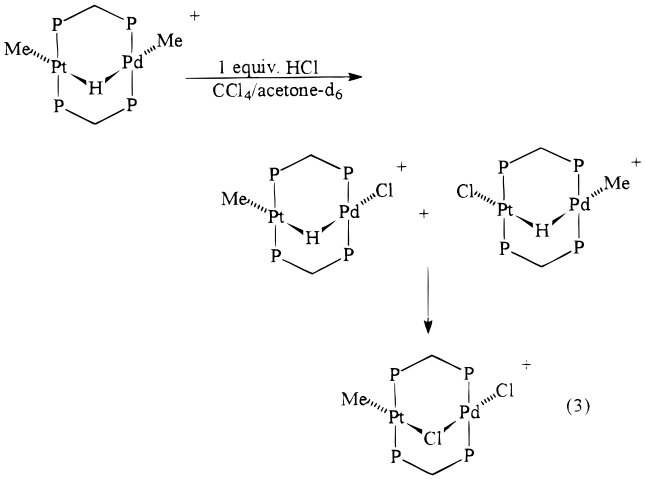


(2)

to cleavage of the Pd−C and Pt−C bonds, respectively. Each compound gives rise to two complex multiplets in the $^{31}P\{^1H\}$ NMR spectrum (Table 1), one of which exhibits coupling to ^{195}Pt in each case. The ^1H signal due to the bridging hydride appears at −11.71 ppm in the case of $[MePt(\mu\text{-}H)(\mu\text{-dppm})_2PdCl]^+$, with a $^1J_{PtH}$ value of 513 Hz, and at −15.02 ($^1J_{PtH}$ = 1205 Hz) for $[ClPt(\mu\text{-}H)(\mu\text{-dppm})_2PdMe]^+$. As found for the diplatinum complexes of this type (*vide supra*), the magnitude of $^1J_{PtH}$ is determined by the *trans*-influence of the terminal group attached to platinum. The major isomer exhibits a triplet resonance at 0.41 ppm ($^3J_{PH}$ = 14 Hz) with ^{195}Pt satellites ($^2J_{PtH}$ = 73 Hz), whereas the minor isomer produces a triplet at δ(H) 0.61 without observable ^{195}Pt satellites. The other methylpalladium complexes $[RPt(\mu\text{-}H)(\mu\text{-dppm})_2PdMe]^+$ (R = Et, Ph) react exclusively by cleavage of the Pd−C bond to generate the appropriate chloropalladium species (Table 1). The product mixtures are stable in solution for only short periods of time at ambient temperature; only 2 h after the addition of HCl signals due to $[PtCl_2(dppm)]$ and $[PdCl_2(dppm)]$ are clearly observable in the ^{31}P NMR spectrum. Attempts to isolate the hydride-bridged products have been unsuccessful.

The reaction of $[PhPt(\mu\text{-}H)(\mu\text{-dppm})_2PdPh]^+$ with excess HCl requires several hours in order to go to completion at ambient temperature, and it results in a mixture of products, identified as $[PhPt(\mu\text{-}H)(\mu\text{-dppm})_2PdCl]^+$ and $[ClPt(\mu\text{-}H)(\mu\text{-dppm})_2PdPh]^+$ (Table 1), in an approximately 2:1 ratio. The former exhibits NMR parameters identical to those for $[PhPt(\mu\text{-}H)(\mu\text{-dppm})_2PdCl]^+$ formed from the reaction of $[PhPt(\mu\text{-}H)(\mu\text{-dppm})_2PdMe]^+$, whereas the assignment of the latter is based on the large $^1J_{PtH}$ value observed for the bridging hydride lying *trans* to the low *trans*-influence chloride. The product ratio again indicates that Pd−C bond cleavage occurs more rapidly. More surprisingly, when $[RPt(\mu\text{-}H)(\mu\text{-dppm})_2PdPh]^+$ (R = Me, Et) is allowed to react with excess HCl, the alkyl group is replaced exclusively, but some migration of the phenyl group from palladium to platinum occurs to generate a 4:1 mixture of $[PhPt(\mu\text{-}H)(\mu\text{-dppm})_2PdCl]^+$ and $[ClPt(\mu\text{-}H)(\mu\text{-dppm})_2PdPh]^+$. It has not proved possible to determine whether this ratio changes with time, because further reaction takes place.

When an acetone-d_6 solution of $[RPt(\mu\text{-}H)(\mu\text{-dppm})_2PdCl]^+$, or a $[RPt(\mu\text{-}H)(\mu\text{-dppm})_2PdCl]^+/[ClPt(\mu\text{-}H)(\mu\text{-dppm})_2PdR]^+$ mixture, formed by treatment of the diorgano precursor with excess HCl , is allowed to stand at ambient temperature, gradual replacement of the bridging hydride by chloride occurs. This process is slow and is accompanied by decomposition to $[PdCl_2(dppm)]$ and $[PtCl_2(dppm)]$. When only 1 equiv of HCl is employed (using CCl_4 as cosolvent) the same hydride-bridged complex, or mixture of complexes, is obtained, but further conversion to $[RPt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]^+$ is much faster. Again, migration of the organic group from palladium to platinum takes place. Treatment of $[MePt(\mu\text{-}H)(\mu\text{-dppm})_2PdMe]^+$, for example, with 1 equiv of HCl in CCl_4/acetone-d_6 produces a mixture of methylplatinum and methylpalladium species, but further reaction yields the methylplatinum complex only (eq 3). In fact,



(3)

when $[MePt(\mu\text{-}H)(\mu\text{-dppm})_2PdMe]PF_6$ is dissolved in acetone-d_6 to which a small amount of CCl_4 is added, rapid conversion to $[MePt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]^+$ takes place; in this case, the hydride-bridged intermediates are not detected. The rapid replacement of hydride by chloride in the presence of CCl_4 may involve a radical process, but this has not been investigated.

The identities of the complexes of the form $[RPt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]PF_6$ have been confirmed by their independent synthesis from $[PtR(dppm\text{-}PP)(dppm\text{-}P)]PF_6$ and $[PdCl_2(cod)]$. Slow addition of $[PdCl_2(cod)]$ to

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a solution of the platinum precursor in CH_2Cl_2 solution, followed by concentration of the solution, allows their isolation as yellow, air-stable powders. Their $^{31}P\{^1H\}$ NMR parameters are given in Table 2.

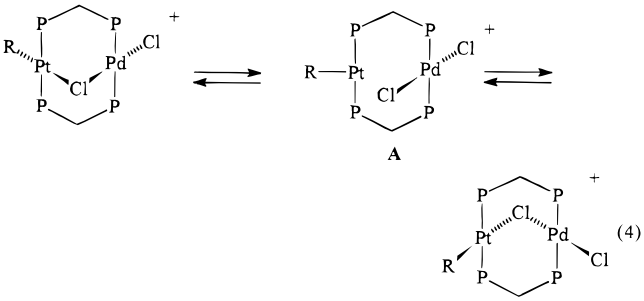
It is uncertain at this stage whether the organic fragment migrates from palladium to platinum prior or subsequent to replacement of the bridging hydride by chloride, although the latter seems more likely. The driving force for the migration is presumably the greater strength of the Pt−C σ-bond. We believe the migration proceeds by means of a transient alkyl- or aryl-bridged species. A small number of complexes containing bridging alkyl groups have been isolated although, in general, they involve electron-deficient metal centers.[13,14] Addition of iodomethane to the ortho-metalated diplatinum complex $[Pt_2(\mu\text{-}C_6H_4PPhCH_2CH_2PPh_2)_2]$ results in a species that may contain a bridging methyl group (alternatively, the methyl may undergo rapid migration between the two platinum centers, presumably by means of a bridging methyl complex).[15] Diplatinum complexes with bridging alkenyl[16] or aryl[17] groups are also known. Phenyl group transfer between platinum centers has been observed in the $[Ph_2Pt(\mu\text{-dmpm})_2PtMe]^+$ cation,[18] and reductive elimination of ethane from the dipalladium system $[Pd_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ has been proposed to occur *via* a transient methyl-bridged intermediate.[5]

The ^1H NMR spectra of the $[RPt(\mu\text{-Cl})(\mu\text{-dppm})_2\text{-}PdCl]^+$ complexes reveal that they are fluxional at ambient temperature. At 298 K the ^1H NMR spectrum of $[MePt(\mu\text{-Cl})(\mu\text{-dppm})_2PdCl]^+$ in acetone-d_6 solution consists of a triplet at 0.78 ppm ($^2J_{PtH}$ = 90 Hz) due to the methyl group, an apparent quintet (with unresolved platinum satellites) at 4.49 ppm ($^2J_{PH}$ = 4.8 Hz) due to the dppm CH_2 group, and a series of multiplets in the range 7.4−8.0 ppm due to the phenyl groups. At 213 K the methyl resonance is virtually unchanged, although the ^{195}Pt satellites are very broad, but the dppm methylene resonance is split into two multiplets centered at 4.48 and 4.75 ppm. Each is a doublet of triplets, with a $^2J_{HH}$ coupling of 13.6 Hz and $^2J_{PH}$ values of 4.0 and 5.9 Hz, respectively. The lower frequency multiplet exhibits broad, poorly resolved platinum satellites, with a $^3J_{PtH}$ coupling of about 60 Hz.[19] As the temperature is raised, these signals broaden and eventually coalesce at 266 K. The free energy of activation for the fluxional process at the coalescence temperature is calculated to be 13.1 ± 0.3 kcal/mol.[20]

The ethyl and phenyl derivatives behave similarly. At 298 K, the ethyl complex exhibits resonances at 0.05 (t, $^3J_{HH}$ = 7.6 Hz, $^3J_{PtH}$ = 83 Hz, CH_3) and 1.40 ppm (q, $^3J_{HH}$ = 7.6 Hz, $^2J_{PtH}$ = 76 Hz, CH_2) and a broad quintet centered at 4.46 ppm. At 213 K the dppm methylene hydrogens are nonequivalent, appearing as two doublets of triplets at 4.41 ($^2J_{HH}$ = 13.9 Hz, $^2J_{PH}$ = *ca.* 4 Hz) and 4.72 ppm ($^2J_{HH}$ = 13.9 Hz, $^2J_{PH}$ = 6.0 Hz). As the temperature is raised, the CH_2 signals broaden and coalesce at 261 K. The phenyl complex exhibits a coalescence temperature of 257 K. The $\Delta G^{\ddagger}$ values for the ethyl and phenyl species are calculated to be 12.6 ± 0.3 and 12.5 ± 0.3 kcal/mol, respectively.

The chloride-bridged complexes $[RPt(\mu\text{-Cl})(\mu\text{-dppm})_2MR]^+$ (M = Pt, Pd) have static structures at ambient temperature,[21,22] whereas the hydride-bridged complexes $[RPt(\mu\text{-H})(\mu\text{-dppm})_2PtR]^+$ (R = H, Me) exhibit fluxional behavior.[21] When R = H, the coalescence temperature is 253 K (at 400 MHz), from which a $\Delta G^{\ddagger}$ value of 11.1 kcal/mol has been calculated; when R = Me, the coalescence temerature is 183 K (at 100 MHz), corresponding to a much lower activation barrier.[21] The hydride-bridged species are believed to undergo inversion of the A-frame structure *via* an intermediate containing a linear R−Pt−H−Pt−R unit, thus averaging the environments of the methylene hydrogens and rendering them equivalent in the NMR spectrum at higher temperatures. It has been reasoned that the chloride-bridged species are not fluxional because the chloride is too large to permit formation of a linear R−Pt−Cl−Pt−R fragment.[21]

In the present case the $\Delta G^{\ddagger}$ values are only 1.5−2.0 kcal/mol higher than that found for $[HPt(\mu\text{-H})(\mu\text{-dppm})_2PtH]^+$, but inversion by means of a linear R−Pt−Cl−Pd−Cl unit is highly unlikely. We propose that averaging of the dppm CH_2 environments occurs by means of a reversible bridge opening process as shown in eq 4. The intermediate **A** would contain a plane of symmetry, which would cause the two hydrogens to become equivalent on the NMR time scale at higher temperatures.



This type of fluxional process suggests a mechanism for the alkyl or aryl group transfer from palladium to platinum. Bridge opening and closure to give a short-lived methyl- or phenyl-bridged intermediate, followed by a second bridge opening and re-formation of a chloride bridge, would effect the transfer (eq 5).

In summary, the diplatinum or platinum−palladium complexes $[RPt(\mu\text{-H})(\mu\text{-dppm})_2MR']PF_6$ react with HCl by cleavage of one of the metal−carbon bonds. The rate of cleavage decreases in the order Me > Et > Ph, and reaction at palladium is faster than at platinum. In the

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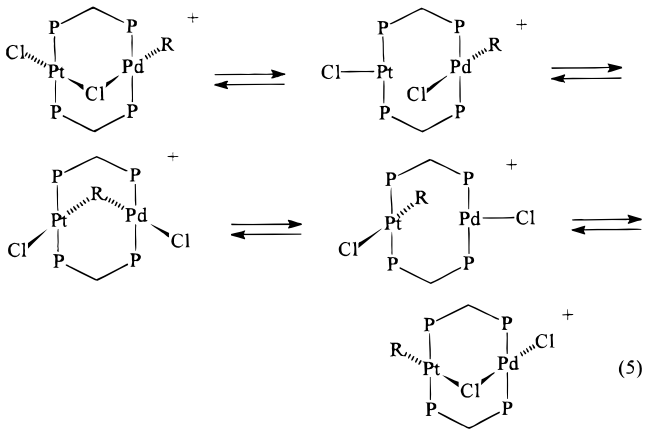

(5)

mixed-metal complexes, Pt−C bond cleavage is followed by migration of the remaining R group from palladium to platinum. This is proposed to occur by means of a transient alkyl- or aryl-bridged species. Further reaction with HCl or CCl_4 yields species of the type $[RPt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]^+$, which are fluxional at ambient temperature. A mechanism involving reversible bridge opening is proposed to account for this behavior.

Experimental Section

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-300 or Varian Unity plus 300 NMR spectrometer. NMR spectroscopic simulations were carried out on a Sun workstation using the VNMR software. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. The hydride-bridged complexes were prepared as described previously.[7]

Preparation of $[MePt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]PF_6$. To a CH_2Cl_2 solution (5 mL) of [PtMe(dppm-*PP*)(dppm-*P*)]PF_6[22] (0.076 g, 0.068 mmol) was added dropwise over 20 min a CH_2Cl_2 solution (7 mL) of $[PdCl_2(cod)]$ (0.019 g, 0.068 mmol). The solution was stirred for a further 2 h and then concentrated, and ether was added to precipitate a fine, yellow powder (0.065 g, 74%). Anal. Found: C, 46.50; H, 3.66. Calcd for $C_{51}H_{47}Cl_2F_6P_5PdPt$: C, 47.08; H, 3.64.

The ethyl and phenyl complexes were prepared analogously. $[EtPt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]PF_6$ was obtained as a yellow powder in 76% yield. Anal. Found: C, 46.90; H, 3.76. Calcd for $C_{52}H_{49}Cl_2F_6P_5PdPt$: C, 47.49; H, 3.76. $[PhPt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]PF_6$ was isolated as a yellow powder in 83% yield. Anal. Found: C, 49.87; H, 3.81. Calcd for $C_{56}H_{49}Cl_2F_6P_5PdPt$: C, 49.34; H, 3.62.

Reactions of Hydride-Bridged Complexes with HCl. In a typical experiment the complex (10−15 mg) was dissolved in acetone-d_6 in a 5-mm NMR tube. Excess acetyl chloride (1 drop) was added (forming HCl by reaction with moisture in the solvent), and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (the hydride resonances were also monitored by ^1H NMR spectroscopy). In stoichiometric reactions the appropriate volume of a 0.14 M solution of acetyl chloride in CCl_4 was introduced, and the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Variable-Temperature NMR Experiments. Approximately 10 mg of the complex $[RPt(\mu\text{-}Cl)(\mu\text{-dppm})_2PdCl]PF_6$ (R = Me, Et, Ph) was dissolved in acetone-d_6 solution. The ^1H NMR spectrum was recorded over the temperature range 193−298 K, and the CH_2 resonance of the dppm ligand was monitored. In the slow exchange regime two signals were observed, and the frequency difference ($\Delta\upsilon$) for the two hydrogens at the coalescence temperature (T_c) was obtained by extrapolation from the low-temperature data. Exchange rate constants, k_c, at the coalescence temperature were calculated using the equation $k_c = \pi(\Delta\upsilon)/2^{1/2}$. The exchange constants were used to determine $\Delta G^{\ddagger}$ at the coalescence temperature from the Eyring equation, $k_c = (k'/h)T_c \exp(-\Delta G^{\ddagger}/RT_c)$, where k' = Boltzmann's constant, h = Planck's constant, and R = the ideal gas constant.[20]

Acknowledgment. Thanks are expressed to the National Science Foundation (Grant No. CHE-9101834) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work, to Johnson Matthey Aesar/Alfa for generous loans of platinum and palladium salts, and to the National Science Foundation (Grant No. CHE-9318696) and the U.S. Department of Energy (Grant No. DE-FG02-92CH10499) for funding to purchase the Varian Unity Plus NMR spectrometer.

OM950931X

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Published on April 2, 1996 on http://pubs.acs.org | doi: 10.1021/om950931x