Organometallics **2000,** *19,* 5071−5076

Synthesis and Structures of Platinum A-Frame Complexes

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Received April 20, 2000

Reactions of [$PtCl_2$(cod)] with the appropriate Grignard reagents produce [PtR_2(cod)] (R = C_6H_5, $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $CH_2C_6H_5$), which, on treatment with 1 mol equiv of HCl, yield the corresponding chloroplatinum complexes [PtClR(cod)]. The 2-tolyl compounds exhibit hindered rotation about the Pt−C bonds at ambient temperature, the barrier to rotation being greater in [PtCl($C_6H_4CH_3$-2)(cod)] than in the ditolyl derivative. The chloroplatinum compounds react with 1 mol equiv of dppm to give [PtClR(dppm)], which are in equilibrium with the A-frame complexes [Pt_2R_2(μ-Cl)(μ-dppm)$_2$]Cl. The extent of dimerization depends on the nature of R, but in each case the A-frame complex could be obtained quantitatively by treatment of the solution with NH_4PF_6 or $TlPF_6$. The structures of [Pt_2R_2(μ-Cl)(μ-dppm)$_2$]-PF_6 (R = $CH_2C_6H_5$, $C_6H_4CH_3$-4) were determined by X-ray crystallography. In the benzyl derivative, one of the *ortho* hydrogens on each phenyl (benzyl) ring points towards the centroid of a dppm phenyl ring, and this may account for the low-frequncy signal associated with the *ortho* hydrogens in solution. The chloride-bridged A-frames could be converted to the corresponding hydride-bridged derivatives, [Pt_2R_2(μ-H)(μ-dppm)$_2$]PF_6 (R = C_6H_5, C_6H_4-CH_3-4, $CH_2C_6H_5$), by treatment with $NaBH_4$.

Introduction

The bis(diphenylphosphino)methane (dppm) ligand has been used extensively in the construction of bimetallic complexes. For platinum(II), these structures include *cis,cis*, *cis,trans*, and *trans,trans* dimers, as well as A-frame derivatives where, in addition to the two bridging dppm ligands, the metals are connected through another bridging atom or group.[1] A-frame complexes of platinum(II) have been known for over 20 years, and compounds with a number of different bridging groups have been structurally characterized.[2−16] Cationic halide-bridged A-frames of the form [Pt_2R_2(μ-X)(μ-dppm)$_2$]$^+$ have been generated by cleavage of a Pt−C bond in [$PtMe_2$(dppm)] by HCl[17] or by displacement of cyclooctadiene from [PtClR(cod)] by dppm.[18] In either case, the reaction proceeds via the monomeric species [PtClR(dppm)]. Although these types of complexes have been known for some time, no structures of halide-bridged platinum(II) A-frames have been determined by X-ray crystallography.

In this paper we describe the preparation and solution behavior of a series of cyclooctadieneplatinum(II) complexes of the types [PtR_2(cod)] and [PtClR(cod)] (R = C_6H_5, $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $CH_2C_6H_5$), their reactions with dppm to form the chloride-bridged compounds [Pt_2R_2(μ-Cl)(μ-dppm)$_2$]PF_6, the molecular structures of the 4-tolyl and benzyl derivatives, and conversion of the phenyl, 4-tolyl, and benzyl A-frames to the corresponding hydride-bridged species.

Results and Discussion

Cyclooctadieneplatinum Precursors. Treatment of [$PtCl_2$(cod)] with at least 2 mol equiv of the appropriate Grignard reagent RMgBr produced the diorganoplatinum complexes [PtR_2(cod)] (R = C_6H_5, $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $CH_2C_6H_5$). Further reaction with 1 mol equiv of HCl, generated in situ from acetyl chloride and methanol, resulted in cleavage of one of the Pt−C bonds

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10.1021/om000337+ CCC: $19.00
Publication on Web 10/27/2000

to give the [PtClR(cod)] derivatives. The complexes were isolated as white or off-white solids that were stable to air and moisture, and they were characterized by elemental analysis and ^{1}H NMR spectroscopy.

The NMR spectra of the phenyl, 4-tolyl, and benzyl complexes are unremarkable. The diorganoplatinum species exhibit a broad multiplet for the methylene hydrogens of the cyclooctadiene, a single resonance for the coordinated olefinic hydrogens (with a coupling to ^{195}Pt of 37−39 Hz), and the expected signals for the R groups. In [Pt($CH_2C_6H_5$)$_2$(cod)], the benzylic CH_2 resonance exhibits a ^2J(Pt,H) value of 114 Hz. The two olefinic groups lie *trans* to different ligands in the [PtClR(cod)] compounds, so two resonances are observed for the olefinic hydrogens, in addition to the signals for the R group and the four CH_2 groups. The olefinic hydrogens that lie *trans* to the R group are shifted to higher frequency compared with their diorganoplatinum precursors, and they exhibit a smaller coupling to platinum (24−32 Hz). In contrast, the olefinic hydrogens *trans* to chloride appear at lower frequency and have greater J(Pt,H) values (75−77 Hz). The ^2J(Pt,H) value in [PtCl($CH_2C_6H_5$)(cod)] is 102 Hz, slightly smaller than that in its dibenzylplatinum analogue.

The bulky 2-tolylplatinum derivatives give rise to broad NMR spectra, suggesting that in these cases rotation about the Pt−C bonds is relatively slow on the NMR time scale. At ambient temperature, a $CDCl_3$ solution of [Pt($C_6H_4CH_3$-2)$_2$(cod)] exhibits a singlet for the two methyl groups, but two very broad signals for the olefinic hydrogens. The latter signals coalesce at 305 K, and they sharpen as the temperature is lowered. At 250 K, two resonances are observed at 4.89 and 5.02 ppm, each with a J(Pt,H) value of 39 Hz. These data lead to a $\Delta G^‡$ value of 14.7 kcal/mol for the bond rotation process. The detection of only two olefinic CH signals at low temperatures indicates that only one rotamer is present in appreciable concentration, unless the signals for both species are coincident. If a single isomer is present, it could be the *syn* or *anti* form, but the latter, in which the two methyl groups are directed away from each other, is the more likely. The di-2-tolylplatinum complex [Pt($C_6H_4CH_3$-2)$_2$(dppm)] exhibited a single resonance in its ^{31}P NMR spectrum at ambient temperature, but both *syn* and *anti* isomers were observed at 203 K.[19]

The chloroplatinum derivative, [PtCl($C_6H_4CH_3$-2)(cod)], gives rise to a single methyl resonance, but three signals due to the olefinic hydrogens in a 1:1:2 ratio at 298 K. The two resonances at 4.45 and 4.59 ppm each exhibit a large coupling to platinum, indicating that they lie *trans* to the chloride. The most intense signal, which is presumably due to two overlapping resonances, has a J(Pt,H) value of only 32 Hz and therefore may be assigned to the olefinic hydrogens *trans* to the tolyl group. A ^{1}H−^{1}H TOCSY spectrum recorded at 298 K reveals that all four CH signals are coupled to each other and also to the methylene hydrogens of the cyclooctadiene. This confirms that all of the signals are due to a single compound. The nonequivalence of the four olefinic hydrogens indicates that there is hindered rotation about the Pt−C bond, and the favored rotamer is that in which the aryl ring lies perpendicular to the platinum square plane. In dmso-d_6 solution, the signals appear at 4.32, 4.49, and 5.62 (1:1:2). As the temperature is raised, the lower frequency signals broaden, and coalescence is reached at 370 K, leading to a $\Delta G^‡$ value of 18.1 kcal/mol. Although coalescence of the signals could be clearly observed, dissociation of cyclooctadiene begins to occur at 350 K, as evidenced by ^{1}H signals at 2.50 and 5.71 ppm, although the solution remains clear. Complete displacement of cyclooctadiene occurs after 20 min at 405 K. Presumably, displacement of cyclooctadiene by dmso-d_6 takes place to yield a species of the type [PtCl($C_6H_4CH_3$-2)(dmso-d_6)$_2$]. The higher barrier to rotation about the Pt−C bond in [PtCl($C_6H_4CH_3$-2)(cod)], compared with its di-2-tolylplatinum analogue, may indicate that the Pt−C bond is stronger in the chloroplatinum complex.

Reactions of [PtClR(cod)] with dppm. When a solution of [PtCl(C_6H_5)(cod)] was treated with 1 mol equiv of dppm, conversion to the dimeric A-frame complex [Pt_2(C_6H_5)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ was complete within 1 h. Addition of NH_4PF_6 to the reaction mixture allowed isolation of the A-frame as its PF_6^- salt. When the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy, the intermediate monomer [PtCl(C_6H_5)(dppm)] (δP −40.5 d, ^2J(P,P) = 41 Hz, ^1J(Pt,P) = 1239 Hz; δP −42.0 d, ^1J(Pt,P) = 3913 Hz) could be detected. When the 4-tolyl complex was treated with dppm, a mixture of monomer (δP −40.4 d, ^2J(P,P) = 41 Hz, ^1J(Pt,P) = 1213 Hz; δP −42.3 d, ^1J(Pt,P) = 3944 Hz) and dimer was obtained, even after 24 h, but addition of excess NH_4PF_6 led to isolation of [Pt_2($C_6H_4CH_3$-4)$_2$(μ-Cl)(μ-dppm)$_2$]PF_6. The reaction of [PtCl($CH_2C_6H_5$)(cod)] with dppm produced [PtCl($CH_2C_6H_5$)(dppm)] (δP −34.5 d, ^2J(P,P) = 48 Hz, ^1J(Pt,P) = 1235 Hz; δP −38.2 d, ^1J(Pt,P) = 4049 Hz) only, and addition of NH_4PF_6 produced a mixture of the monomer and [Pt_2($CH_2C_6H_5$)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$, which persisted even after 48 h. It proved necessary to use $TlPF_6$, which would generate a very insoluble precipitate of TlCl, to drive the reaction to completion. In the bulky 2-tolyl case, conversion of [PtCl($C_6H_4CH_3$-2)(dppm)] (δP −39.6 d, ^2J(P,P) = 41 Hz, ^1J(Pt,P) = 1214 Hz; δP −42.9 d, ^1J(Pt,P) = 3885 Hz) to the A-frame required 24 h, even when $TlPF_6$ was used. In the sequence shown in eq 1, substitution of the diene by dppm occurs rapidly in each case, but the rate and degree of dimerization is strongly dependent on the nature of the R group. In the benzyl and 2-tolyl cases only [PtClR(dppm)] can be observed by ^{31}P NMR spectroscopy, and rearrangement to the A-frame is slow even after addition of NH_4PF_6 or $TlPF_6$. The dimerization probably proceeds by dissociation of one end of a dppm ligand, which then attacks a second molecule of [PtClR(dppm)], displacing a chloride ligand. The larger R groups most likely inhibit attack of the free phosphino group on the second platinum center.

The chloride-bridged A-frame complexes were isolated as their PF_6^- salts, which were characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. They are white or yellow solids, which are stable to air and moisture. Crystals of the 4-tolyl and benzyl derivatives were grown from CH_2Cl_2/Et_2O solution, and their structures were determined by single-crystal X-ray diffraction. With the exception of the 2-tolyl complex, the ^{31}P{^{1}H} NMR

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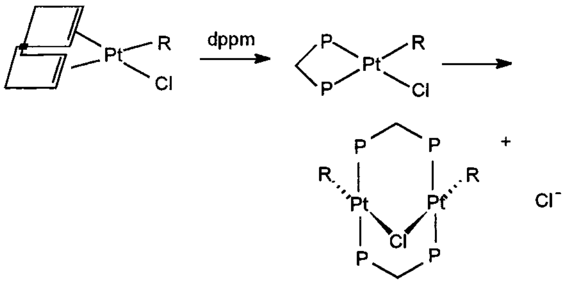

(1)

spectrum consists of a single central resonance, flanked by two sets of satellites due to ^1J(Pt,P) and ^3J(Pt,P) couplings. The coupling patterns have been analyzed in detail previously.[20] The ^1J(Pt,P) values are consistently in the range 3000−3100 Hz, which is typical for species of the form *trans*-[PtClAr(PR$_3$)$_2$].[21] In the 2-tolyl case two central resonances at 9.2 and 9.5 ppm, in an approximate 2:1 ratio, are observed. This may be due to hindered rotation about the Pt−C bonds at ambient temperature. Since all four P atoms are equivalent in each species, the two 2-tolyl groups must lie perpendicular to the Pt$_2$P$_4$ plane, as found previously for the mesitylpalladium complex [Pd$_2${C$_6$H$_2$(CH$_3$)$_3$-2,4,6}$_2$(μ-Br)(μ-dppm)$_2$]PF$_6$.[22] One can imagine three such rotamers for [Pt$_2$(C$_6$H$_4$CH$_3$-2)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$, with the methyl groups both directed into the pocket of the A-frame, both on the outside face, or one on the inside and one on the outside face of the A-frame. Only two are observed, however. Consideration of space-filling models of the three rotamers reveals that no serious steric interactions should be present in any of them provided the tolyl rings remain nearly perpendicular to the Pt$_2$P$_4$ plane, but rotation of the methyl substituents past the dppm phenyls may be restricted. In dmso-d_6 solution, the two signals are found at 12.9 and 13.2 ppm. As the solution is heated, the signals move closer together, but they appear to coalesce at 415 K. By extrapolating the chemical shift difference to the coalescence temperature, a minimum value of $\Delta G^‡$ of 21.3 kcal/mol is obtained. If the signals are indeed due to two rotamers, it is unclear which two are observed.

The ^{1}H NMR spectra of the four chloride-bridged A-frames exhibit the expected numbers of resonances for the organic groups attached to platinum and the phenyl groups on phosphorus. Two signals are observed for the two pairs of methylene hydrogens of the dppm ligands that lie *syn* and *anti* to the bridging chloride. In the benzyl derivative the CH$_2$ group resonates at 2.67 ppm, and it exhibits a coupling to ^{195}Pt of 97 Hz. The *ortho* hydrogens of the benzyl fragment give rise to an unusually low-frequency resonance at 5.17 ppm (vide infra).

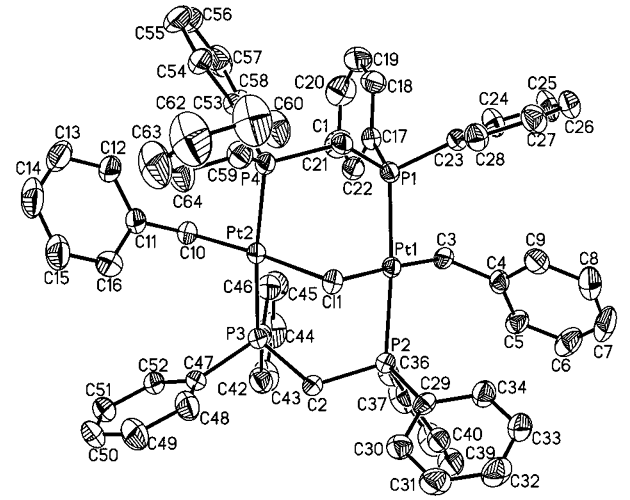

Figure 1. Molecular structure of the [Pt$_2$(CH$_2$C$_6$H$_5$)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ cation, showing the atom-labeling scheme.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [Pt$_2$(CH$_2$C$_6$H$_5$)$_2$(μ-Cl)(μ-dppm)$_2$]PF$_6$

Pt1−C3	2.079(5)	Pt2−C10	2.087(5)
Pt1−Cl	2.4810(11)	Pt2−Cl	2.4602(11)
Pt1−P1	2.2897(13)	Pt2−P3	2.2892(13)
Pt1−P2	2.3078(13)	Pt2−P4	2.3022(13)
Pt1−Pt2			
P1−Pt1−P2	175.09(4)	P3−Pt2−P4	173.82(4)
P1−Pt1−C3	89.30(14)	P3−Pt2−C10	89.56(15)
P1−Pt1−Cl	91.91(4)	P3−Pt2−Cl	91.63(4)
C3−Pt1−Cl	174.25(14)	C10−Pt2−Cl	171.75(14)
C3−Pt1−P2	94.66(15)	C10−Pt2−P4	94.74(15)
P2−Pt1−Cl	84.43(4)	P4−Pt2−Cl	84.75(4)
Pt1−C3−C4	113.2(3)	Pt2−C10−C11	111.9(4)
C3−Pt1−Pt2		C10−Pt2−Pt1	
Pt1−Cl−Pt2	83.45(4)		

X-ray Structure Determinations. [Pt$_2$(CH$_2$C$_6$H$_5$)$_2$(μ-Cl)(μ-dppm)$_2$]PF$_6$ crystallizes in the space group $P\bar{1}$. The molecular structure of the cation is shown in Figure 1, and selected bond distances and angles are presented in Table 1. The Pt$_2$P$_4$ unit is almost planar. The eight-membered Pt$_2$P$_4$C$_2$ ring adopts an elongated, eight-membered chair conformation such that one CH$_2$ group is oriented towards the bridging chloride, and the other lies on the opposite face of the Pt$_2$P$_4$ plane. The bridging chloride is nearly equidistant from the two Pt atoms, the Pt−Cl distances differing by only 0.021 Å, and the Pt−Cl−Pt angle is 83.45(4)°. The Pt−Pt separation is 3.289 Å. The Pt−P distances lie within the range 2.289(1)−2.308(1) Å, and the Pt−C distances are 2.079(5) and 2.087(5) Å. These are typical for platinum(II) units of the form *trans*-[PtXR(PR$_3$)$_2$].[23] The benzyl groups exhibit the expected bend at C3 and C10, and the phenyl rings are tilted such that the *ortho* hydrogens attached to C9 and C16 point directly toward the centroids of the C23−C28 and C47−C52 rings, respectively. These hydrogens will experience significant shielding due to the ring current of the aromatic ring. Although rotation about the Pt−C and C−C bonds in solution will average the environments of H5 and H9 (and H12 and H16), this feature must account for the low-frequency signal associated with the *ortho* hydrogens observed in the ^{1}H NMR spectrum.

The 4-tolyl analogue crystallizes in the $P2_1/c$ space group. The molecular structure of the [Pt$_2$(C$_6$H$_4$CH$_3$-4)$_2$(μ-Cl)(μ-dppm)$_2$]$^+$ cation is shown in Figure 2, and selected bond distances and angles are given in Table 2. As in the first structure, the Pt$_2$P$_4$ unit is nearly planar, and the Pt$_2$P$_4$C$_2$ ring adopts an elongated chair

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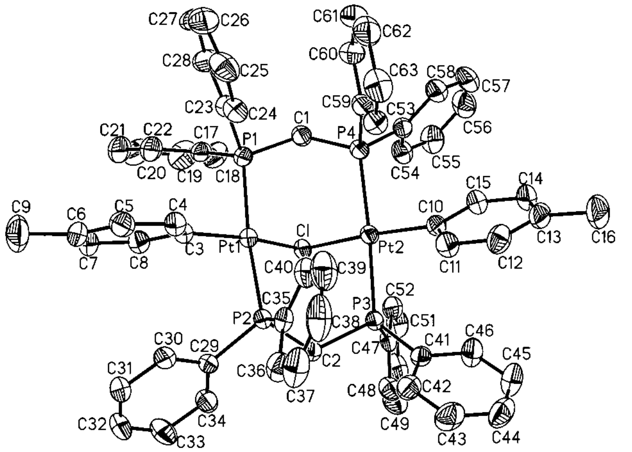

Figure 2. Molecular structure of the $[Pt_2(C_6H_4CH_3\text{-}4)_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$ cation, showing the atom-labeling scheme.

Table 2. Selected Bond Distances and Angles for $[Pt_2(C_6H_4CH_3\text{-}4)_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]PF_6$

Pt1−C1	2.015(4)	Pt2−C8	2.024(3)
Pt1−Cl	2.4368(8)	Pt2−Cl	2.4519(8)
Pt1−P1	2.3020(10)	Pt2−P3	2.3074(9)
Pt1−P2	2.3049(9)	Pt2−P4	2.3125(10)
Pt1−Pt2	3.2337(2)		
P1−Pt1−P2	172.88(3)	P3−Pt2−P4	173.35(3)
P1−Pt1−C1	92.97(11)	P3−Pt2−C8	94.10(10)
P1−Pt1−Cl	86.03(3)	P3−Pt2−Cl	82.80(3)
C1−Pt1−Cl	162.10(11)	C8−Pt2−Cl	170.37(10)
C1−Pt1−P2	89.43(11)	C8−Pt2−P4	91.69(10)
P2−Pt1−Cl	93.72(3)	P4−Pt2−Cl	90.96(3)
C1−Pt1−Pt2	149.09(11)	C8−Pt2−Pt1	141.10(10)
Pt1−Cl−Pt2	82.82(3)		

conformation. The bridging chloride is again nearly equidistant from the two Pt atoms, the Pt−Cl distances being 2.4368(8) and 2.4519(8) Å, and the Pt−Cl−Pt angle is 82.82(3)°. The Pt−Pt separation is 3.2337(2) Å. The Pt−P distances fall between 2.302(1) and 2.313(1) Å, and the Pt−C distances are 2.015(5) and 2.024(5) Å. The Pt−C(aryl) distances are slightly shorter than the Pt−C(alkyl) distances in the previous structure. The 4-tolyl groups lie almost perpendicular to the Pt_2P_4 plane, the C1−C6 and C8−C13 rings being tilted with respect to the Pt_2P_4 plane by 88.6° and 60.7°, respectively.

In contrast to these two structures, the $[Pt_2(COCH_3)_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$ cation adopts a twisted boat conformation, with a Pt−Pt separation of 3.1130(5) Å.[24] In that case, the Pt−Cl−Pt bridge is slightly asymmetric and the Pt−Cl distances are greater (2.556(2) and 2.519(2) Å) than those found in the present complexes. The Pt−Cl−Pt angle of 75.67(6)° is considerably more acute than those observed here. The M−Cl−M angles are also close to 75° in $[Pd_2H(CH_3)(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$ and $[Hg_2Cl_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$,[25,26] whereas in $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$, $[PtRhPh(CO)\ (\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$, and $[Cu_2Cl(NCNMe_2)(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$ the M−Cl−M angles are more similar to those found here.[27−29] There is no clear correlation between the M−M distance and the M−Cl−M angle, the smallest angle being found in $[Hg_2Cl_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$, which also exhibits the greatest metal−metal distance.[26]

The Pt−Pt distances found here lie at the high end of the range of previously reported values for platinum A-frame complexes, which vary from 2.71 Å in $[Pt_2Cl_2(\mu\text{-}HgCl_2)(\mu\text{-dppm})_2]$,[30] where there is a significant Pt−Pt interaction, to over 3.2 Å in $[Pt_2Cl_2(\mu\text{-}L)(\mu\text{-dppm})_2]^+$ (L = NO, $N_2C_6H_4OCH_3$-4)[31,32] and $[Pt_2(C{\equiv}CPh)_2(\mu\text{-}C{\equiv}CPh)(\mu\text{-dppm})_2]^+$.[33] A survey of the previously reported platinum(II) A-frame complexes reveals that they all adopt an elongated boat conformation, in which the bridging moiety lies on the same face of the Pt_2P_4 plane as the dppm methylene groups. The present structures are unusual, therefore, in that they exist in the solid state as elongated chairs. The reasons for this are unclear.

Synthesis of Hydride-Bridged A-Frames. The chloride-bridged complexes $[Pt_2R_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]PF_6$ (R = C_6H_5, $C_6H_4CH_3$-4, $CH_2C_6H_5$) could be converted to the corresponding hydride-bridged derivatives by treatment of a CH_2Cl_2 solution of the A-frame (generated in situ) with 1 mol equiv of $NaBH_4$ at low temperature. After purification, the complexes $[Pt_2R_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$ were isolated as yellow solids. The hydride-bridged 2-tolyl complex could not be isolated because, although it could be detected in solution, it formed only slowly and it decomposed almost as rapidly as it was formed. The three isolable hydride-bridged derivatives were characterized by microanalysis and by NMR spectroscopy. In each case, the complex gives rise to a single resonance with ^{195}Pt satellites in its $^{31}P\{^1H\}$ NMR spectrum. The resonance is shifted slightly to higher frequency, compared with the chloride-bridged precursors. The value of $^1J(Pt,P)$ in $[Pt_2Ph_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ is 130 Hz smaller than that in $[Pt_2Ph_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$, but the couplings are nearly identical in the hydride- and chloride-bridged derivatives where R = $C_6H_4CH_3$-4 or $CH_2C_6H_5$. In the ^1H NMR spectrum, a quintet is observed in the range −9.0 to −9.5 ppm due to the bridging hydride, with $^1J(Pt,H)$ values of 486-496 Hz.[9,34] A broad resonance is observed around 4.5 ppm, due to the methylene hydrogens of the dppm ligands, and the expected signals for the organic substituents attached to platinum and the dppm phenyls are also present. A single, broad resonance is observed for the dppm methylene hydrogens at all accessible temperatures, indicating that they are equivalent on the NMR time scale. This is due to the fluxional nature of the complexes, resulting from rapid migration of the bridging hydride between the two metal centers.[35]

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Summary

We have prepared the platinum(II) complexes [PtR_2(cod)] and [PtClR(cod)] (R = C_6H_5, $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $CH_2C_6H_5$). The 2-tolyl derivatives exhibit restricted rotation about the Pt−C bonds. Reactions of the chloroplatinum species with dppm generate first [PtClR(dppm)], which is in equilibrium with the A-frame complex [Pt_2R_2(μ-Cl)(μ-dppm)$_2$]Cl. The position of equilibrium favors the dimer when R = C_6H_5, but with the bulkier R groups only the monomer is observed. Addition of NH_4PF_6 or $TlPF_6$ results in quantitative conversion to [Pt_2R_2(μ-Cl)(μ-dppm)$_2$]PF_6. The solid state structures of the benzyl and 4-tolyl derivatives have been determined. These represent the first structures of halide-bridged platinum(II) A-frames, and the first examples that adopt an elongated chair conformation. With the exception of the 2-tolyl complex, the chloride-bridged A-frames could be converted to their hydride-bridged analogues.

Experimental Section

All reactions were carried out under an atmosphere of argon. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker ARX-500 or a Varian Unity plus 300 or XL-300 spectrometer. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

[Pt(C_6H_5)$_2$(cod)] and [PtCl(C_6H_5)(cod)] were prepared as reported previously.[36] [Pt(C_6H_5)$_2$(cod)], ^{1}H NMR ($CDCl_3$): δ 2.52 (br, 8H, CH_2), 5.11 (br s, J(Pt,H) = 39 Hz, 4H, CH), 6.65−7.31 (m, 10H, C_6H_5). [PtCl(C_6H_5)(cod)]. ^{1}H NMR ($CDCl_3$): δ 2.65 (m, 8H, CH_2), 4.67 (br s, J(Pt,H) = 77 Hz, 2H, CH), 5.80 (Br s, J(Pt,H) = 30 Hz, 2H, CH), 6.81−7.29 (m, 5H, C_6H_5).

Preparation of [Pt($C_6H_4CH_3$-4)$_2$(cod)]. [PtCl_2(cod)] (0.44 g, 1.2 mmol) was suspended in ether (60 mL), and 4-$CH_3C_6H_4$-MgBr (5.9 mL of a 1.0 M solution in ether) was added. The solution was allowed to stir overnight, then the mixture was quenched with methanol and water. The ether layer was separated, and the aqueous layer was washed with three 10 mL portions of ether. The solvent was removed from the combined ether solution under reduced pressure to leave the product as a white powder (0.45 g, 78%). ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 6H, CH_3), 2.53 (m, 8H, CH_2), 5.12 (br s, J(Pt,H) = 37 Hz, 4H, CH), 6.84−7.31 (m, 8H, C_6H_4).

Preparation of [Pt($C_6H_4CH_3$-2)$_2$(cod)]. This complex was prepared similarly from [PtCl_2(cod)] (0.50 g, 1.3 mmol) and 2-$CH_3C_6H_4$MgBr (3.3 mL of a 2.0 M solution in ether) and isolated as a white powder (0.41 g, 63%). ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 6H, CH_3), 2.61 (m, 8H, CH_2), 4.94 and 5.05 (v br, 4H, CH), 6.77−7.37 (m, 8H, C_6H_4).

Preparation of [Pt($CH_2C_6H_5$)$_2$(cod)]. This complex was prepared similarly from [PtCl_2(cod)] (0.52 g, 1.4 mmol) and $C_6H_5CH_2$MgBr (14 mL of a solution prepared from 1.2 g of Mg and 3.0 mL of $C_6H_5CH_2$Br in 50 mL of dry ether) and isolated as a white powder (0.46 g, 68%). ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 8H, CH_2), 2.91 (s, ^2J(Pt,H) = 114 Hz, 4H, PtCH_2), 4.61 (br s, J(Pt,H) = 39 Hz, 4H, CH), 6.65−7.31 (m, 10H, C_6H_5).

Preparation of [PtCl($C_6H_4CH_3$-4)(cod)]. [Pt($C_6H_4CH_3$-4)$_2$(cod)] (0.21 g, 0.43 mmol) was dissolved in ether (30 mL), and CH_3COCl (3.2 mL of a 0.5 M solution in CCl_4) and methanol (5 drops) were added. The mixture was allowed to stir overnight, then the solvents were removed under reduced pressure. The resulting solid was washed twice with pentane to leave the product as an off-white powder (0.16 g, 70%). Anal. Calcd for $C_{15}H_{19}$ClPt: C, 41.91; H, 4.46. Found: C, 41.90; H, 4.62. ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H, CH_3), 2.52 (m, 8H, CH_2), 4.59 (br s, J(Pt,H) = 75 Hz, 2H CH), 5.79 (br s, J(Pt,H) = 24 Hz, 2H, CH), 6.91−7.31 (m, 4H, C_6H_4).

Preparation of [PtCl($C_6H_4CH_3$-2)(cod)]. This compound was prepared analogously from [Pt($C_6H_4CH_3$-2)$_2$(cod)] (0.14 g, 0.29 mmol) and CH_3COCl (2.1 mL of a 0.5 M solution in CCl_4) and isolated as an off-white powder (0.093 g, 75%). Anal. Calcd for $C_{15}H_{19}$ClPt: C, 41.91; H, 4.46. Found: C, 41.87; H, 4.60. ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 3H, CH_3), 2.52 (m, 8H, CH_2), 4.45 (br, J(Pt,H) = 79 Hz, 1H, CH), 4.59 (br, J(Pt,H) = 73 Hz, 1H, CH), 5.81 (br, J(Pt,H) = 32 Hz, 2H, CH), 6.91−7.31 (m, 4H, C_6H_4).

Preparation of [PtCl($CH_2C_6H_5$)(cod)]. This compound was prepared similarly from [Pt($CH_2C_6H_5$)$_2$(cod)] (0.23 g, 0.47 mmol) and CH_3COCl (3.4 mL of a 0.5 M solution in CCl_4) and isolated as an off-white powder (0.18 g, 86%). Anal. Calcd for $C_{15}H_{19}$ClPt: C, 41.91; H, 4.46. Found: C, 41.42; H, 4.51. ^{1}H NMR ($CDCl_3$): δ 2.38 (m, 8H, CH_2), 3.16 (s, ^2J(Pt,H) = 102 Hz, 2H, PtCH_2), 4.33 (br s, J(Pt,H) = 76 Hz, 2H, CH), 5.59 (br s, J(Pt,H) = 32 Hz, 2H, CH), 7.01−7.31 (m, 5H, C_6H_5).

Preparation of [Pt_2Ph_2(μ-Cl)(μ-dppm)$_2$]PF_6. [PtClPh(cod)] (0.21 g. 0.50 mmol) and dppm (0.19 g, 0.50 mmol) were dissolved in CH_2Cl_2 (30 mL). To this stirred solution was added NH_4PF_6 (0.24 g, 1.5 mmol) and methanol (3 mL). After 1 h the solvents were removed and the resulting solid was washed twice with pentane. The solid was extracted with CH_2Cl_2 (15 mL) and passed down a short alumina column, then the column was washed with CH_2Cl_2 (15 mL) in small portions. The total effluent was collected, and the solvent was removed. The residue was washed twice with pentane, leaving the product as a white powder (0.53 g, 70%). ^{1}H NMR ($CDCl_3$): δ 3.94 (dq, ^2J(H,H) = 13.7 Hz, ^2J(P,H) = 3.4 Hz, 2H, CH_2), 4.29 (dq, ^2J(H,H) = 13.7 Hz, ^2J(P,H) = 4.9 Hz, 2H, CH_2), 6.37 (d, ^3J(H,H) = 6.3 Hz, 4H, CH-2,6), 6.50 (t, ^3J(H,H) = 6.3 Hz, 4H, CH-3,5), 6.81 (t, ^3J(H,H) = 6.3 Hz, 2H, CH-4), 6.98−7.60 (m, 40H, PPh_2). ^{31}P{^{1}H} NMR: δ 9.1, ^1J(Pt,P) = 3027 Hz.

Preparation of [Pt_2($C_6H_4CH_3$-4)$_2$(μ-Cl)(μ-dppm)$_2$]PF_6. This complex was prepared in the same manner from [PtCl($C_6H_4CH_3$-4)(cod)] (0.21 g. 0.50 mmol), dppm (0.19 g, 0.50 mmol), and NH_4PF_6 (0.32 g, 2.0 mmol), but the mixture was allowed to stir for 24 h. The product was obtained as a yellow powder (0.55 g, 72%). Anal. Calcd for $C_{64}H_{58}ClF_6P_5Pt_2$: C, 50.52; H, 3.84. Found: C, 50.78; H, 3.88. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 6H, CH_3), 3.90 (dq, ^2J(H,H) = 14.0 Hz, ^2J(P,H) = 3.0 Hz, 2H, CH_2), 4.28 (dq, ^2J(H,H) = 14.0 Hz, ^2J(P,H) = 4.0 Hz, 2H, CH_2), 6.20 (d, ^3J(H,H) = 7.6 Hz, 4H, CH-2,6), 6.76 (d, ^3J(H,H) = 7.6 Hz, 4H, CH-3,5), 6.98−7.60 (m, 40H, PPh_2). ^{31}P{^{1}H} NMR: δ 8.5, ^1J(Pt,P) = 3055 Hz.

Preparation of [Pt_2($C_6H_4CH_3$-2)$_2$(μ-Cl)(μ-dppm)$_2$]PF_6. [PtCl($C_6H_4CH_3$-2)(cod)] (0.21 g. 0.50 mmol) and dppm (0.19 g, 0.50 mmol) were dissolved in CH_2Cl_2 (30 mL). To this stirred solution was added $TlPF_6$ (0.17 g, 0.50 mmol) and methanol (3 mL). The reaction was allowed to proceed overnight, then the solvents were removed and the resulting solid was washed twice with pentane. The solid was extracted with CH_2Cl_2 (10 mL) and passed down a short alumina column, then the column was washed with CH_2Cl_2 (15 mL) in small portions. The total effluent was collected, and the solvent was removed. The residue was washed with small portions of pentane, leaving the product as a yellow powder (0.50 g, 66%). Anal. Calcd for $C_{64}H_{58}ClF_6P_5Pt_2$: C, 50.52; H, 3.84. Found: C, 50.60; H, 4.20. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 9.2, ^1J(Pt,P) = 3101 Hz; δ 9.5, ^1J(Pt,P) = 3101 Hz.

Preparation of [Pt_2($CH_2C_6H_5$)$_2$(μ-Cl)(μ-dppm)$_2$]PF_6. This complex was prepared in a similar manner from [PtCl($CH_2C_6H_5$)(cod)] (0.21 g, 0.50 mmol), dppm (0.19 g, 0.50 mmol), and $TlPF_6$ (0.17 g, 0.50 mmol), but the reaction was allowed to proceed for only 3 h. The product was obtained as a yellow powder (0.47 g, 62%). Anal. Calcd for $C_{64}H_{58}ClF_6P_5Pt_2$: C, 50.52; H, 3.84. Found: C, 50.47; H, 4.23. ^{1}H NMR ($CDCl_3$): δ 2.67 (s, ^2J(Pt,H) = 97 Hz, 4H, CH_2), 3.76 (dq, ^2J(H,H) = 14.0 Hz, ^2J(P,H) = 3.7 Hz, 2H, CH_2), 4.42 (dq, ^2J(H,H) = 14.0 Hz,

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^2J(P,H) = 5.8 Hz, 2H, CH_2), 5.17 (d, ^3J(H,H) = 7.5 Hz, 4H, C*H-2,6*), 6.31 (t, ^3J(H,H) = 7.5 Hz, 4H, C*H-3,5*), 6.54 (t, ^3J(H,H) = 7.5 Hz, 2H, C*H-4*), 6.95−7.80 (m, 40H, PPh_2). ^{31}P{^{1}H} NMR: δ 8.6, ^1J(Pt,P) = 3044 Hz.

Preparation of [$Pt_2Ph_2(\mu$-H)(μ-dppm)$_2$]PF_6. [PtClPh(cod)] (0.21 g, 0.51 mmol) and dppm (0.19 g, 0.51 mmol) were dissolved in CH_2Cl_2 (30 mL) and stirred magnetically. NH_4PF_6 (0.24 g, 1.5 mmol) was then added to form a suspension, and MeOH (3.0 mL) was added to assist the dissolution of NH_4PF_6. The reaction was allowed to proceed for 1 h, then cooled to 0 °C. $NaBH_4$ (1.0 mL of a 0.50 M solution in dimethoxyethane) was added, and the reaction was allowed to proceed for a further 1 h. The solvent was removed under reduced pressure, and the solid was washed twice with pentane. The solid was extracted with CH_2Cl_2 (10 mL), and the resulting solution was carefully decanted and passed through a short column of neutral alumina. The column was washed with CH_2Cl_2 (15 mL) in small portions. The effluent was collected, and the solvent was removed under reduced pressure. The solid was washed with small portions of pentane to give the product as a yellow powder (0.29 g, 78%). ^{1}H NMR ($CDCl_3$): δ −9.29, (quintet, ^2J(P,H) = 9 Hz, ^1J(Pt,H) = 486 Hz, 1H, Pt*H*), 4.59 (br, 4H, CH_2), 6.19−7.80 (m, 50H, C_6H_5). ^{31}P{^{1}H} NMR: δ 12.6 (s, ^1J(Pt,P) = 2898 Hz).

Preparation of [$Pt_2(C_6H_4CH_3$-4)$_2(\mu$-H)(μ-dppm)$_2$]PF_6. This complex was prepared similarly from [PtCl(4-tolyl)(cod)] (0.21 g, 0.51 mmol) and dppm (0.19 g, 0.51 mmol) and isolated as a yellow powder (0.27 g, 73%). Anal. Calcd for $C_{64}H_{59}F_6P_5Pt_2$: C, 51.68; H, 3.97. Found: C, 51.89; H, 4.11. ^{1}H NMR ($CDCl_3$): δ −9.54 (quintet, ^2J(P,H) = 12 Hz, ^1J(Pt,H) = 496 Hz, 1H, Pt*H*), 1.85 (s, 6H, CH_3), 4.62 (br, 4H, CH_2), 6.15 (d, ^3J(H,H) = 6.4 Hz, 4H, C*H-2,6*), 6.25 (d, ^3J(H,H) = 6.4 Hz, 4H, C*H-3,5*), 7.10−7.70 (m, 40H, PPh_2). ^{31}P{^{1}H} NMR: δ 12.8 (s, ^1J(Pt,P) = 3036 Hz).

Preparation of [$Pt_2(CH_2C_6H_5)_2(\mu$-H)(μ-dppm)$_2$]PF_6. This complex was prepared similarly from [PtCl($CH_2C_6H_5$)(cod)] (0.21 g, 0.51 mmol) and dppm (0.19 g, 0.51 mmol) and isolated as a yellow powder (0.24 g, 65%). ^{1}H NMR ($CDCl_3$): δ −9.03 (quintet, ^2J(P,H) = 10 Hz, ^1J(Pt,H) = 493 Hz, 1H, Pt*H*), 2.39 (s, ^{2}J(Pt,H) = 96 Hz, 4H, PtCH_2), 4.37 (br, 4H, CH_2), 6.02 (d, ^3J(H,H) = 6.9 Hz, 4H, C*H-2,6*), 6.50 (t, ^3J(H,H) = 6.9 Hz, 4H, C*H-3,5*), 6.60 (t, ^3J(H,H) = 6.9 Hz, 2H, C*H-4*), 7.27−7.65 (m, 40H, PPh_2). ^{31}P{^{1}H} NMR: δ 14.2, ^1J(Pt,P) = 3059 Hz.

X-ray Structure Determinations. Preliminary examination and data collection were performed using a Siemens SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed tube X-ray source (50 kV × 40 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary unit cell constants were determined with a set of 45 narrow frame (0.3° in ω) scans. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. The SMART software package[37] was used for data collection, and SAINT[37] was used for frame integration. Final cell constants were determined by a global refinement of *xyz* centroids of 8192 reflections. An empirical absorption correction was applied using SADABS.[38] Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package.[39] Crystallographic data are collected in Table 3.

Table 3. Crystallographic Data for [$Pt_2R_2(\mu$-Cl)(μ-dppm)$_2$]PF_6 (R = $C_6H_4CH_3$-4, $CH_2C_6H_5$)

	R = $C_6H_4CH_3$-4	R = $CH_2C_6H_5$
cryst syst	monoclinic	triclinic
space group, *Z*	$P2_1/c$, 4	$P\bar{1}$, 2
a, Å	16.1901(5)	11.7628(12)
b, Å	21.3483(7)	14.2670(8)
c, Å	17.0454(6)	20.3564(14)
α, deg	90	78.712(5)
β, deg	97.147(2)	85.531(8)
γ, deg	90	85.851(5)
cell vol, Å^3	5845.6(3)	3334.2(5)
D(calcd), Mg/m^3	1.729	1.674
temp, K	218(2)	218(2)
abs coeff, mm^{-1}	5.023	4.491
θ range, deg	1.27−26.42	1.02−27.57
no. of reflns collected	88 341	64 918
no. of ind reflns	11 999	14 928
abs corr	empirical	empirical
no. of params refined	705	793
$R(F)$, $R_w(F^2)$ ($F^2 > 2.0\sigma(F^2)$)	0.0235, 0.0528	0.0417, 0.0761
$R(F)$, $R_w(F^2)$ (all data)	0.0360, 0.0578	0.0494, 0.0784
goodness of fit	1.016	1.259
largest difference peak and hole, e Å^{-3}	0.966, −0.609	1.203, −1.356

Acknowledgment. Thanks are expressed to the National Science Foundation (grant no. CHE-9530085) and the University of Missouri Research Board for support of this work. Acknowledgment is made to the National Science Foundation (grant nos. CHE-9318696 and 9309690), the U.S. Department of Energy (grant no. DE-FG02-92CH10499), and the University of Missouri Research Board for instrumentation grants.

Supporting Information Available: A listing of crystal data and structure refinement parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for [$Pt_2R_2(\mu$-Cl)(μ-dppm)$_2$]PF_6 (R = $CH_2C_6H_5$, $C_6H_4CH_3$-4). This material is available free of charge via the Internet at http://pubs.acs.org.

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