Factors Influencing the Formation of Cis and Trans Isomers in Long-Chain Bis(phosphine) Complexes of Platinum(II)

William E. Hill,[*1a] **David M. A. Minahan,**[1a] **John G. Taylor,**[1a] **and Charles A. McAuliffe**[*1b]

Contribution from the Departments of Chemistry, Auburn University, Auburn, Alabama 36849, and The University of Manchester Institute of Science and Technology, Manchester M60 IQD, United Kingdom. Received October 14, 1981

Abstract: The square-planar platinum(II) complexes of a series of bis(diphenylphosphine)alkanes have been synthesized and characterized by infrared and phosphorus-31 NMR spectroscopy, elemental analysis, and vapor-phase osmometry. Cis complexes are formed when the complex precursor is potassium tetrachloroplatinate(II), while the corresponding trans complexes are preferred when the starting material is Zeise's salt. An unusual trans-bonded complex with dpe has also been isolated. The trans isomers revert to their cis analogues in the presence of heat or excess bis(phosphine). The cis dimers are the most stable isomers for the majority of the cis complexes. The preferred ring sizes for the cis chelated monomers are 14- and 19-membered chelate rings. The amount of trans monomer increases with increasing chain length and reaches a maximum with a chelate ring size of 15 members and can be correlated directly with ring contributions to the chemical shift—thus ring contributions in trans monomeric complexes can be used as a measure of ring strain for these ligands. Large flexible chelate rings (19 members or above) appear to be unstable in the trans configuration.

Introduction

Since the synthesis of the first trans-bonded square-planar bis(tertiary phosphine) complex by Issleib[2] in 1961, a number of trans-bonded complexes have been prepared. Venanzi[3–6] showed that trans bonding can be accomplished if the chelate ring is rigid and of suitable size, while Shaw and co-workers have prepared a number of trans complexes of the type MLCl$_2$ [M = Pd, Pt; L = (*t*-Bu)$_2$P(CH$_2$)$_n$P(*t*-Bu)$_2$, *n* = 5–10], from which they conclude that bulky *tert*-butyl groups induce favorable conformational and entropy effects which promote trans chelation by ligands possessing flexible backbones.[7–10] Evidence that bulky substituent groups are not a prerequisite for trans chelation has been presented by Alcock with the observation that ligands of the type Ph$_2$P-(CH$_2$)$_2$(OCH$_2$CH$_2$)$_n$PPh$_2$ (*n* = 1, 2, and 3) can form trans-bonded square-planar complexes with rhodium.[11–13] Subsequently, we have shown that trans square-planar complexes with Ph$_2$P-(CH$_2$)$_2$(OCH$_2$CH$_2$)$_2$PPh$_2$ can be synthesized with nickel(II), palladium(II), and platinum(II),[14,15] and indeed trans complexes of the type PdLX$_2$ [L = Ph$_2$P(CH$_2$)$_n$PPh$_2$, *n* = 6, 8, 10, and 12; X = Cl, Br, I, and CNS] have been synthesized by us and all possess a trans configuration despite the smaller steric requirements of the phenyl groups attached to the donor phosphorus atoms.[16] Furthermore, the complex *trans*-[Pd(Me$_2$As(CH$_2$)$_{12}$AsMe$_2$)Cl$_2$]

has been isolated, where the donor arsenic atoms have even less bulky methyl substituents attached.[17]

Therefore, other factors must play vital roles in determining the stereochemistry of complexes of this type. We report here an investigation into the factors influencing the formation of cis and trans isomers in platinum(II) complexes with long-chain bis(tertiary phosphines) with phenyl substituents attached to the donor phosphorus atoms.

Experimental Section

A. Materials. Potassium tetrachloroplatinate(II) and the solvents employed were reagent grade and were used without further purification. Zeise's salt was prepared by the standard literature route.[18] The ligands Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dpe), Ph$_2$P(CH$_2$)$_6$PPh$_2$ (dph), Ph$_2$P(CH$_2$)$_7$PPh$_2$ (dphp), Ph$_2$P(CH$_2$)$_8$PPh$_2$ (dpo), Ph$_2$P(CH$_2$)$_9$PPh$_2$ (dpn), Ph$_2$P-(CH$_2$)$_{10}$PPh$_2$ (dpd), Ph$_2$P(CH$_2$)$_{11}$PPh$_2$ (dpu), Ph$_2$P(CH$_2$)$_{12}$PPh$_2$ (dpdod), and Ph$_2$P(CH$_2$)$_{16}$PPh$_2$ (dphd) were prepared and characterized as previously described.[16]

B. Preparation of the Complexes. *cis*-[Pt(ligand)Cl$_2$]. Potassium tetrachloroplatinate(II) (0.83 g, 2 mmol) and the ligand (2 mmol) were stirred and refluxed in 2-methoxyethanol (50 mL) for 4 h. The solution was filtered hot and evaporated to dryness under reduced pressure. The residue was dissolved in chloroform (10 mL) and filtered. A fivefold excess of pentane was added to the filtrate to precipitate the product. After the filtrate and precipitate were cooled in a refrigerator, the complex was collected by vacuum filtration and washed successively with 10-mL portions of water and ethanol and finally with pentane.

Due to low solubility, the complex *cis*-[Pt(dpe)Cl$_2$] was recrystallized directly from 2-methoxyethanol and collected as above.

trans-[Pt(ligand)Cl$_2$]. The ligand (0.5 mmol) dissolved in a 50:50 acetone/chloroform solution (30 mL) was added dropwise to a stirred solution of Zeise's salt, K[Pt(C$_2$H$_4$)Cl$_3$] (0.184 g, 0.5 mmol), in acetone (100 mL) over a 30-min period. After addition, stirring was continued for a further hour. The solution was then evaporated to dryness under reduced pressure at room temperature. The resulting residue was dissolved in chloroform (10 mL) and filtered. A fivefold excess of pentane was added subsequently to the filtrate to precipitate the product. After it was cooled in a refrigerator, the complex was collected by vacuum filtration and washed successively with 10-mL portions of water and ethanol and finally with pentane.

In the case of the complexes with the ligands dpn, dpd, dpu, and dpdod, a more soluble component was crystallized out from the chloroform/pentane filtrate after prolonged refrigeration. These complexes were collected as described above.

All other complexes were collected on sintered-glass filters and dried under vacuum.

C. Physical Measurements. The phosphorus-31 NMR spectra of the complexes were recorded on a Varian CFT-20 Fourier transform spec-

(1) (a) Auburn University. (b) The University of Manchester Institute of Science and Technology.

(2) Issleib, V. K.; Hohlfeld, G. *Z. Anorg. Allg. Chem.* **1961**, *312*, 169.

(3) DeStefano, N. J.; Johnson, D. K.; Lane, R. M.; Venanzi, L. M. *Helv. Chim. Acta* **1976**, *59*, 2674.

(4) DeStefano, N. J.; Johnson, D. K.; Venanzi, L. M. *Helv. Chim. Acta* **1976**, *59*, 2683.

(5) Reed, F. J. S.; Venanzi, L. M. *Helv. Chim. Acta* **1977**, *60*, 2804.

(6) Bachechi, F.; Zambonelli, L.; Venanzi, L. M. *Helv. Chim. Acta* **1977**, *60*, 2815.

(7) Pryde, A.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1976**, *322*.

(8) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972.

(9) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.*, **1980**, *102*, 4373.

(10) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856.

(11) Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Chem. Commun.* **1974**, 829.

(12) Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Dalton Trans.* **1976**, 583.

(13) Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 888.

(14) Hill, W. E.; Taylor, J. G.; McAuliffe, C. A.; Muir, K. W.; Manojlovic-Muir, L. *J. Chem. Soc., Dalton Trans.* **1982**, 833.

(15) Falshaw, C. P.; King, T. J.; Hill, W. E.; Taylor, J. G.; Beagley, B.; McAuliffe, C. A., to be submitted for publication in *J. Chem. Soc. Chem. Commun.*

(16) Hill, W. E.; McAuliffe, C. A.; Niven, I.E.; Parish, R. V. *Inorg. Chim. Acta* **1979**, *38*, 273.

(17) Levason, W.; McAuliffe, C. A.; Murray, S. G. *J. Organomet. Chem.* **1976**, *110*, C25.

(18) Choici, P. B.; Halpern, J.; Paulik, F. E. *Inorg. Synth.* **1973**, *14*, 90.

Table I. Elemental Analyses and Molecular Weight Data for the Complexes *cis*-[Pt(Ph$_2$P(CH$_2$)$_n$PPh$_2$)Cl$_2$]

complex	% C	% H[a]	% Cl[a]	mol wt (obsd)[b]	mol wt (calcd)[d]
Pt(dpe)Cl$_2$	45.8 (45.7)[a]	3.9 (3.8)	10.9 (10.4)	c	
Pt(dph)Cl$_2$	49.2 (50.0)	4.8 (4.4)	9.6 (9.9)	c	
Pt(dphp)Cl$_2$	51.2 (50.7)	5.0 (4.6)	9.8 (9.7)	c	
Pt(dpo)Cl$_2$	51.4 (51.3)	4.9 (4.8)	9.9 (9.5)	1490 (748)[e]	1496
Pt(dpn)Cl$_2$	50.7 (50.8)	5.3 (5.1)	9.8 (9.1)	1041 (762)[e]	1039
Pt(dpd)Cl$_2$	52.6 (52.6)	5.0 (5.1)	8.3 (9.2)	c	
Pt(dpu)Cl$_2$	53.4 (53.2)	5.2 (5.3)	9.5 (9.2)	1368 (790)[e]	1359
Pt(dpdod)Cl$_2$	53.6 (53.7)	5.5 (5.5)	9.2 (8.8)	c	
Pt(dphd)Cl$_2$	55.6 (55.8)	6.1 (6.0)	8.3 (8.3)	1289 (860)[e]	1230

[a] Calculated values given in parentheses. [b] Molecular weights determined in chloroform. [c] Too insoluble for molecular weight determination. [d] Molecular weight estimated from NMR data. [e] Molecular weight calculated for the monomer in parentheses.

Table II. Elemental Analyses and Molecular Weight Data for the Complex *trans*-[Pt(Ph$_2$P(CH$_2$)$_n$PPh$_2$)Cl$_2$]

complex	% C[a]	% H[a]	% Cl[a]	mol wt (obsd)[b]	mol wt (calcd)[d]
[Pt(dpe)Cl$_2$]·H$_2$O	45.9 (45.7)	3.9 (3.8)	11.0 (10.4)	c	
[Pt(dph)Cl$_2$]·H$_2$O	48.5 (48.7)	4.7 (4.6)	9.9 (10.4)	c	
[Pt(dphp)Cl$_2$]·2H$_2$O	48.3 (48.3)	4.8 (4.9)	10.2 (9.2)	1239 (734)[e]	1385
[Pt(dpo)Cl$_2$]·H$_2$O	50.1 (50.2)	5.0 (5.0)	9.2 (9.3)	c	
[Pt(dpn)Cl$_2$]	51.9 (52.0)	5.0 (5.0)	9.3 (9.3)	1150 (762)[e]	1148
[Pt(dpd)Cl$_2$]	52.5 (52.6)	5.2 (5.2)	9.2 (9.2)	1020 (776)[e]	1032
[Pt(dpu)Cl$_2$]	53.0 (53.2)	5.4 (5.3)	9.0 (9.0)	c	
[Pt(dpdod)Cl$_2$]	53.6 (53.7)	5.5 (5.5)	9.1 (8.8)	709 (804)[e]	909
[Pt(dphd)Cl$_2$]·H$_2$O	54.8 (54.7)	6.3 (6.2)	8.6 (8.1)	1711 (860)	1720

[a] Calculated values given in parentheses. [b] Molecular weights determined in chloroform. [c] Too insoluble for molecular weight determination. [d] Molecular weights estimated from NMR data. [e] Molecular weights calculated for the monomer in parentheses. dpn, dpd, dpu, and dpdod monomeric isomers were isolated from mixtures by fractional crystallization.
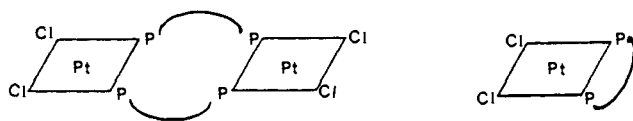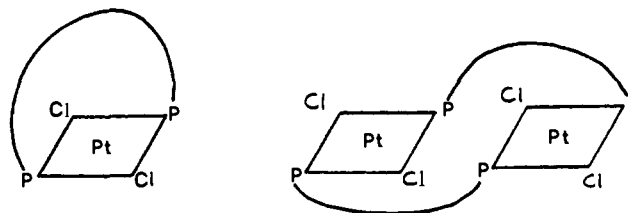

Figure 1. Structures of the cis dimer and the cis monomer.

Figure 2. Structures of the trans monomer and the trans dimer.

trometer at 32.1 MHz. Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer using polyethylene plates for the region 600–200 cm^{-1} in a Nujol mull. Molecular weights were determined in chloroform by vapor-phase osmometry. Elemental analyses were carried out by the microanalytical laboratories at UMIST.

Results and Discussion

Platinum(II) complexes of the type *cis*-Pt(ligand)Cl$_2$, where ligand = bis(phosphine), were prepared by refluxing the ligand and potassium tetrachloroplatinate(II) in a 1:1 molar ratio in 2-methoxyethanol. The corresponding trans complexes were prepared by the reaction of the ligand with Zeise's salt in a 1:1 molar ratio in acetone/chloroform; the reaction was carried out in a large volume of solvent to minimize the formation of oligomeric species. The mode of addition was deliberately designed so that a large excess of Zeise's salt was present; i.e., the phosphine was added dropwise to a solution of Zeise's salt, since the presence of excess phosphine causes trans–cis isomerization.[19] The elemental analyses and molecular weight data are reported in Tables I and II.

The geometries of the complexes were assigned by phosphorus-31 NMR and infrared spectroscopy. Much valuable information can be obtained from the magnitudes of $^1J_{Pt-P}$ observed in the phosphorus-31 NMR spectra. The use of this parameter allows the unambiguous distinction between the cis and trans isomeric forms of complexes of the general formula [Pt(PR$_3$)$_2$X$_2$] if the value of $^1J_{Pt-P}$ for the phosphorus atom in the trans position to ligand X is not of the same order of magnitude as that for a phosphorus atom in a trans position to another phosphorus atom.[20,21] It should be noted that while this ^1J criterion holds

good for the assignment of molecular geometries in complexes where X = Cl$^-$, Br$^-$, and I$^-$, it gives ambiguous results when X = NO$_2^{-22}$ and R$_2$S.[23]

Platinum-195 has the highest NMR frequency and sensitivity of the transition metals which possess a nuclear spin $I = {}^1/_2$.[24] The isotope occurs in 33.7% natural abundance, and the phosphorus-31 NMR spectrum of any phosphorus-containing species will exhibit a 1:4:1 triplet when phosphorus is coupled to ^{195}Pt: the central portion of the spectrum is that which is not coupled to ^{195}Pt, while the separation between the two satellites gives the value for $^1J_{Pt-P}$. For symmetrical bis(phosphine) complexes of platinum(II), the phosphorus-31 NMR spectrum should appear as a simple A$_2$X system and can be analyzed by first-order methods.[7,8] Complexes of the type *cis*-[Pt(PR$_3$)$_2$Cl$_2$] normally have $^1J_{Pt-P}$ = ca. 3500 Hz, whereas those of the type *trans*-[Pt(PR$_3$)$_2$Cl$_2$] have $^1J_{Pt-P}$ = ca. 2500 Hz.[21,25] The values of $^1J_{Pt-P}$ in the complexes studied here fell into one or the other of these distinct classes, allowing unambiguous assignment of the geometry of the complexes (see Table III and IV).

The assignments made on the basis of $^1J_{Pt-P}$ were confirmed by examination of the far-infrared spectra of the complexes. The symmetry of the cis and trans isomers is clearly different: the cis isomer possesses local C_{2v} symmetry, while the more symmetrical trans isomer possesses the higher D_{2h} local symmetry classification. Group theory predicts that, for metal–chlorine stretching vibrations, a square-planar MP$_2$Cl$_2$ donor set should give rise to one band (B$_u$) for D_{2h} symmetry (trans chlorine atoms) and to two bands (A$_1$ and B$_2$) for C_{2v} symmetry (cis chlorine

(19) Farez, R. Roulet, R.; Pinkerton, A. A.; Schwartzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356 and references therein.

(20) Pregosin, P. S.; Kunz, R. W. "Phosphorus-31 and Carbon-13 Nuclear Magnetic Resonance Studies of Transition Metal Complexes Containing Phosphorus Ligands"; Springer-Verlag: New York, 1979.

(21) Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133 and references therein.

(22) Kunz, R. W.; Pregosin, P. S., unpublished results.

(23) Lai, R. D.; Shaver, A. *Inorg. Chem.* **1981**, *20*, 477.

(24) Harris, R. K. *Chem. Soc. Rev.* **1976**, *5*, 1.

(25) McFarlane, W. *J. Chem. Soc. A* **1967**, 1922.

Table III. Phosphorus-31 NMR and Infrared Data for the Complexes cis-[Pt(Ph$_2$P(CH$_2$)$_n$PPh$_2$)Cl$_2$]

complex	δ(^{31}P)^a	$^1J_{Pt-P}$^{b}	% composition	ν(Pt–Cl)^c
cis-[Pt(dpe)Cl$_2$]	−41.0 (monomer)	3617	low sol	294, 315
	−7.8 (dimer)	3654		
cis-[Pt(dph)Cl$_2$]	−7.4	3655		295, 320
cis-[Pt(dphp)Cl$_2$]	−7.4 (monomer)			294, 321
	−7.1			
cis-[Pt(dpo)Cl$_2$]	−7.1 (dimer)	3649	100	292, 320
cis-[Pt(dpn)Cl$_2$]	−7.4 (monomer)	3654	39	291, 321
	−7.1 (dimer)	3639	58	
	−13.0 (trans)	2570	3	
cis-[Pt(dpd)Cl$_2$]	−7.3 (monomer)	3648	50	294, 320
	−7.1 (dimer)	3650	50	
cis-[Pt(dpu)Cl$_2$]	−7.5 (monomer)	3657	68	295, 320
	−7.1 (dimer)	3654	28	
	−13.0 (trans)	2564	4	
cis-[Pt(dpdod)Cl$_2$]	−7.1 (dimer)	3649	100	294, 320
cis-[Pt(dphd)Cl$_2$]	−7.3 (monomer)	3638	57	289, 314
	−7.1 (dimer)	3650	38	
	−12.6 (trans)	2564	5	

^{a} Measured relative to 85% H$_3$PO$_4$ external standard with CDCl$_3$ as the lock solvent. ^{b} Measured in hertz. ^{c} Measured in cm^{-1}.

Table IV. Phosphorus-31 NMR and Infrared Data for the Complexes trans-[Pt(Ph$_2$P(CH$_2$)$_n$PPh$_2$)Cl$_2$]

complex	δ(^{31}P)^a	$^1J_{Pt-P}$^{b}	% composition	ν(Pt–Cl)^c
trans-[Pt(dpe)Cl$_2$]	−47.3	2359	low sol	340
trans-[Pt(dph)Cl$_2$]	−12.4	2548	low sol	340
trans-[Pt(dphp)Cl$_2$]	−17.5 (monomer)	2544	12	340
	−12.4 (dimer)	2548	82	
	−13.4	2573		
	−6.9 (cis)	3648	6	
trans-[Pt(dpo)Cl$_2$]	−16.0 (monomer)	2587	54	338
	−12.4 (dimer)	2550	48	
	−12.8	2562		
trans-[Pt(dpn)Cl$_2$]	−15.9 (monomer)	2595	51	340
	−12.5 (dimer)	2550	45	
	−13.3	2569		
	−7.0 (cis)	3644	4	
trans-[Pt(dpd)Cl$_2$]	−15.5 (monomer)	2595	67	340
	−12.5 (dimer)	2550	33	
	−12.9	2563		
trans-[Pt(dpu)Cl$_2$]	−14.2 (monomer)	2585	62	
	−12.5 (dimer)	2549	25	340
	−13.1	2564		
	−7.1 (cis)	3648	13	
trans-[Pt(dpdod)Cl$_2$]	−13.5 (monomer)	2579	87	
	−12.5 (dimer)	2580	13	340
	−12.9	2569		
trans-[Pt(dphd)Cl$_2$]	−12.6 (dimer)	2566	92	338
	−7.0 (cis)	3648	8	

^{a} Measured relative to 85% H$_3$PO$_4$ external standard with CDCl$_3$ as the lock solvent. ^{b} Measured in hertz. ^{c} Measured in cm^{-1}.

atoms). Therefore, the far-infrared spectra of the complexes (600–180 cm^{-1}) should provide the necessary information required to confirm the geometry of the complexes, as it is in this area that the platinum–chlorine stretching vibrations are observed.[26,27] The far-infrared spectral data are displayed in Tables III and IV. The complexes prepared with potassium tetrachloroplatinate(II) as the precursor exhibit two bands at ca. 285 and 320 cm^{-1}, characteristic of cis chlorine atoms,[26-28] while the corresponding

complexes prepared from Zeise's salt show only one band at ca. 340 cm^{-1}, characteristic of trans chlorine atoms.[26-29] The far-infrared spectral data are consistent with the geometries assigned to the complexes on the basis of $^1J_{Pt-P}$.

The molecular weights of a number of the complexes were determined and are displayed in Tables I and II, and the values indicate that the isomers formed in each synthesis are usually a mixture of monomeric and dimeric species. The phosphorus-31 NMR spectra of the cis complexes of the ligands dpn, dpu, and dphd showed the presence of three distinct resonances. One resonance was present as a very small percentage of the total (ca. 5%) and possessed a coupling constant of ca. 2500 Hz and could therefore be identified as a trans impurity. The other two resonances, one at −7.1 ppm, the other at −7.3 to −7.5 ppm (relative to 85% H$_3$PO$_4$ external standard), were assigned as the dimeric cis isomer and the monomeric cis isomer, respectively, by comparison of the peak areas with the molecular weights determined for these complexes: typically, good agreement was obtained; e.g., the Pt(dpn)Cl$_2$ molecular weight observed from vapor-phase osmometry was 1041, while the molecular weight calculated from assignment of resonances at −7.1 ppm to the dimer (58%), at −7.4 to the monomer (39%), and at −13.0 to the trans impurity (4%) gave a value of 1039. With use of this technique, the peak at −7.1 ppm present in all of the cis complexes could be assigned to a dimeric species and those at lower field to the corresponding monomers.

For the trans complexes, as many as four distinct resonances could be observed in the ^{31}P NMR spectrum. The resonance at ca. −7.0 ppm with $^1J_{Pt-P}$ = ca. 3600 Hz could be assigned immediately as a cis impurity due to both the value of $^1J_{Pt-P}$ and the fact that this resonance was only present in a small percentage of the total. Once again, comparison of the molecular weights determined by vapor-phase osmometry with those from the ^{31}P NMR spectra suggested that the lowest field resonance was due to the monomeric trans-chelated isomer while the two resonances at higher field represented two distinct conformers of the dimeric binuclear macrocyclic species. Shaw[7] noted that the reaction of (t-Bu)$_2$P(CH$_2$)$_8$P(t-Bu)$_2$ with [PtCl$_2$(NCPh)$_2$] gave two signals in the ^{31}P NMR spectrum which were ascribed to two distinct trans conformers present in solution as the tert-butyl groups gave a triplet pattern in the ^{1}H NMR spectrum ("virtual coupling") which could only arise if the two phosphorus nuclei were equivalent. Similarly the mononuclear trans-PdCl$_2$[(t-Bu)$_2$P-(CH$_2$)$_{10}$P(t-Bu)$_2$] showed a singlet ^{31}P NMR resonance whereas the corresponding binuclear species showed two singlets in the ^{31}P NMR spectrum. Again the appearance of "virtual coupling" in the ^{1}H NMR spectrum showed that the phosphorus nuclei were equivalent. Shaw once again suggested that this behavior must be due to the existence of two conformational isomers in solution. We have observed similar behavior in the systems studied here and have assigned the resonances in a similar manner. The reason for the presence of two conformers in the trans binuclear complexes is not clear at this time. Trans dimeric complexes with a chemical shift of −12.5 ppm ($^1J_{Pt-P}$ = 2548–2550 Hz) were observed in each case; the chemical shift of the other trans dimeric conformer increased slightly with increasing chain length but remained in the range of −12.6 to −13.4 ppm ($^1J_{Pt-P}$ = 2563–2575 Hz) with the exception of trans-[Pt(dphd)Cl$_2$], for which only one conformer was observed (δ(^{31}P) = 12.6). The major dimeric species for the complexes was always the high-field conformer.

An interesting feature of the study was the isolation of a trans-bonded complex with dpe (see Table IV) which possessed δ(^{31}P) = −47.3 and $^1J_{Pt-P}$ = 2359 Hz and exhibited one band in the far-infrared spectrum at 340 cm^{-1}. To our knowledge, this is the first report of dpe acting as a trans-bonding ligand. The complex was extremely insoluble and probably possesses a polymeric structure. The product was isolated from the reaction of the ligand with Zeise's salt as described in the Experimental Section. Reaction of dpe with potassium tetrachloroplatinate(II)

(26) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 203.

(27) Adams, D. M. "Metal-Ligand and Related Vibrations"; St. Martin's: New York, 1968; p 319.

(28) Adams, D. M.; Chatt, J.; Gerratt, J.; Westland, A. D. *J. Chem. Soc.* **1964**, 734.

(29) Duddell, D. A.; Goggin, P. L.; Goodfellow, R. R.; Norton, M. G.; Smith, J. G. *J. Chem. Soc. A* **1970**, 545.

6004   *J. Am. Chem. Soc., Vol. 104, No. 22, 1982*

Hill et al.

Table V. Ring Contributions to the ^{31}P Chemical Shift for the Cis Complexes

	δ(free ligand)[a]	δ(^{31}P)[b]	Δ[c]	Δ$_R$[d]
dph	+15.5	−7.4	−22.9	+1.2
dphp	+15.6	−7.4	−23.0	+1.1
dpo	+15.6	e	e	e
dpn	+15.6	−7.4	−23.0	+1.1
dpd	+15.7	−7.3	−23.0	+1.1
dpu	+15.5	−7.5	−23.0	+1.1
dpdod	+15.6	e	e	e
dphd	+15.5	−7.3	−22.8	+1.3

[a] Values from ref 42 relative to 85% H_3PO_4.   [b] Chemical shift of chelated monomer relative to 85% H_3PO_4.   [c] Coordination shift.   [d] Ring contribution to the chemical shift with cis-[Pt(n-BuPh$_2$P)$_2$Cl$_2$][21] as reference (δ(^{31}P) = −24.1).   [e] The complex was dimeric.

Table VI. Ring Contributions to the ^{31}P Chemical Shift for the Trans Complexes

	δ(free ligand)[a]	δ(^{31}P)[b]	Δ[c]	Δ$_R$[d]
dph	+15.5			
dphp	+	−17.5	−33.1	−4.0
dpo	+15.6	−16.0	−33.6	−2.5
dpn	+15.6	−15.9	−31.5	−2.4
dpd	+15.7	−15.5	−31.2	−2.1
dpu	+15.5	−14.2	−29.7	−0.6
dpdod	+15.6	−13.5	−29.1	0
dphd	+15.5	e	e	e

[a] Values from ref 42 relative to 85% H_3PO_4.   [b] Chemical shift of chelated monomer relative to 85% H_3PO_4.   [c] Coordination shift.   [d] Ring contribution to the chemical shift with trans-[Pt(n-BuPh$_2$P)$_2$Cl$_2$][21] as reference (δ(^{31}P) = −29.1).   [e] The complex was dimeric.

results in the formation of the expected cis-chelated monomer with δ(^{31}P) = −41.0 and $^1J_{Pt-P}$ = 3617 Hz in agreement with literature reports[30-32] and also a species at −7.8 ppm with $^1J_{Pt-P}$ = 3654 Hz, which we assign to a dimeric species. Solubility problems prevented an accurate assessment of the relative abundances of the two cis-bonded species. The extremely large downfield shift that occurs on coordination of dpe is a well-known phenomenon[30-33] that has been explained in terms of "ring strain",[34] but this interpretation has been open to dispute.[35]   The isolation of a trans-bonded polymeric dpe complex that cannot be chelated but also exhibits a large downfield shift upon coordination clearly shows that this effect cannot be due to "ring strain".

For the cis complexes, the dimer is generally preferred over the monomer and indeed is the exclusive product when the ligand is dpo or dpdod. On the other hand, the monomeric cis-chelated complexes are preferred with dpu and dphd, indicating that the preferred ring sizes for cis-chelated monomers are 14- and 19-membered chelate rings. The corresponding trans-bonded complexes show an increase in the relative amount of monomer present, which reaches a maximum with dpdod, showing that for trans-chelated monomers the preferred chelate ring size is 15 members. It is interesting to note that dpo can form a monomeric trans-bonded complex: earlier work by Shaw reported only dinuclear and trinuclear complexes should be synthesized with the *tert*-butyl-substituted analogue (t-Bu)$_2$P(CH$_2$)$_8$P(t-Bu)$_2$.[7] These observations are in agreement with the work of Ogino and Fujita on cobalt(III) chelates with long-chain diammines,[36] who noted that the yields of large ring chelates passed through a minimum for 10-membered rings and a maximum for 15-membered rings.

In Tables V and VI are listed the "coordination shifts", Δ, of the monomeric chelated complexes (i.e., the difference in ^{31}P chemical shift between the free and complexed phosphine) and the "ring contribution", Δ$_R$, for the same compounds (i.e., the difference between the coordination shift of a similar bis(monophosphine) complex, in this case cis- or trans-Pt[(n-Bu)Ph$_2$P]$_2$Cl$_2$, and the coordination shift of the corresponding diphosphine complex[33,37]). The values of Δ$_R$ for the cis-chelated monomeric complexes remain relatively constant at +1.1 to +1.3. However, the corresponding trans-chelated monomeric complexes show a steady decrease of Δ$_R$ with increasing ring size, and Δ$_R$ reaches zero for the complex [Pt(dpdod)Cl$_2$]. There is therefore a direct correlation between Δ$_R$ and the amount of monomer formed, and thus ring contributions to the chemical shift can be used as a measure of ring strain for these ligands. Large flexible chelate rings (19 members or above) appear to be unstable in the trans configuration: for trans-[Ph(dphd)Cl$_2$], only the dimer was observed. This suggests that 38-membered ring dinuclear species might be more stable because of an inherent rigidity in the ring. There does not appear to be a simple relationship between $^1J_{Pt-P}$ and the ring size for the trans-chelated monomeric complexes. The values calculated for Δ$_R$ indicate that no metalation has occurred on the large ring backbone.[37]

Addition of a trace of an excess bis(phosphine) to a solution of the trans species, followed by the application of heat, results in rapid trans–cis isomerization. The majority of the trans complexes showed a minor cis component, indicating some isomerization. Since the experimental conditions avoid the presence of excess bis(phosphine), this is an interesting observation, as most mechanisms proposed for cis–trans isomerization in platinum(II) complexes have involved catalysis by excess phosphine.[19] Comparison with the results in Table III makes it possible to assign the cis component to the cis dimeric species in each case. The cis isomers of square-planar platinum(II) phosphine complexes are more stable thermodynamically than their trans analogues,[38,39] and the use of polar solvents in the synthesis of this type of complex also favors the formation of the cis isomer.[21] The expected product from the reaction of bis(phosphines) with potassium tetrachloroplatinate(II) in 2-methoxyethanol is therefore the cis isomer as observed. For the trans isomer, the product of kinetic control, to be obtained, a suitably high trans-labilizing group must be introduced into the complex precursor: in the case of the compounds studied here, the trans-labilizing group employed is the ethylene group present in Zeise's salt[40,41] and the use of this precursor results in the formation of the trans product.

Conclusions

The formation of cis and trans isomers of long-chain flexible bis(phosphine) ligands is critically dependent on the choice of complex precursor: the use of potassium tetrachloroplatinate(II) gives the cis isomer, while the use of Zeise's salt yields the trans analogue. The presence of bulky terminal substituents on the donor phosphorus atoms is not a prerequisite for trans chelation. The absence of a strong trans-labilizing group in the complex precursor results in the formation of the thermodynamically more stable cis isomer, a fact confirmed by the tendency of the trans isomer to revert to the corresponding cis isomer in the presence of heat or excess bis(phosphine).

The *cis* dimers are the most stable isomers for the majority of the cis complexes. The cis monomers are preferred for complexes with the ligands dpu and dphd, which suggests that the preferred ring sizes for cis-chelated monomeric complexes of long-chain

(30) Appleton, T. G.; Bennett, M. A.; Tompkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439.

(31) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971.

(32) Slack, D. A.; Baird, M. C. *Inorg. Chim. Acta* **1977**, 24, 277.

(33) Garrou, P. E. *Inorg. Chem.* **1975**, 14, 1435.

(34) Connor, J. A.; Day, J. P.; Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1978**, 347.

(35) Grim, S. O.; Briggs, W. L.; Barton, R. C.; Tolman, C. A.; Jenson, J. P. *Inorg. Chem.* **1974**, 13, 1095.

(36) Fujita, J.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1975**, 48, 1863.

(37) Garrou, P. E. *Chem. Rev.* **1981**, 81, 229 and references therein.

(38) Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* **1952**, 4300.

(39) Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* **1956**, 525.

(40) Green, M.; Wilson, C. J. *J. Chem. Soc., Dalton Trans.* **1977**, 23, 2302.

(41) Green, M.; Swanwick, M. G. *J. Chem. Soc., Dalton Trans.* **1978**, 2, 158.

ligands are 14- and 19-membered rings.

Trans monomers are formed in solution even with the dphp ligand (10-membered chelate ring), albeit in small amounts. The percentage of trans monomer increases from dphp to dpdod (15-membered chelate ring) in agreement with literature reports for the trans-bonded cobalt(III) complexes with long-chain diammines. Ring contributions, Δ_R, for the trans monomers decrease with increasing ring size and reach zero at a ring size of 15 members—thus we conclude that Δ_R in trans monomeric complexes is a measure of ring strain for these large-ring chelates. For ligands with short chelate backbones such as *cis*-[Pt(dpe)Cl$_2$] the anomalous coordination chemical shift observed for this and other five-membered ring systems cannot be due to "ring strain", as the complex *trans*-[Pt(dpe)Cl$_2$] has been isolated, which also possesses an anomalous coordination chemical shift but which cannot be chelated.

Finally, trans-bonded monomeric complexes appear to be unstable for 19-membered chelate rings and above.

Photochemistry of Metal Carbonyl Alkyls. Study of Thermal β-Hydrogen Transfer in Photogenerated, 16-Valence-Electron Alkyldicarbonylcyclopentadienylmolybdenum and -tungsten Complexes

Romas J. Kazlauskas and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received March 30, 1982

Abstract: Near-UV irradiation of (η^5-C$_5$R$'_5$)M(CO)$_3$R (R' = H, Me; M = Mo, W; R = CH$_3$, C$_2$H$_5$, *n*-pentyl) results in efficient (Φ_{366} > 0.1) dissociative loss of CO. If the photoreaction is carried out at 77 K, the 16-valence-electron species resulting from CO loss can be accumulated and characterized by infrared spectroscopy. Relative intensities of the two carbonyl stretching absorptions suggest that the structure of these species is similar to that of the 18-valence-electron (η^5-C$_5$H$_5$)Fe(CO)$_2$R, that is, a relaxed structure. Upon warming, (η^5-C$_5$R$'_5$)M(CO)$_2$R reacts with CO or added PPh$_3$ to regenerate starting material or form (η^5-C$_5$R$'_5$)M(CO)$_2$(PPh$_3$)R, respectively. In the case where R contains β-hydrogens, warming in the absence of ligand results in β-hydrogen transfer to form *trans*-(η^5-C$_5$R$'_5$)M(CO)$_2$(alkene)(H). For the R groups having β-hydrogens, optical and infrared spectroscopy give evidence for a second (η^5-C$_5$R$'_5$)M(CO)$_2$R species that is not completely coordinatively unsaturated and is proposed to be the immediate precursor to β-hydrogen transfer. This species can be formed by warming or irradiating samples of the photogenerated 16-valence-electron complex and is thought to have a weak M–(β-H) bond. This species does not react rapidly with CO or PPh$_3$ at 195 K as do the (η^5-C$_5$R$'_5$)M(CO)$_2$CH$_3$ complexes. The activation energy $\Delta G^\ddagger$ for the conversion of all such 16-valence-electron species to an alkene–hydride is 10 ± 2 kcal/mol, and the C$_2$H$_5$ and C$_2$D$_5$ species react at the same rate. Irradiation of (η^5-C$_5$H$_5$)W(CO)$_3$CD$_2$CH$_3$ gives a mixture of *trans*-(η^5-C$_5$H$_5$)W(CO)$_2$(C$_2$H$_3$D)(D) and *trans*-(η^5-C$_5$H$_5$)W(CO)$_2$(C$_2$H$_2$D$_2$)(H) at a temperature where both are inert. The β-hydrogen transfer is proposed to involve a preequilibrium between the 16-valence-electron species and a cis-alkene–hydride complex that isomerizes to the trans alkene–hydride in the rate-determining step. (η^5-C$_5$R$'_5$)M(CO)$_2$(alkene)(H) reacts with PPh$_3$ at 298 K to form (η^5-C$_5$R$'_5$)M(CO)$_2$(PPh$_3$)(alkyl). For (η^5-C$_5$H$_5$)W(CO)$_2$(C$_5$H$_{10}$)(H) the reaction rate is proportional to PPh$_3$ concentration up to ~0.1 M, after which little further increase in rate is observed. The kinetics for this reaction are treated as a preequilibrium between the 16-valence-electron dicarbonyl–alkyl and an 18-valence-electron alkene–hydride with the PPh$_3$ reacting with the dicarbonyl–alkyl. The rate constant for the conversion of the pentene–hydride to the dicarbonyl–pentyl is determined to be 1.7 × 10^{-3} s^{-1} at 298 K. In the case of M = Mo, R = C$_2$H$_5$ the equilibrium constant for this interconversion is ~2 and both species are observed in alkane solution at temperatures as high as 250 K.

Introduction

Photochemistry can serve as a useful tool for the generation and characterization of reactive organometallic intermediates. Among the organometallic intermediates that can be formed photochemically are 17-valence-electron metal-centered radicals via metal–metal bond cleavage and 16-valence-electron coordinatively unsaturated metal carbonyls via ligand dissociation or reductive elimination.[1] Generally, an intermediate is a transient

molecular entity formed in the course of a reaction and is not accumulated in appreciable amounts, since the activation energy for the formation is larger than the activation energy for the decomposition or further reaction. Photochemistry offers an alternative pathway for generation of certain thermally reactive intermediates having the advantage that at sufficiently low temperatures an intermediate can be accumulated.[2] This study

---

(1) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(2) (a) Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakoff, M. *Pure Appl. Chem.* **1977**, *49*, 271. (b) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.