available lone pair in the deprotonated form over the metal and other ligands.[6,13] The extent of the increase is no doubt related to factors such as the net charge on the complex (consider $[Ru(NH_3)_5(RSH)]^{2+}$)[4] and the donor-acceptor character of other ligands. This seems to us to be a subject which has not yet been sufficiently studied, and we hope that our work, albeit qualitative, will encourage further consideration of this topic.

Registry No. I, 76136-83-9; II, 12110-44-0; THF, 109-99-9; Me_2SO, 67-68-5; Ph_2NH, 122-39-4; $[Fe(C_5H_5)(CO)_2(THF)]BF_4$, 63313-71-3.

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Steric Control in the Synthesis and Reactions of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$

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Dimeric halide-bridged complexes[1] of platinum(II) of the type $[Pt_2Cl_2(\mu\text{-}Cl)_2(ER_3)_2]$ (E = P, As, Sb; R = alkyl, aryl) are generally prepared by heating a slurry of platinum(II) chloride with the appropriate *cis*-$[PtCl_2(ER_3)_2]$ complex in an inert solvent.[2,3] If the cis isomer of the $[PtCl_2(ER_3)_2]$ complex is not available, two alternative methods may be employed; the trans isomer may be fused with the platinum(II) halide[4,5] or the ER_3 ligand may be reacted with the dimeric ethylene complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$.[4] The former method requires a high degree of thermal stability from both reactants and products while the latter method is generally employed only for tertiary stibines, since phosphines and arsines yield mainly monomeric products via bridge cleavage.[1b] Neither method is available when ER_3 is a sterically demanding phosphine ligand. Our interest in platinum complexes of such ligands[6,7] has led us to develop an efficient synthesis of the dimeric complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ (Cy = cyclohexyl), a synthesis in which a high degree of steric control is observed. In addition, bridge-cleavage reactions with neutral ligands are now reported which yield several interesting products of trans geometry; the reaction with carbon monoxide yields an exceptionally stable trans complex which shows little tendency to isomerize to the more common, thermodynamically preferred, cis isomer. Cleavage by large nucleophiles is slow; a probable consequence of steric hindrance during an associative process.[8]

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Experimental Section

$[K][PtCl_3(C_2H_4)]$ was prepared by the literature method.[9] Phosphine ligands were obtained from Strem Chemicals and 90% ^{13}C-enriched carbon monoxide from Prochem. Spectrograde acetone was distilled from activated 3-Å molecular sieve immediately prior to use. All manipulations involving tertiary phosphines were performed under strictly anaerobic conditions. ^{13}C and ^{31}P NMR spectra were obtained on a Bruker WP60 instrument operating in the Fourier transform mode at 15 (^{13}C) or 24 MHz (^{31}P). Infrared spectra were obtained on a Perkin-Elmer 180 spectrometer either as Nujol mulls with use of CsI optics or as chloroform solutions with use of KBr solution cells of 0.1-mm path length.

Synthesis of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$. A solution of PCy_3 (0.280 g, 1.0 mmol) in acetone (500 mL) was added dropwise over 48 h to a vigorously stirred solution of $[K][PtCl_3(C_2H_4)]$ (0.369 g, 1.0 mmol) in acetone (500 mL). The solution was stirred for a further 24 h and then reduced to dryness in vacuo at room temperature. The residue was extracted with chloroform (3 × 15 mL aliquots), and the extracts were filtered and reduced to small volume in vacuo. Careful addition of petroleum ether (bp 30-40 °C) caused a yellow solid to crystallize which was filtered, recrystallized from chloroform-petroleum ether, and dried in vacuo. The yield was 0.358 g (70%). Anal. Calcd for $Pt_2Cl_4P_2C_{36}H_{66}$: C, 39.56; H, 6.09. Found: C, 39.53; H, 6.00.

Cleavage Reactions of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$. (A) SMe_2 and C_5H_5N. A 10-fold excess of the ligand was added to a solution of the dimer (~30 mg) in $CDCl_3$, and the solution was examined spectroscopically after 15 min and again after being treated at 55 °C for 2 h.

(B) PCy_3, $P(o\text{-}CH_3C_6H_4)_3$, $PMePh_2$, $AsPh_3$, and *t*-BuNC. A stoichiometric amount of the ligand was added to a solution of the dimer (~30 mg) in $CDCl_3$, and the solution was examined spectroscopically. Reactions of $PMePh_2$, $AsPh_3$, and *t*-BuNC were complete within ~15 min while reactions with PCy_3 and $P(o\text{-}CH_3C_6H_4)_3$ required several hours.

(C) CO and ^{13}CO. Solutions of the dimer (~30 mg) in $CDCl_3$ were either purged with a gentle stream of CO for 1 h or stirred under an atmosphere of ^{13}CO for 2 h and then examined spectroscopically.

Results and Discussion

The slow addition of PCy_3 to $[K][PtCl_3(C_2H_4)]$ under anaerobic conditions gives the dimeric complex $[Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$ in high yield. Its far infrared spectrum shows bands at 353 cm^{-1} and 326, 250 cm^{-1} attributed largely to terminal and bridging metal-chlorine vibrations.[1c] The $^{31}P\{^1H\}$ NMR spectrum is entirely typical of the AA'XX' spin system,[10] characteristic of dimeric complexes of this type ($\delta(P)$ = 20.2, $^1J(Pt, P)$ = 3875 Hz, $^3J(Pt, P)$ = 20 Hz, $^4J(P, P)$ < 2 Hz, $^2J(Pt, Pt)$ = 138 Hz).[11]

The preparative route described here is specific for sterically demanding phosphine ligands, and attempts to utilize this method in the preparation of dimeric analogues of less bulky ligands such as PEt_3 and PPh_3,[12] lead to the isolation of other products. Thus, the slow addition of dilute solutions of these ligands to $[K][PtCl_3(C_2H_4)]$ yields *trans*-$[PtCl_2(PR_3)_2]$ as the only phosphine-containing products. Similar experiments at low temperature (-60 °C) also yield only these monomeric species. The trans geometry of the $[PtCl_2(PR_3)_2]$ complexes

(8) Nucleophilic attack on bridged $[Pt_2X_2(\mu\text{-}X)_2L_2]$ (X = halide, L = neutral ligand) complexes follows the same rate law as ligand displacement reactions of mononuclear complexes and is thus assumed to be associative. See R. G. Pearson and M. M. Muir, *J. Am. Chem. Soc.*, **88**, 2163 (1966).
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(11) $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data are relative to external H_3PO_4 and internal Me_4Si, respectively. More positive values of δ represent deshielding.
(12) The cone angle data of Tolman allow some relative comparisons of ligand steric effects to be made. Cone angles of ligands employed here, or used in discussion, are as follows: ~95° for CO, 122° for PMe_2Ph, 132° for PEt_3 and P-*n*-Bu_3, 136° for $PMePh_2$, 145° for PPh_3, 170° for PCy_3, and 194° for $P(o\text{-}CH_3C_6H_4)_3$. See for discussion C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).

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Table I. $^{31}P\{^1H\}$ NMR Data of *trans*-$[PtCl_2(PCy_3)L]$ Complexes

L	δ(P)	^1J(Pt, P),[21] Hz
PCy_3	16.3	2393
$PMePh_2$[a]	19.5	2512
	3.9	2422
$P(o\text{-}CH_3C_6H_4)_3$[b]	17.6	2478
	17.8	2495
CO[c]	16.2	2910
SMe_2	19.3	3320
C_5H_5N	9.0	3389
$AsPh_3$	17.7	3120
t-BuNC[d]	10.5	2842

[a] In this AB spectrum, where $\delta(P_1) >> \delta(P_2)$, coupling between the inequivalent phosphorus atoms is observed; ^2J(P, P) = 454 Hz. [b] In this closely spaced AB spectrum, where $\delta(P_1) \approx \delta(P_2)$, no coupling between the inequivalent phosphorus atoms can be observed. [c] ^2J(P, ^{13}C) = 150 Hz. [d] ^3J(P, ^{14}N) = 7 Hz.

was confirmed by $^{31}P\{^1H\}$ NMR (δ(P) = 11.6, ^1J(Pt, P) = 2415 Hz for *R* = Et and δ(P) = 19.8, ^1J(Pt, P) = 2637 Hz for R = Ph).[13] Thus, this route is in itself a useful synthetic method as such complexes are more normally prepared by UV irradiation of the corresponding cis isomers[14] or by the reaction of *trans*-$[PtHCl(PR_3)_2]$ with $HgCl_2$ at low temperature.[15]

The exact limitation imposed by the steric demand of the phosphine on the molecularity of the products obtained has yet to be determined, but it is noteworthy that, even with PCy_3, the reaction must be performed under conditions of high dilution; otherwise the dimeric product is contaminated by traces of *trans*-$[PtCl_2(PCy_3)_2]$. Presumably, it is the difference in the rate of bridge cleavage (slow for PCy_3 but rapid for small nucleophiles) which permits use of this synthesis of the dimeric products.

The $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ complexes are mainly used in synthesis as precursors to mononuclear $[PtCl_2(PR_3)(L)]$ species via bridge cleavage by neutral ligands (L). Generally, cleavage by amines yields products of trans configuration[16] while cleavage by olefins or carbon monoxide yields cis products.[17] Recent reports of the cleavage of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (PR_3 = P-*n*-Bu_3, PEt_3, PMe_2Ph, $PMePh_2$[12]) by carbon monoxide have shown that the initial product of trans geometry is rapidly isomerized to the cis isomer under the reaction conditions.[18] We undertook bridge-cleavage reactions with various neutral ligands to determine whether the sterically demanding PCy_3 ligand would influence the rate of cleavage by nucleophiles of differing size and/or the geometries of the products. The effect on reaction rate was clearly observed in cleavage by $P(o\text{-}CH_3C_6H_4)_3$, PCy_3, and $PMePh_2$. Cleavage by either of the two large[12] phosphines is slow, requiring several hours for completion while the much smaller $PMePh_2$ ligand reacts rapidly and cleavage is essentially complete in a few minutes.[19] The reactions were monitored by $^{31}P\{^1H\}$ NMR (see Table I), the magnitudes of ^1J(Pt, P) and ^2J(P, P) defining the trans geometry.[13]

In the cleavage reaction with carbon monoxide, the $^{31}P\{^1H\}$ NMR of a deuterochloroform solution showed 100% conversion to a mononuclear species δ(P) = 16.2, ^1J(Pt, P) = 2910 Hz after ~1 h. The infrared spectrum of this solution showed a band assigned as ν(CO) at 2125 cm^{-1}. For determination of the geometry of this carbonyl-containing species unequivocally, the ^{13}C-labeled carbonyl analogue was prepared. The $^{13}C\{^1H\}$ NMR spectrum confirmed the presence of a platinum carbonyl (δ(CO) = 168.7, ^1J(Pt, C) = 1162 Hz, ^2J(P, C) = 150 Hz), and the magnitude of ^2J(P, C) defines the geometry as trans.[18] The infrared spectrum of this solution showed the expected band assigned as $\nu(^{13}CO)$ at 2075 cm^{-1}. Isomerization of the previously reported[18] *trans*-$[PtCl_2(CO)(PR_3)]$ complexes to the thermodynamically preferred cis geometry was catalyzed by free carbon monoxide; under such conditions isomerization was generally complete in ~1 h. However, when the complex *trans*-$[PtCl_2(CO)(PCy_3)]$ was purged with carbon monoxide and then allowed to stand in a carbon monoxide saturated solution for 24 h, examination by $^{31}P\{^1H\}$ NMR and solution infrared spectroscopies showed formation of only trace amounts of the cis isomer (δ(P) = 36.0, ^1J(Pt, P) not observed, ν(CO) = 2090 cm^{-1}, $\nu(^{13}CO)$ = 2040 cm^{-1}), thus demonstrating the exceptional stability imposed on this system by the sterically demanding phosphine ligand.

Finally, cleavage by other small nucleophiles (SMe_2, C_5H_5N, $AsPH_3$, *t*-BuNC) was examined. The products were assigned the trans geometry on the basis of ^1J(Pt, P) values (Table I) and, in the case of *t*-BuNC, the rarely observed parameter ^3J(P, N).[20] Attempts to isomerize the complexes of SMe_2 and C_5H_5N by heating solutions containing a 10-fold excess of the ligand at 55 °C for 2 h were unsuccessful.

The selectivity of these reactions is exemplified by comparison with the cleavage reactions of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$. Reaction of this complex with SMe_2 was monitored by $^{31}P\{^1H\}$ NMR and showed formation of both isomers of $[PtCl_2(SMe_2)(PEt_3)]$ (for the cis isomer δ(P) = 8.4 and ^1J(Pt, P) = 3408 Hz and for the trans isomer δ(P) = 10.3 and J(Pt, P) = 3291 Hz), the cis isomer being more favored. Both isomeric products are similarly formed in the cleavage reaction with *t*-BuNC, the $^{31}P\{^1H\}$ NMR spectrum showing a well-defined triplet of 1:1:1 intensity for the trans isomer (δ(P) = 4.2, ^1J(Pt, P) = 2822 Hz, ^3J(P, N) = 7 Hz) but only a singlet (δ(P) = 13.7, ^1J(Pt, P) = 3174 Hz) for the cis isomer.[20]

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Registry No. $Pt_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2$, 76156-54-2; $[K][PtCl_3(C_2H_4)]$, 12012-50-9; *trans*-$[PtCl_2(PCy_3)_2]$, 60158-99-8; *trans*-$[PtCl_2(PCy_3)(PMePh_2)]$, 76136-75-9; *trans*-$[PtCl_2(PCy_3)(P(o\text{-}CH_3C_6H_4)_3)]$, 76136-76-0; *trans*-$[PtCl_2(PCy_3)(CO)]$, 76189-24-7; *trans*-$[PtCl_2(PCy_3)(SMe_2)]$, 76136-77-1; *trans*-$[PtCl_2(PCy_3)(C_5H_5N)]$, 66005-41-2; *trans*-$[PtCl_2(PCy_3)(AsPh_3)]$, 76136-78-2; *trans*-$[PtCl_2(PCy_3)(BuNC)]$, 76136-79-3; *cis*-$[PtCl_2(SMe_2)(PEt_3)]$, 76136-80-6; *trans*-$[PtCl_2(SMe_2)(PEt_3)]$, 76189-25-8; *trans*-$[PtCl_2(BuNC)(PEt_3)]$, 76136-81-7; *cis*-$[PtCl_2(BuNC)(PEt_3)]$, 76189-26-9; *cis*-$[PtCl_2(CO)(PCy_3)]$, 19618-81-6; ^{13}C, 14762-74-4.

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(19) The possibility that electronic effects also modify the reaction rate cannot be ignored; however Tolmans electronic parameters for PCy_3 (2056.4), $PMePh_2$ (2066.6), and $P(o\text{-}CH_3C_6H_4)_3$ (2067.0) suggest that these are not important as $PMePh_2$ and $P(o\text{-}CH_3C_6H_4)_3$ are of very similar electronic nature.
(20) Observation of a three-bond coupling between phosphorus and a quadrupolar nucleus such as ^{14}N is uncommon due to line broadening; here the trans geometry makes ^3J(P, N) sufficiently large (7 Hz) for unambiguous resolution.
(21) The magnitude of ^1J(Pt, P) is not always definitive in assigning the geometry of a complex; the values here however are exactly as expected in terms of the trans influence of the ligands. Thus the values lie in the order L = P donor < sp C donor < As donor < S donor < N donor. For P trans Cl, the NMR trans influence series predicts a higher value of ^1J(Pt, P) than even the P trans N donor, and on this basis we assign the geometry of these complexes as trans. For fuller discussion of the NMR trans influence see T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).