stable in refluxing toluene, but to a lesser extent than its iodide analogue, since slow appearance of the typical $\delta \rightarrow \delta^*$ electronic transition of $Mo_2Cl_4(PMe_3)_4$ can be detected in the visible spectrum; (iii) thermal treatment of $MoI_3(PEt_3)_3$ as obtained from $MoI_3(THF)_3$ by the procedure described in eq 6 gives rise to a mixture of $Mo_2I_4(PEt_3)_4$ and $[PHEt_3][MoI_4(PEt_3)_2]$.

It would therefore seem that dissociation of a phosphine molecule from $MoI_3(PR_3)_3$ is a much more facile process for PEt_3 than for PMe_3. This is in agreement with the relative basicity of the two ligands and also with their steric requirements. A similar trend was found for the Mo(II) quadruply bonded dimers $Mo_2Cl_4(PR_3)_3$ in their reaction with CO: kinetic studies indicated that the dissociation of a phosphine is the necessary primary step, and the dimer with PMe_3 was found to be much less reactive than those containing phosphines with longer alkyl substituents.[30]

Finally, we would like to remark that the chemistry depicted in Scheme I may be related to other phosphine-molybdenum carbonyl reactions that were found to lead to salts of phosphonium cations.[4,11a,31]

Conclusions

A convenient route to $MoI_3(THF)_3$ has been developed by diiodine oxidation of molybdenum(0) and molybdenum(II) carbonyl starting materials. This route represents a new strategy for the preparation of THF adducts of transition-metal halides, the commonly used ones being direct interaction of the metal(III) halide with THF or reduction of higher valent starting materials. We anticipate that other unknown $MX_3(THF)_3$ complexes, particularly $MoBr_3(THF)_3$ and $WX_3(THF)_3$ (X = Br, I), could possibly be obtained in the same way.

Acknowledgment. We thank the National Science Foundation for support of this work, Dr. Cynthia Day of Crystalytics, Lincoln, NB, for collection of intensity data on $MoI_3(THF)_3$, and Professor H. D. Kaesz for helpful discussion.

Registry No. $MoI_3(THF)_3$, 107680-52-4; $Mo(CO)_3(\eta^6\text{-}C_6H_5CH_3)$, 12083-34-0; $Mo_2I_4(CO)_8$, 22547-54-2; $MoI_2(CO)_3(THF)_2$, 103904-36-5; $MoI_3(PMe_3)_3$, 107680-53-5; $MoI_3(PEt_3)_3$, 107680-54-6; $Mo_2Cl_4(PMe_3)_4$, 67619-17-4; $MoCl_3(PMe_3)_3$, 73534-30-2; $Mo_2I_4(PEt_3)_4$, 107680-55-7; $[MoI_4(PEt_3)_2][PHEt_3]$, 107680-57-9; $Mo_2I_4(PMe_3)_4$, 89637-15-0; I_2, 7553-56-2.

Supplementary Material Available: Full tables of bond distances and angles and a listing of anisotropic displacement parameters for $MoI_3(THF)_3$ (3 pages); a listing of observed and calculated structure factors for $MoI_3(THF)_3$ (5 pages). Ordering information is given on any current masthead page.

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Reactions of Dichloro(diphosphine)platinum(II) Complexes with Tertiary Phosphines: $^{31}P\{^1H\}$ NMR Studies of $[PtCl(PR_3)(P^\frown P)]^+$ and $[Pt(PR_3)_2(P^\frown P)]^{2+}$ ($P^\frown P$ = 1,2-Bis(diphenylphosphino)ethane (dppe), 1,2-Bis(dimethylphosphino)ethane (dmpe), or Bis(diphenylphosphino)methane (dppm))

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$[PtCl_2(dppe)]$ reacts with L (L = PBu_3, PEt_3, $PMePh_2$, PPh_3) to yield $[PtCl(L)(dppe)]Cl$. Likewise, $[PtCl_2(dppm)]$ reacts with L (L = PBu_3, $PMePh_2$) to give $[PtCl(L)(dppm)]Cl$. When $[PtCl_2(dppe)]$ is treated with 2 equiv of L, $[PtCl(L)(dppe)]^+$ is the only platinum-containing species observed. In contrast, when $[PtCl_2(dppm)]$ is treated with 2 equiv of $PMePh_2$, both chloride ligands are displaced to yield $[Pt(PMePh_2)_2(dppm)]Cl_2$. $[Pt(PMePh_2)_2(dppe)]^{2+}$ can be generated, although not quantitatively, by treatment of $[PtCl_2(dppe)]$ with 2 equiv of $PMePh_2$ in the presence of silver perchlorate. $[PtCl_2(dppe)]$ reacts with dppm to give the unsymmetrical cation $[Pt(dppm)(dppe)]^{2+}$, which has been isolated as both its chloride and tetraphenylborate salts. $[PtCl_2(dmpe)]$ can be treated with dppe to form $[Pt(dmpe)(dppe)]Cl_2$. These unsymmetrical dipositive cations $[PtL_2(P^\frown P)]^{2+}$ display second-order $^{31}P\{^1H\}$ NMR spectra that have been analyzed in terms of a four-spin system, and the analyses have been confirmed by spin simulation.

Introduction

We have recently been investigating the reaction chemistry of platinum(II) carboxylate complexes containing chelating diphosphine ligands. During the course of this work we have found that reactions of such complexes with tertiary phosphines are complicated by subsequent reactions with chlorinated solvents.[1] For example, when $[Pt(OBz)_2(dppe)]$ (OBz = benzoate) is treated with PBu_3 in dichloromethane, the initial substitution product, $[Pt(OBz)(PBu_3)(dppe)]^+$, is ultimately converted to $[PtCl(PBu_3)(dppe)]^+$. A detailed account of the substitution chemistry of platinum(II) carboxylate complexes will be presented elsewhere, but in order to fully characterize the products of these reactions in chlorinated solvents, a study of the substitution reactions of the corresponding platinum(II) chloride complexes was undertaken. The results of this latter study are presented here.

Although ligand substitution reactions of square-planar platinum(II) complexes are well documented in general,[2] surprisingly little has appeared in the literature regarding the substitution chemistry of $[PtCl_2(P^\frown P)]$ complexes. Davies et al. have reported the formation of $[PtCl(PR_3)(dppe)]^+$ (R = Ph, *n*-Pr) complexes upon treatment of $[PtCl_2(dppe)]$ with 1 equiv of PR_3 in the presence of silver perchlorate.[3] The compounds $[PtCl(PR_3)(dppe)][ClO_4]$ were characterized by $^{31}P\{^1H\}$ NMR, infrared, and UV-visible spectroscopies, solution conductivity experiments, and elemental analyses. We have found that the presence of a silver salt is not necessary for the formation of $[PtCl(PR_3)(P^\frown P)]^+$ complexes from the corresponding $[PtCl_2(P^\frown P)]$. One chloride ligand can be displaced readily from $[PtCl_2(dppe)]$ or $[PtCl_2(dppm)]$ by the treatment of such complexes with 1 equiv of a tertiary phosphine ligand. Furthermore, in the case of $[PtCl_2(dppm)]$, both chloride ligands can be displaced by tertiary phosphine ligands in the absence of a silver salt. On the other hand, it is much more difficult to remove the second chloride ligand

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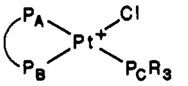
0020-1669/87/1326-1518$01.50/0

Table I. $^{31}P\{^1H\}$ NMR Data[a] for $[PtCl(L)(P\frown P)]^+$ Complexes



complex	$\delta(P_A)$ $\delta(P_B)$ $\delta(P_C)$	$^1J(Pt-P_A)$ $^1J(Pt-P_B)$ $^1J(Pt-P_C)$	$^2J(P_A-P_B)$ $^2J(P_B-P_C)$ $^2J(P_A-P_C)$
$[PtCl(PMePh_2)(dppe)]Cl$	52.6	2266	6
	44.9	3480	17
	8.3	2342	389
$[PtCl(PBu_3)(dppe)]Cl$	53.2	2255	6
	42.8	3551	15
	8.3	2281	368
$[PtCl(PEt_3)(dppe)]Cl$	53.1	2263	6
	43.3	3527	16
	16.6	2282	368
$[PtCl(PPh_3)(dppe)]Cl$	53.7	2414	6
	46.3	3505	17
	23.9	2370	387
$[PtI(PMePh_2)(dppe)][ClO_4]$	52.6	2368	6
	45.1	3481	17
	8.4	2350	390
$[PtCl(PMePh_2)(dppm)][ClO_4]$	-50.9	1968	66
	-51.1	2995	8
	6.1	2361	414
$[PtCl(PMePh_2)(dppm)]Cl$[b]	-50.7	1941	66
	-51.4	3006	9
	5.6	2359	408
$[PtCl(PBu_3)(dppm)]Cl$[b]	-49.7	1867	66
	-50.3	3042	9
	8.2	2312	396
$[PtCl(PPh_3)(dmpe)]Cl$	48.4	2354	4
	25.3	3304	16
	22.6	2342	390
$[PtCl(PMePh_2)(dmpe)]Cl$	48.0	2323	c
	24.9	3381	17
	9.1	1938	391

[a] Chemical shifts are in ppm relative to external phosphoric acid. All coupling constants are given in hertz. The spectra were recorded for solutions in $CDCl_3$. [b] Recorded at -40 °C. [c] Not resolved.

from the dppe complex. These reactions are discussed in detail below.

$[PtCl_2(dppe)]$ has been shown to react with dppe to form $[Pt(dppe)_2]Cl_2$, and $[PtCl_2(dppm)]$ reacts likewise with dppm to form $[Pt(dppm)_2]Cl_2$.[4] In a similar manner we have prepared two unsymmetrical dipositive cations of the type $[Pt(P\frown P)(dppe)]^{2+}$ ($P\frown P$ = dppm or dmpe), and these are also discussed here.

Results and Discussion

Treatment of a $CDCl_3$ solution of $[PtCl_2(dppe)]$ with 1 equiv of $PMePh_2$ yields the cationic complex $[PtCl(PMePh_2)(dppe)]^+$ in quantitative yield, as determined by phosphorus-31 NMR spectroscopy. This complex displays a first-order $^{31}P\{^1H\}$ NMR spectrum, which is characteristic of three different phosphino groups bound to a platinum(II) center.[3] Each phosphino group appears as a doublet of doublets, with satellites due to coupling to platinum-195. The $^{31}P\{^1H\}$ NMR data for $[PtCl(PMePh_2)(dppe)]Cl$ are listed in Table I. The resonances due to the phosphino groups of the dppe ligand appear well downfield of that for free dppe. Such an observation is indicative of a five-membered chelate ring.[5] The resonance due to the phosphorus atom trans to the $PMePh_2$ ligand is readily identified by its one-bond platinum–phosphorus coupling constant of 2266 Hz, which is typical of a trans arrangement of phosphine ligands.[6] For the other dppe phosphino group, $^1J(Pt-P)$ = 3480 Hz, which is typical for a phosphorus atom trans to a chloride ligand. The resonance due to $PMePh_2$ appears at 8.3 ppm with $^1J(Pt-P)$ = 2342 Hz, which again is typical for phosphino groups bound to platinum(II) in a trans arrangement. Furthermore, the three two-bond phosphorus–phosphorus coupling constants are all resolved, and these can be used to further confirm the above assignment of peaks. As expected, coupling between phosphino groups in a cis arrangement is small ($^2J(P-P)_{cis} < 20$ Hz), whereas that for phosphorus atoms arranged trans to one another is much larger ($^2J(P-P)_{trans} > 350$ Hz) (Table I).

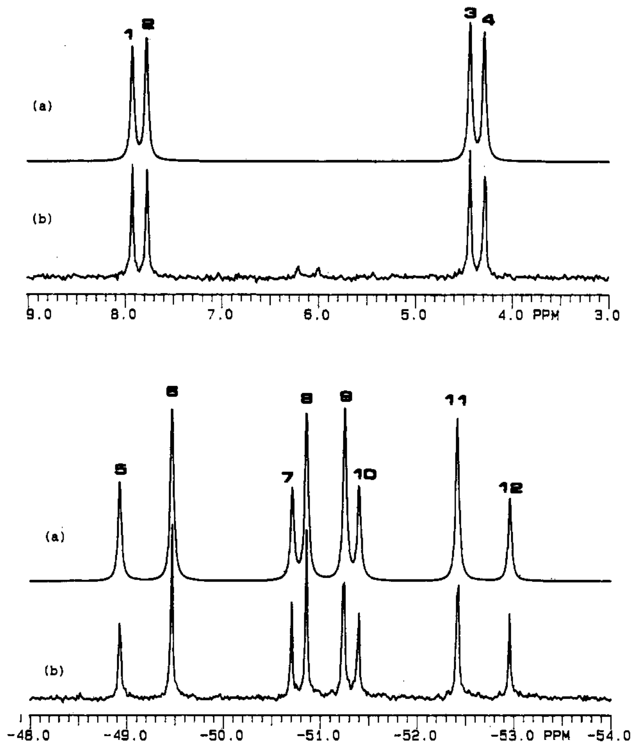


Figure 1. Calculated (a) and experimental (b) $^{31}P\{^1H\}$ NMR spectra of $[PtCl(PMePh_2)(dppm)][ClO_4]$ in $CDCl_3$. The platinum-195 satellites have been omitted.

In a similar manner $[PtCl_2(dppe)]$ reacts to give other $[PtCl(L)(dppe)]^+$ complexes by treatment with L (L = PBu_3, PEt_3, or PPh_3). Interestingly, in the case of L = PEt_3 or PPh_3 a small amount of $[PtCl_2L_2]$ is observed in the product mixture. It is somewhat surprising (especially for PPh_3) that these monodentate ligands displace the strongly chelating dppe ligand. The $^{31}P\{^1H\}$ NMR data for these cationic complexes are similar to those for $[PtCl(PMePh_2)(dppe)]Cl$, and they are compiled in Table I.

$[PtCl_2(dppm)]$ undergoes an analogous reaction when treated with 1 equiv of a phosphine ligand. When a $CDCl_3$ solution of $[PtCl_2(dppm)]$ is treated with 1 equiv of $PMePh_2$, the cationic complex $[PtCl(PMePh_2)(dppm)]^+$ is formed readily. This complex has been isolated as its perchlorate salt. $[PtCl(PMePh_2)(dppm)][ClO_4]$ displays a $^{31}P\{^1H\}$ NMR spectrum that is qualitatively similar to that of $[PtCl(PMePh_2)(dppe)]Cl$, but the very small difference between the chemical shifts of the two dppm phosphino resonances leads to second-order effects. Figure 1 compares the calculated and experimental $^{31}P\{^1H\}$ NMR spectra for $[PtCl(PMePh_2)(dppm)][ClO_4]$, and the spectroscopic parameters are compiled in Table I. This complex displays an ABX type spectrum,[7] in which the resonances for the dppm ligand (P_A and P_B) appear upfield of the resonances of free dppm. Such an upfield shift is characteristic for phosphino groups incorporated into a four-membered chelate ring.[5] Lines 1–4 are assigned to the $PMePh_2$ (P_C) ligand on the basis of its chemical shift, which is well downfield of that of free $PMePh_2$. Furthermore, the $^1J(Pt-P_C)$ value is 2361 Hz, which is characteristic of a phosphorus atom bound to platinum(II) in a site that is trans to another

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(7) Those molecules not containing platinum-195 display ABX type spectra. This accounts for approximately two-thirds of the molecules present in solution. For those molecules containing platinum-195, the spectrum is further split by coupling to ^{195}Pt ($I = {}^1/_2$; 33.8% natural abundance).

phosphorus atom.[6] Lines 5, 6, 11, and 12 are assigned to the dppm phosphino group (P_A), which is trans to $PMePh_2$. This assignment is based on the magnitude of ${}^1J(Pt-P_A)$ (1968 Hz), which suggests that this phosphino group is trans to another phosphino group. This is further confirmed by the magnitude of ${}^2J(P_A-P_C)$ (414 Hz), which is also characteristic of a trans arrangement of phosphine ligands. Lines 7–10 are thus assigned to P_B, which is trans to a chloride ligand. This is supported by the magnitudes of ${}^1J(Pt-P_B)$ (2995 Hz), ${}^2J(P_A-P_B)$ (66 Hz), and ${}^2J(P_B-P_C)$ (8 Hz); the ${}^2J(P-P)$ values are indicative of phosphino groups bound in a cis arrangement.[6]

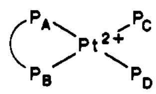
There are few examples in the literature of platinum complexes containing chelated dppm in which the two phosphino groups are chemically inequivalent, such that ${}^2J(P_A-P_B)$ may be observed directly. For complexes of the type [PtClR(dppm)][8-10] the ${}^2J(P_A-P_B)$ values lie in the range 40–46 Hz, but in $[PtCl(PMePh_2)(dppm)]^+$ the value of ${}^2J(P_A-P_B)$ is significantly larger. This contrasts with the very small ${}^2J(P_A-P_B)$ values observed for dppe complexes; the $[PtCl(L)(dppe)]^+$ complexes described above give rise to couplings of 6 Hz, $[Pt(CH_3)(L)(dppe)]^+$ species produce couplings in the range 6–9 Hz,[11] and for [PtClR(dppe)][12] and $[Pt(CH_3)X(dppe)]$[11] ${}^2J(P_A-P_B)$ is too small to be resolved. The larger ${}^2J(P_A-P_B)$ values in complexes containing chelated dppm are due to the existence of two coupling paths, through the metal and through the carbon.

In $[PtCl(PMePh_2)(dppm)]^+$ the magnitudes of the two-bond phosphorus–phosphorus couplings are 414, 66, and 8 Hz. Where the sign of the large coupling constant involving mutually trans phosphines has been determined for square-planar complexes, it has been found to be positive.[13-19] Thus, we assume that ${}^2J(P_A-P_C)$ in $[PtCl(PMePh_2)(dppm)]^+$ is +414 Hz. On the other hand two-bond couplings between mutually cis phosphines may be positive or negative.[14,18,19] In simulating the ${}^{31}P\{{}^1H\}$ NMR spectrum of $[PtCl(PMePh_2)(dppm)]^+$, we have found that a good correlation of the relative line intensities with those in the experimental spectrum is only obtained if ${}^2J(P_B-P_C)$ is −8 Hz, whereas ${}^2J(P_A-P_B)$ may be of either sign.

Interestingly, when the cation $[PtCl(PMePh_2)(dppm)]^+$ is not isolated as its perchlorate salt, that is the counterion is chloride, the lines in the ${}^{31}P\{{}^1H\}$ NMR spectrum are somewhat broad at ambient temperature, but when the sample is cooled to −40 °C, the lines become sharp. Furthermore, the resonances due to P_A are shifted to slightly lower field relative to the resonances due to P_B for $[PtCl(PMePh_2)(dppm)]Cl$ compared to those for the perchlorate salt. Since the ${}^{31}P\{{}^1H\}$ NMR spectrum of $[PtCl(PMePh_2)(dppm)][ClO_4]$ shows virtually no change on cooling to −40 °C, it is likely that the chemical shift changes observed in the spectrum of $[PtCl(PMePh_2)(dppm)]Cl$ are due to an interaction of the chloride ion with the metal complex.

The compound $[PtCl(PBu_3)(dppm)]Cl$ can be formed by treating a solution of $[PtCl_2(dppm)]$ in $CDCl_3$ with 1 equiv of PBu_3. In contrast to the analogous compound containing $PMePh_2$, the lines in the ${}^{31}P\{{}^1H\}$ NMR spectrum of $[PtCl(PBu_3)(dppm)]Cl$ are sharp at room temperature. The spectrum for this complex is very similar to that for $[PtCl(PMePh_2)(dppm)][ClO_4]$ (Table I). In both $[PtCl(PMePh_2)(dppm)]Cl$ and $[PtCl(PBu_3)(dppm)]Cl$ it is necessary that ${}^2J(P_B-P_C)$ be negative in order to obtain a satisfactory correlation of the experimental and simulated spectra.

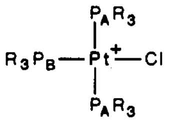
Table II. ${}^{31}P\{{}^1H\}$ NMR Data[a] for $[PtL_2(P\frown P)]^{2+}$ Complexes



complex	$\delta(P_{A,B})$ (${}^1J(Pt-P_{A,B})$) $\delta(P_{C,D})$ (${}^1J(Pt-P_{C,D})$)	J_{AB} J_{AC} (J_{BD}) J_{AD} (J_{BC}) J_{CD}
$[Pt(PMePh_2)_2(dppm)]Cl_2$[b]	−36.7 (2085) −6.7 (2604)	±59.6 −20.9 +337.1 ±19.2
$[Pt(PBu_3)_2(dppm)]Cl_2$[b]	−38.2 (2032) −9.2 (2609)	±55.1 −22.1 +327.1 ±21.2
$[Pt(PMePh_2)_2(dppe)][ClO_4]_2$	48.8 (2280) −3.2 (2377)	±6.5 −24.1 +311.4 ±25.5
$[Pt(dppm)(dppe)][BPh_4]_2$[c]	−38.9 (1959) 48.8 (2312)	±57.5 −11.1 +309.8 ±5.7
$[Pt(dmpe)(dppe)]Cl_2$[d]	44.0 (2370) 32.1 (2512)	±12.1 −21.6 +313.0 ±8.4

[a] Chemical shifts are in ppm relative to external 85% H_3PO_4. Coupling constants are given in hertz. Spectra were recorded for $CDCl_3$ solutions. [b] Recorded at −40 °C. [c] $P_A\frown P_B$ = dppm; $P_C\frown P_D$ = dppe. [d] $P_A\frown P_B$ = dppe; $P_C\frown P_D$ = dmpe. Assignments of J_{AB} and J_{CD} are uncertain.

Table III. ${}^{31}P\{{}^1H\}$ NMR Data[a] for $[PtClL_3]^+$ Complexes



L	$\delta(P_A)$	${}^1J(Pt-P_A)$	$\delta(P_B)$	${}^1J(Pt-P_B)$	${}^2J(P_A-P_B)$
$PMePh_2$	12.2 (d)	2393	−4.8 (t)	3599	20
PBu_3	11.1 (d)	2270	1.9 (t)	3461	19

[a] Chemical shifts are reported in ppm relative to external 85% phosphoric acid. Coupling constants are given in hertz. Spectra were recorded for solutions in $CDCl_3$.

When 2 equiv of L (L = PBu_3, PEt_3, $PMePh_2$, PPh_3) are added to a $CDCl_3$ solution of $[PtCl_2(dppe)]$, the only platinum-containing product observed is $[PtCl(L)(dppe)]^+$. In contrast, when $[PtCl_2(dppm)]$ is treated with 2 equiv of $PMePh_2$, the dipositive cationic complex $[Pt(PMePh_2)_2(dppm)]^{2+}$ is formed virtually quantitatively, as determined by ${}^{31}P\{{}^1H\}$ NMR spectroscopy. At ambient temperature the resonances due to this compound in the ${}^{31}P\{{}^1H\}$ NMR spectrum are very broad, but when the solution is cooled to −40 °C a second-order spectrum is obtained. $[Pt(PMePh_2)_2(dppm)]^{2+}$ gives rise to an AA'XX' type of spectrum,[20] which has been analyzed by the method of Bovey.[21] The ${}^{31}P\{{}^1H\}$ NMR data for this complex are compiled in Table II, and the assignments have been confirmed by spin simulation. Again we

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(20) Those molecules containing platinum-195 have been omitted for the spin-simulation experiments. The molecules $[{}^{195}Pt(PMePh_2)_2(dppm)]^{2+}$ give rise to an AA'MXX' type spectrum.
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have assumed that $^2J(P_A-P_D)$ is of positive sign; it is then necessary that $^2J(P_A-P_C)$ be negative in order to simulate the spectrum correctly. It is also necessary that $^2J(P_A-P_B)$ and $^2J(P_C-P_D)$ should have the same sign, but it is not possible to determine from the $^{31}P\{^1H\}$ NMR spectrum whether they are positive or negative.

The $[Pt(PMePh_2)_2(dppm)]^{2+}$ ion has been isolated as its chloride salt, but attempts to prepare it with perchlorate counterions by reacting $[PtCl_2(dppm)]$ with 2 equiv of $PMePh_2$ in the presence of excess silver perchlorate resulted in mixtures of $[Pt(PMePh_2)_2(dppm)][ClO_4]_2$ and $[PtCl(PMePh_2)_3][ClO_4]$ (Table III). It should be noted that the $^{31}P\{^1H\}$ NMR spectrum of $[Pt(PMePh_2)_2(dppm)][ClO_4]_2$ is virtually identical with that of $[Pt(PMePh_2)_2(dppm)]Cl_2$, which suggests that in this case the chloride ions do not interact with the dipositive cationic complex.

A somewhat different situation arises when $[PtCl_2(dppm)]$ is treated with 2 equiv of PBu_3 in $CDCl_3$ solution. Two platinum-containing species are formed, namely $[PtCl(PBu_3)_3]^+$, which displays a doublet and a triplet (both with platinum satellites) in its $^{31}P\{^1H\}$ NMR spectrum (Table III), and $[PtCl(PBu_3)(dppm)]^+$. When the mixture is allowed to stand for 3 days, the $[PtCl(PBu_3)_3]^+$ complex disappears and a signal due to Bu_3PO grows in at 49.9 ppm, but the signals due to $[PtCl(PBu_3)(dppm)]^+$ remain unchanged. This suggests that $[PtCl(PBu_3)_3]^+$ is involved in the oxidation of PBu_3. When an additional amount of PBu_3 is added, the resonances due to $[PtCl(PBu_3)(dppm)]^+$ and PBu_3 become quite broad. When the solution is cooled to −40 °C, this exchange is stopped with the observed products being $[Pt(PBu_3)_2(dppm)]^{2+}$, for which all the peaks in the $^{31}P\{^1H\}$ NMR spectrum have not been resolved, and $[PtCl(PBu_3)_3]^+$. Although all the peaks for $[Pt(PBu_3)_2(dppm)]Cl_2$ have not been resolved, a reasonable fit of the calculated $^{31}P\{^1H\}$ NMR spectrum to that obtained experimentally has been achieved by successively approximating where the missing peaks are located. The $^{31}P\{^1H\}$ NMR data for this dipositive complex cation appear in Table II.

The reactions of $[PtCl_2(dppe)]$ with $PMePh_2$ have been investigated by using dimethylformamide, acetonitrile, and acetone as solvent in order to determine whether the reactions are solvent-dependent. The complex itself is quite insoluble in these solvents but, upon addition of 1 mol equiv of $PMePh_2$, yields $[PtCl(PMePh_2)(dppe)]^+$ quantitatively in each case (in acetone some precipitate is formed, and the $^{31}P\{^1H\}$ NMR spectrum is broad). Addition of a second mole equivalent of $PMePh_2$ to each of these solutions causes no change (except for the appearance of a signal due to free $PMePh_2$), indicating that the difficulty in displacing the second chloride from $[PtCl(L)(dppe)]^+$, which was previously observed in $CDCl_3$ solution, is indeed a general phenomenon. Introduction of a large excess of Et_4NCl to a DMF solution of $[PtCl(PMePh_2)(dppe)]^+$ causes no reaction, indicating that chloride does not compete effectively with tertiary phosphine for coordination sites at the metal center; $[PtCl_2(dppe)]$ is also stable to treatment with excess chloride ions.

The complex $[Pt(PMePh_2)_2(dppe)]^{2+}$ has been generated by treatment of $[PtCl_2(dppe)]$ with 2 equiv of $PMePh_2$ in the presence of silver perchlorate, but complete conversion to the dipositive cation could never be achieved, with $[PtCl(PMePh_2)(dppe)][ClO_4]$ always being in the product mixture. Attempts to prepare pure $[Pt(PMePh_2)_2(dppe)][ClO_4]_2$ by reaction of $[PtI_2(dppe)]$ with 2 equiv of $PMePh_2$ in the presence of excess $AgClO_4$ yielded only $[PtI(PMePh_2)(dppe)][ClO_4]$ (Table I). Like the analogous dppm complex, $[Pt(PMePh_2)_2(dppe)]^{2+}$ displays a second-order $^{31}P\{^1H\}$ NMR spectrum. The spectrum consists of a 20-line pattern, characteristic of an AA′XX′ spin system, with corresponding platinum-195 satellites. The spectrum has been analyzed,[21] and the spectroscopic assignments have been confirmed by spin simulation. The $^{31}P\{^1H\}$ NMR data for this complex are compiled in Table II.

When $[PtCl_2(dppe)]$ is treated with 1 equiv of dppe, the two chloride ligands are displaced quantitatively to give $[Pt(dppe)_2]Cl_2$.[4] Similarly, when $[PtCl_2(dppe)]$ is treated with 1 equiv of dppm, the novel complex $[Pt(dppm)(dppe)]^{2+}$ is formed. This complex can be isolated as its chloride or tetraphenylborate salt. Although both these salts give $^{31}P\{^1H\}$ NMR spectra that are consistent with an AA′XX′ type spin system, the spectrum for the chloride salt differs somewhat from that for the tetraphenylborate salt. In the case of $[Pt(dppm)(dppe)]Cl_2$, the resonances due to the dppm phosphorus atoms appear at −30.2 ppm with $^1J(Pt-P)$ = 2035 Hz, whereas for $[Pt(dppm)(dppe)][BPh_4]_2$ these peaks are shifted upfield to −38.9 ppm with $^1J(Pt-P)$ = 1959 Hz. The resonances due to the dppe phosphorus atoms are not shifted significantly from one salt to the other, but the one-bond platinum–phosphorus coupling constant for the chloride salt (2476 Hz) is greater than that for the tetraphenylborate salt (2312 Hz). These differences are presumed to be due to an interaction of the chloride ions with the metal complex. Similar increases in $^1J(Pt-P)$ have been observed in $[Pt(dppm)_2]I_2$ that were attributed to ion-pairing.[4] The second-order splitting patterns are also somewhat different for the two salts, namely, only eight of the possible twenty lines are observed in the $^{31}P\{^1H\}$ NMR spectrum of $[Pt(dppm)(dppe)]Cl_2$, whereas all 20 lines are resolved for $[Pt(dppm)(dppe)][BPh_4]_2$. The spectrum for the latter species has been fully analyzed,[21] and the assignments have been confirmed by spin simulation. The $^{31}P\{^1H\}$ NMR data for this compound appear in Table II. As we have noted above, when $[PtCl_2(dppe)]$ is treated with a monodentate phosphine ligand, the presence of a silver salt is necessary for removal of the second chloride ligand. Thus the chelate effect of the dppe and dppm ligands apparently provides sufficient driving force for the displacement of the second chloride ligand.

For the $[PtL_2(P^\frown P)]^{2+}$ complexes discussed up to this point the chemical shift difference between the two sets of phosphino resonances is large enough that AA′XX′ type spectra are obtained. When the diphosphine ligands have comparable chemical shifts, a much more complicated spectrum of the type AA′BB′ is obtained. Such is the case with $[Pt(dmpe)(dppe)]Cl_2$. When $[PtCl_2(dmpe)]$ and 1 equiv of dppe are mixed together in $CDCl_3$ solution, an off-white precipitate is formed (the nature of this precipitate is not known for certain, but it is believed to be a mixture of $[Pt(dppe)_2]Cl_2$, $[Pt(dmpe)(dppe)]Cl_2$, and possibly $[Pt(dmpe)_2]Cl_2$, all of which have low solubility in $CDCl_3$). $^{31}P\{^1H\}$ NMR analysis of the solution above this precipitate indicates the presence of two species: (1) $[Pt(dppe)_2]^{2+}$ (δ(P) 47.9; $^1J(Pt-P)$ = 2365 Hz)[4] and (2) $[Pt(dmpe)(dppe)]^{2+}$. As expected, the latter complex gives a complicated $^{31}P\{^1H\}$ NMR spectrum, which has been interpreted in terms of an AA′BB′ spin system.[21] The dppe and dmpe resonances appear as complex multiplets well downfield of phosphoric acid at 44.0 and 32.1 ppm respectively (Table II). Each is accompanied by platinum satellites, with $^1J(Pt-P)$ being 2370 Hz for dppe and 2512 Hz for dmpe. Such values are consistent with phosphine ligands bound to platinum(II) in a trans arrangement.[6] The coupling constants $^2J(P_A-P_B)$ and $^2J(P_C-P_D)$ are 12.1 and 8.4 Hz, but these cannot be assigned specifically, since such small couplings are typical of both dppe and dmpe ligands. The remaining two coupling constants, $^2J(P_A-P_D)$ and $^2J(P_A-P_C)$ are 313 and −21.6 Hz respectively. These assignments have been confirmed by spin simulation (Figure 2).

Interestingly, when the reaction of $[PtCl_2(dmpe)]$ with dppe is carried out in a larger volume of solvent, a different product distribution is obtained. When a solution of dppe in CH_2Cl_2/CH_3CN (1:4) is added dropwise to a solution of $[PtCl_2(dmpe)]$ in 300 mL of CH_3CN, three products are obtained, namely $[Pt(dppe)_2]^{2+}$, $[Pt(dmpe)_2]^{2+}$, (δ(P) 29.0; $^1J(Pt-P)$ = 2353 Hz), and only a small amount of the unsymmetrical cation $[Pt(dmpe)(dppe)]^{2+}$. The formation of $[Pt(dppe)_2]^{2+}$ must involve displacement of the dmpe ligand from the platinum(II) center. This is somewhat surprising in view of the fact that dmpe, with its electron-donating methyl groups, should be a better donor ligand than dppe. However, dmpe is displaced more readily than one might expect (vide infra).

When $[PtCl_2(dmpe)]$ is treated with 1 equiv of PPh_3 in $CDCl_3$ solution, a mixture of *cis*-$[PtCl_2(PPh_3)_2]$ (δ(P) 14.9; $^1J(Pt-P)$ = 3677 Hz)[22] and $[PtCl(PPh_3)(dmpe)]^+$ (Table I) is obtained.

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[22] Anderson, G. K.; Clark, H. C.; Davies, J. A.; Ferguson, G.; Parvez, M. *J. Crystallogr. Spectrosc. Res.* **1982**, *12*, 449.

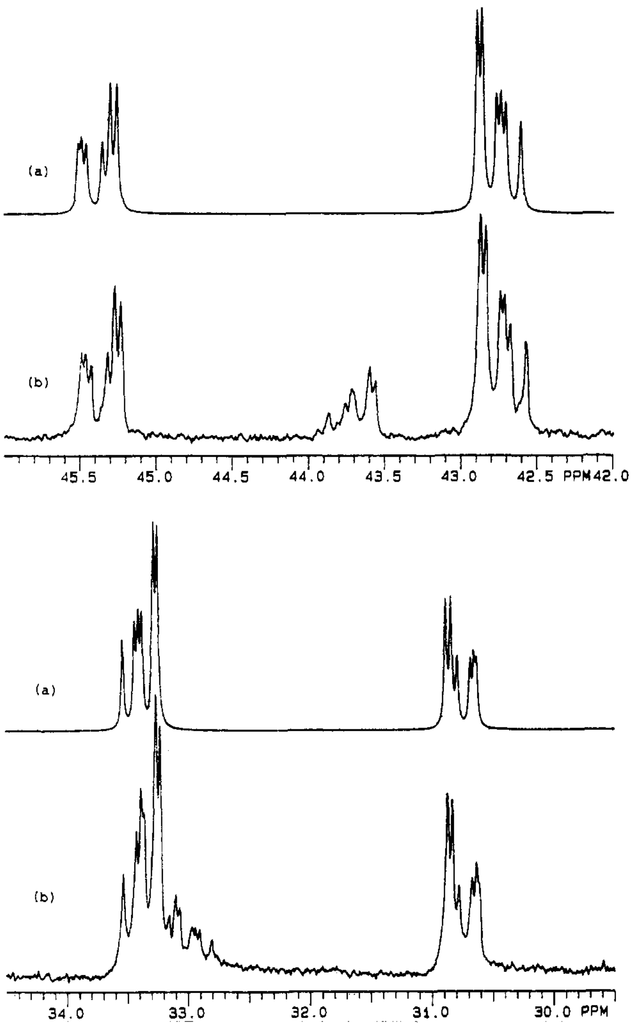


Figure 2. Calculated (a) and experimental (b) $^{31}P\{^1H\}$ NMR spectra of $[Pt(dmpe)(dppe)]^{2+}$. The peaks in the 43.5–44.0 and 32.7–33.2 ppm regions in the experimental spectrum are platinum satellites.

Scheme I

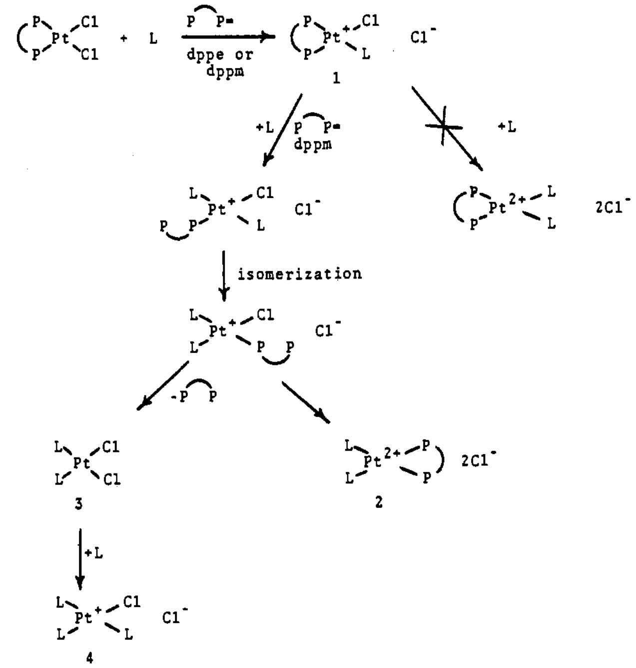
$$[PtCl_2(dmpe)] + 2PPh_3 \rightarrow cis\text{-}[PtCl_2(PPh_3)_2] + dmpe$$

$$[PtCl_2(dmpe)] + dmpe \rightarrow [Pt(dmpe)_2]Cl_2$$

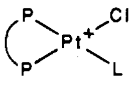
Again, the displacement of dmpe by PPh_3 is a surprising result. Stoichiometry dictates that there should be some $[PtCl_2(dmpe)]$ remaining in the product mixture, but this species was not observed in the $^{31}P\{^1H\}$ NMR spectrum (there was a considerable amount of precipitate in the NMR tube that is thought to have contained the remaining dmpe complex). Reaction with a second equivalent of PPh_3 does little to change the product mixture in solution. However, when the reaction is carried out in a large volume of solvent, a different mixture of products is obtained. When a solution of PPh_3 is added dropwise to a solution of $[PtCl_2(dmpe)]$ in acetonitrile, the three species observed in the product mixture are $[PtCl_2(dmpe)]$, *cis*-$[PtCl_2(PPh_3)_2]$, and $[Pt(dmpe)_2]Cl_2$. (The distribution of products obtained in this experiment suggests that slightly less than 1 equiv of PPh_3 was actually used.) It would appear that PPh_3 displaces the dmpe ligand from half of the $[PtCl_2(dmpe)]$ molecules present to give *cis*-$[PtCl_2(PPh_3)_2]$. The remaining $[PtCl_2(dmpe)]$ then reacts with the free dmpe that has been displaced by PPh_3 (Scheme I). When 2 equiv of PPh_3 are used, the $[PtCl_2(dmpe)]$ is converted completely to $[PtCl_2(PPh_3)_2]$ and $[Pt(dmpe)_2]Cl_2$, with free PPh_3 also being observed in solution.

The reason why PPh_3 displaces dmpe is unclear. $PMePh_2$ is generally considered to be a better donor ligand than PPh_3 because of the replacement of an electron-withdrawing phenyl group with an electron-donating methyl group. However, when $[PtCl_2(dmpe)]$ is mixed with 1 equiv of $PMePh_2$ in $CDCl_3$, the predominant platinum-containing species formed is $[PtCl(PMePh_2)(dmpe)]^+$ (Table I), whereas *cis*-$[PtCl_2(PMePh_2)_2]$ is not observed. On the other hand, when $[PtCl_2(dmpe)]$ is treated with 2 equiv of $PMePh_2$, the predominant platinum-containing species observed in solution is $[PtCl(PMePh_2)_3]^+$. Some free $PMePh_2$ is detected in solution. A precipitate is formed in this reaction, but its nature has not been ascertained.

Scheme II



In summary, the reactions of complexes of the type $[PtCl_2(P\frown P)]$ with other diphosphines lead to unsymmetrical bis(diphosphine)platinum(II) dications, although some symmetrization occurs, particularly when dmpe is involved. Analogous reactions with monodentate phosphines result in the formation of four types of products (**1**–**4**), where **4** is formed by subsequent reaction of **3** with free phosphine. Complexes of type **1** are formed readily for each of the three diphosphines studied; **2**, which is formed readily for dppm, can only be produced to a limited extent for dppe even in the presence of a chloride-abstracting agent and is not observed at all for dmpe. Displacement of the diphosphine to give **3** and/or **4** occurs under certain conditions for dppm or dmpe but not for dppe.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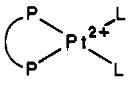
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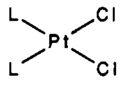
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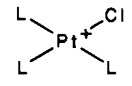
4

It would be expected that the electron-releasing methyl groups in dmpe would cause that ligand to coordinate strongly to platinum and also to stabilize the positive charge in **1** and **2**, yet dmpe is displaced from platinum more readily than is dppe and complexes of type **2** are not detected with dmpe. On the other hand, $[Pt(dmpe)_2]^{2+}$ is apparently readily formed and the stability of this complex may be the overriding factor in determining the products formed in the reactions of $[PtCl_2(dmpe)]$.

A comparison of the reactions of $[PtCl_2(dppe)]$ and $[PtCl_2(dppm)]$ with monodentate phosphines reveals that complexes of type **1** are readily formed, but $[PtCl(L)(dppe)]^+$ undergoes no reaction with excess L whereas $[PtCl(L)(dppm)]^+$ yields complexes of type **2** and/or **4** depending on the nature of L. The strained four-membered ring in the dppm complex should result in more facile displacement of that ligand (which we observe), but the trans effect of the phosphino groups in dppm should be lower than that in dppe; thus, if formation of **2** from **1** were to occur by simple chloride displacement by L then such reactions should be more favorable for the dppe complexes (which is contrary to what we observe). We propose the reaction sequence shown in Scheme

II to account for both of these observations. The intrinsic stability of the five-membered chelate ring would resist displacement of dppe by L, so reaction does not proceed beyond **1** (except in the presence of a silver salt). With dppm, the phosphino group trans to L would be displaced (since the trans effect of a tertiary phosphine is greater than that of chloride[23]), and subsequent isomerization would yield *cis*-$[PtCl(L)_2(\eta^1\text{-dppm})]^+$, from which Cl^- or dppm elimination would yield **2** or **3** respectively. Continuing aspects of this work will include determination of the factors that control the course of these reactions.

Experimental Section

Dmpe, dppe, dppm, PBu_3, PEt_3, $PMePh_2$, and PPh_3 were all obtained from commercial suppliers and were used as received. $[PtCl_2(dppe)]$ and $[PtCl_2(dppm)]$ were prepared according to established procedures.[12] The preparation of $[PtCl_2(dmpe)]$ is described below. $^{31}P\{^1H\}$ NMR spectra were recorded for $CDCl_3$ solutions on a Varian XL-300 NMR spectrometer. Spin-simulation experiments were carried out by using the LAME program, which is included in the XL-300 software package. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, TN.

Preparation of $[PtCl_2(dmpe)]$. The reaction was carried out in a glovebag under a nitrogen atmosphere. The dichloromethane was deaerated prior to use by purging with argon for 20 min. $[PtCl_2(cod)]$ (3.07 g, 8.21 mmol) was dissolved in CH_2Cl_2 (150 mL), and then dmpe (1.37 mL, 8.21 mmol) was added by syringe to this solution. A yellow precipitate formed immediately. The mixture was stirred for 1 h. (At this point all the dmpe was assumed to be coordinated to the platinum center and the complex thus formed was assumed to be air stable, so the rest of the procedure was performed outside the glovebag.) The solvent was removed by rotary evaporation, yielding a yellow microcrystalline solid. This solid was collected, washed with ether, and dried by suction to give $[PtCl_2(dmpe)]$ in virtually quantitative yield. The compound was characterized by infrared spectroscopy (KBr pellet; ν(Pt–Cl) 276 and 284 cm^{-1}) and $^{31}P\{^1H\}$ NMR spectroscopy ($CDCl_3$; $\delta(P)$ 30.6; $^1J(Pt\text{–}P)$ = 3523 Hz).

Reaction of $[PtCl_2(dppe)]$ with $PMePh_2$. $[PtCl_2(dppe)]$ (0.023 g, 0.035 mmol) was placed in a 5-mm NMR tube, and $CDCl_3$ was added. After the tube had been thoroughly flushed with argon, $PMePh_2$ (6.6 μL, 0.035 mmol) was introduced. The $^{31}P\{^1H\}$ NMR spectrum of the resulting colorless solution indicated that the only platinum-containing species present was $[PtCl(PMePh_2)(dppe)]^+$. Addition of more $PMePh_2$ had no effect upon the spectrum except for the growth of a signal at $\delta(P)$ – 26.2, due to free $PMePh_2$.

Reactions of $[PtCl_2(dppe)]$ with PBu_3, PEt_3, or PPh_3. These reactions of $[PtCl_2(dppe)]$ were carried out in the same way as the reaction with $PMePh_2$.

Reaction of $[PtCl_2(dppm)]$ with 1 equiv of $PMePh_2$. $[PtCl_2(dppm)]$ (0.025 g, 0.038 mmol) was suspended in $CDCl_3$ in a 5-mm NMR tube. After the mixture was purged with argon, $PMePh_2$ (7.1 μL, 0.038 mmol) was added. At room temperature, the lines in the $^{31}P\{^1H\}$ NMR spectrum were broad. However, when the sample was cooled to –40 °C, the lines sharpened considerably, with the resulting spectrum indicating that the main platinum-containing species present in this pale yellow solution was $[PtCl(PMePh_2)(dppm)]Cl$.

Reaction of $[PtCl_2(dppm)]$ with 1 equiv of PBu_3. This reaction was carried out in a manner analogous to that described above for the reaction of $[PtCl_2(dppm)]$ with 1 equiv of $PMePh_2$.

Preparation of $[PtCl(PMePh_2)(dppm)][ClO_4]$. *Caution! Perchlorate salts of metals with organic ligands are potentially explosive.* $[PtCl_2(dppm)]$ (0.095 g, 0.16 mmol) was dissolved in CH_2Cl_2 (30 mL), and the solution was purged with argon for 10 min. $PMePh_2$ (27 μL, 0.14 mmol) was added, and after being stirred for 15 min, the solution was diluted with an equal volume of acetone. To this colorless solution was added dropwise a solution of $AgClO_4$ (0.037 g, 0.18 mmol) in acetone (30 mL). The mixture was stirred for an additional 1.5 h, and then the solvent was evaporated. The residue was dissolved in CH_2Cl_2 and filtered to remove the silver salts. The resulting colorless solution was concentrated to 5 mL and excess ether was added to precipitate $[PtCl(PMePh_2)(dppm)][ClO_4]$ as a white solid (0.066 g, 49%). Anal. Calcd for $C_{38}H_{35}Cl_2O_4P_3Pt$: C, 49.90; H, 3.86. Found: C, 49.41; H, 4.00.

Reaction of $[PtCl_2(dppm)]$ with 2 equiv of $PMePh_2$. (a) $[PtCl_2(dppm)]$ (0.028 g, 0.043 mmol) and $PMePh_2$ (16.1 μL, 0.087 mmol) were mixed together in $CDCl_3$ in a NMR tube under argon. Only very broad lines were observed in the $^{31}P\{^1H\}$ NMR spectrum at ambient temperature. When the sample was cooled to –40 °C, resonances due to $[Pt(PMePh_2)_2(dppm)]^{2+}$ were observed.

(b) $[PtCl_2(dppm)]$ (0.16 g, 0.24 mmol) and excess $AgClO_4$ (0.19 g, 0.92 mmol) were placed together in a test tube, which had been fitted with a rubber serum cap. Dichloromethane (2 mL) was added as solvent. After the tube had been thoroughly flushed with argon, $PMePh_2$ (89.6 μL, 0.48 mmol) was added. The tube was stored in the dark overnight. All solids were then centrifuged, and the colorless solution was decanted. The remaining solid was washed with 2 mL of CH_2Cl_2. This wash was added to the original solution, and the solvent was evaporated. The residue was dissolved in $CDCl_3$ and the $^{31}P\{^1H\}$ NMR spectrum was obtained at –60 °C. This indicated the presence of two platinum-containing species, $[PtCl(PMePh_2)_3][ClO_4]$ and $[Pt(PMePh_2)_2(dppm)][ClO_4]_2$.

Reaction of $[PtCl_2(dppm)]$ with 2 equiv of PBu_3. $[PtCl_2(dppm)]$ (0.017 g, 0.026 mmol) and $CDCl_3$ were mixed together in a 5-mm NMR tube. After the tube had been flushed with argon, PBu_3 (13 μL, 0.052 mmol) was added. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution displayed peaks due to $[PtCl(PBu_3)_3]Cl$ and $[PtCl(PBu_3)(dppm)]Cl$, both at room temperature and at –40 °C. There was no evidence for exchange between $[PtCl(PBu_3)(dppm)]^+$ and PBu_3 at room temperature, but only a trace of free PBu_3 was present according to the $^{31}P\{^1H\}$ NMR spectrum. When the sample was allowed to stand for 3 days, the resonances due to $[PtCl(PBu_3)_3]^+$ had disappeared with a corresponding increase in a signal due to Bu_3PO. The predominant platinum-containing species at room temperature was $[PtCl(PBu_3)(dppm)]^+$. An additional amount of PBu_3 was added to the tube at this point. This led to a collapse of the peaks due the $[PtCl(PBu_3)(dppm)]^+$ ion. When the solution was cooled to –40 °C, the rate of exchange was reduced and the dipositive ion $[Pt(PBu_3)_2(dppm)]^{2+}$ was observed.

Generation of the $[Pt(PMePh_2)_2(dppe)]^{2+}$ Cation. $[PtCl_2(dppe)]$ (0.11 g, 0.16 mmol) and an excess of $AgClO_4$ (0.26 g, 1.24 mmol) were placed together in a test tube, which had been fitted with a serum cap. Dichloromethane (2 mL) was added as solvent, and after the tube had been flushed with argon, $PMePh_2$ (59 μL, 0.32 mmol) was added by syringe. The tube was allowed to stand overnight in the dark. All solids were then centrifuged, and the colorless solution was decanted. The precipitate was washed with several portions of CH_2Cl_2, with these washings being added to the original decantate. The solution was concentrated to 1 mL and excess ether was added to precipitate a white solid. The $^{31}P\{^1H\}$ NMR spectrum of this solid showed it to be a mixture of $[Pt(PMePh_2)_2(dppe)][ClO_4]_2$ and $[PtCl(PMePh_2)(dppe)][ClO_4]$.

Reaction of $[PtCl_2(dppe)]$ with Dppm. A solution of dppm (0.070 g, 0.18 mmol) in CH_2Cl_2 (20 mL) was added dropwise with stirring to a solution of $[PtCl_2(dppe)]$ (0.12 g, 0.18 mmol) in CH_2Cl_2 (150 mL). After being stirred for 1 h, the pale yellow solution was concentrated to 5 mL and a white solid (0.18 g) was precipitated by addition of ether. The $^{31}P\{^1H\}$ NMR spectrum of the product, dissolved in $CDCl_3$, indicated the presence of the $[Pt(dppm)(dppe)]^{2+}$ cation.

Preparation of $[Pt(dppm)(dppe)][BPh_4]_2$. $[PtCl_2(dppe)]$ (0.19 g, 0.29 mmol) was mixed with dppm (0.11 g, 0.29 mmol) in dichloromethane, and the resulting yellow solution was stirred for 0.5 h. $NaBPh_4$ (0.54 g, 1.58 mmol) was added, and the mixture was allowed to stir overnight. After the mixture was filtered through activated charcoal, the resulting yellowish solution was concentrated to 5 mL and excess pentane was added to precipitate a white solid. This solid was filtered, washed with pentane, and dried by suction to give $[Pt(dppm)(dppe)][BPh_4]_2$ (0.39 g, 82%).

Reaction of $[PtCl_2(dmpe)]$ with Dppe. $[PtCl_2(dmpe)]$ (0.015 g, 0.036 mmol) and dppe (0.015 g, 0.038 mmol) were placed together in a test tube. $CDCl_3$ was added, and the mixture was allowed to stand for 15 min. After the mixture was centrifuged, the resulting solution was decanted and the $^{31}P\{^1H\}$ NMR spectrum was recorded. This indicated the presence of two platinum-containing species, $[Pt(dppe)_2]^{2+}$ and $[Pt(dmpe)(dppe)]^{2+}$.

In an attempt to prepare the $[Pt(dmpe)(dppe)]^{2+}$ complex exclusively, $[PtCl_2(dmpe)]$ (0.033 g, 0.079 mmol) was dissolved in acetonitrile (300 mL). A solution of dppe (0.033 g, 0.083 mmol) in CH_2Cl_2/CH_3CN (1:4) (20 mL) was added dropwise. After the solution was stirred overnight, the solvent was removed from the clear, colorless solution to give a white solid. This white solid was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, and it was found to consist of $[Pt(dmpe)(dppe)]^{2+}$, $[Pt(dppe)_2]^{2+}$, and $[Pt(dmpe)_2]^{2+}$ ($\delta(P)$ 29.0; $^1J(Pt\text{–}P)$ = 2352 Hz) in approximately a 2:3:4 ratio.

Reaction of $[PtCl_2(dmpe)]$ with PPh_3. When $[PtCl_2(dmpe)]$ (0.032 g, 0.077 mmol) and PPh_3 (0.020 g, 0.077 mmol) were mixed in $CDCl_3$ in a NMR tube, the observed products were *cis*-$[PtCl_2(PPh_3)_2]$ and $[PtCl(PPh_3)(dmpe)]Cl$, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. Alternatively, if a solution of PPh_3 (0.018 g, 0.070 mmol) in CH_2Cl_2/CH_3CN (1:4) (20 mL) was added dropwise to a solution of $[PtCl_2(dmpe)]$ (0.029 g, 0.069 mmol) in CH_3CN (300 mL), the only species

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observed in the resulting product mixture were [$PtCl_2$(dmpe)], *cis*-[$PtCl_2(PPh_3)_2$], and [Pt(dmpe)$_2$]Cl_2. No evidence for the cationic complex [$PtCl(PPh_3)$(dmpe)]$^+$ was obtained.

Reaction of [$PtCl_2$(dmpe)] with $PMePh_2$. (a) [$PtCl_2$(dmpe)] (0.037 g, 0.088 mmol) was mixed with $CDCl_3$ in a 5-mm NMR tube. After the tube had been flushed with argon, $PMePh_2$ (16.3 μL, 0.088 mmol) was added. $^{31}P\{^1H\}$ NMR analysis of the resulting mixture indicated that the predominant platinum-containing species was [$PtCl(PMePh_2)$(dmpe)]Cl.

(b) When [$PtCl_2$(dmpe)] (0.032 g, 0.077 mmol) was reacted with $PMePh_2$ (28.8 μL, 0.16 mmol) in $CDCl_3$ in the same way as above, the $^{31}P\{^1H\}$ NMR spectrum indicated that the predominant platinum-containing species in solution was [$PtCl(PMePh_2)_3$]Cl.

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Solvolysis Reactions of *cis*- and *trans*-Diamminedichloroplatinum(II) in Dimethyl Sulfoxide. Structural Characterization and DNA Binding of *trans*-[$Pt(NH_3)_2(Me_2SO)Cl$]$^+$

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Dimethyl sulfoxide, Me_2SO, is commonly used to dissolve *cis*- and *trans*-diamminedichloroplatinum(II), *cis*- and *trans*-DDP, prior to use in experiments comparing their biological activities. The solvolysis reactions of *cis*- and *trans*-DDP in Me_2SO have been investigated in this study. Me_2SO substitutes for a single chloride ligand in both cases to form *cis*-[$Pt(NH_3)_2(Me_2SO)Cl$]Cl (**1**-Cl) and *trans*-[$Pt(NH_3)_2(Me_2SO)Cl$]Cl (**2**-Cl). The half-lives of the cis and trans isomers in Me_2SO at 37 °C are 60 and 8 min, respectively, as determined by both optical and ^{195}Pt NMR spectroscopy. Kinetic studies gave activation parameters for *cis*-DDP solvolysis of $\Delta H^{\ddagger} = 18.9\ (1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14.5\ (2)$ eu (optical spectroscopy) and $\Delta H^{\ddagger} = 19.8\ (3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.6\ (3)$ eu (^{195}Pt NMR spectroscopy). Activation parameters for solvolysis of *trans*-DDP were $\Delta H^{\ddagger} = 15.5\ (1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -21.4\ (2)$ eu (optical spectroscopy) and $\Delta H^{\ddagger} = 16.9\ (3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17.7\ (4)$ eu (^{195}Pt NMR spectroscopy). The mixed perchlorate/chloride salt of **2**, *trans*-[$Pt(NH_3)_2(Me_2SO)Cl$]$(ClO_4)_{0.8}Cl_{0.2}$, has been crystallized and its structure determined by single-crystal X-ray diffraction methods. The compound crystallizes in the orthorhombic space group *Pnma* with $a = 10.554\ (3)$ Å, $b = 7.446\ (1)$ Å, $c = 14.161\ (2)$ Å, $V = 1111.79$ Å^3, and $Z = 4$. The final R_1 value was 0.0395 for 799 observed reflections. The geometry of platinum is square planar, with Pt–S, Pt–N, and Pt–Cl distances of 2.204 (4), 2.11 (2) and 2.03 (1), and 2.307 (5) Å, respectively. Since **2** is formed rapidly enough to be a significant contaminant in studies in which *trans*-DDP has been dissolved in Me_2SO, reactions with DNA substrates of *trans*-DDP dissolved in either Me_2SO or aqueous buffer were compared. Use of Me_2SO instead of aqueous buffer to dissolve *trans*-DDP increases the rate of platinum binding to calf thymus DNA. Moreover, significant changes occur in the spectrum of products, as revealed in reactions with the model DNA substrate d(GpTpG). These results are consistent with the conversion of *trans*-DDP in Me_2SO to *trans*-[$Pt(NH_3)_2(Me_2SO)Cl$]$^+$ and the subsequent reaction of this complex with DNA. The use of Me_2SO to dissolve *cis*- or *trans*-DDP in biological studies is therefore strongly discouraged.

Introduction

cis-Diamminedichloroplatinum(II), *cis*-DDP,[2] is a clinically important anticancer drug that apparently acts by binding to DNA and inhibiting replication.[3] Bidentate coordination of DNA to *cis*-DDP is preceded by hydrolysis of at least one labile chloride ligand.[4] Interestingly, the trans isomer, which can bind DNA in a different bifunctional manner, is far less cytotoxic at equimolar doses. A number of studies have focused on the different biological activities of the two isomers in an attempt to explain the detailed mechanism of *cis*-DDP cytotoxicity.[5]

While reviewing data on the different biological effects of *cis*- and *trans*-DDP we became concerned that a number of laboratories[6] employ dimethyl sulfoxide, Me_2SO, as a solvent to dissolve these platinum complexes prior to use in biological experiments, despite the well-known affinity of divalent platinum for sulfur donor ligands.[7] In particular, substitution of a chloride ligand by Me_2SO is expected to occur much faster for *trans*-DDP than for *cis*-DDP, owing to the greater trans-labilizing effect of chloride vs. ammonia.[8] Use of Me_2SO as a solvent may therefore change

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(2) Abbreviations: *cis*- and *trans*-DDP, *cis*- and *trans*-diamminedichloroplatinum(II); Me_2SO, dimethyl sulfoxide; en, ethylenediammine; dach, 1,2-diaminocyclohexane; HPLC, high pressure liquid chromatography; $(D/N)_f$ and $(D/N)_b$, formal and bound drug-to-nucleotide ratios.

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