

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

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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 Issleib² in 1961, a number of trans-bonded complexes have been prepared. Venanzi³⁻⁶ 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 $MLCl_2$ [$M = Pd, Pt$; $L = (t-Bu)_2P(CH_2)_nP(t-Bu)_2$, $n = 5-10$], 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 $Ph_2P(CH_2)_2(OCH_2CH_2)_nPPh_2$ ($n = 1, 2$, and 3) can form trans-bonded square-planar complexes with rhodium.¹¹⁻¹³ Subsequently, we have shown that trans square-planar complexes with $Ph_2P(CH_2)_2(OCH_2CH_2)_nPPh_2$ can be synthesized with nickel(II), palladium(II), and platinum(II),^{14,15} and indeed trans complexes of the type $PdLX_2$ [$L = Ph_2P(CH_2)_nPPh_2$, $n = 6, 8, 10$, 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(Me₂As(CH₂)₁₂AsMe₂)Cl₂]

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 $Ph_2P(CH_2)_2PPh_2$ (dpe), $Ph_2P(CH_2)_6PPh_2$ (dph), $Ph_2P(CH_2)_7PPh_2$ (dphp), $Ph_2P(CH_2)_8PPh_2$ (dpo), $Ph_2P(CH_2)_9PPh_2$ (dppn), $Ph_2P(CH_2)_{10}PPh_2$ (dpd), $Ph_2P(CH_2)_{11}PPh_2$ (dpu), $Ph_2P(CH_2)_{12}PPh_2$ (dpdod), and $Ph_2P(CH_2)_{16}PPh_2$ (dphd) were prepared and characterized as previously described.¹⁶

B. Preparation of the Complexes. *cis*-[Pt(ligand)Cl₂]. 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)Cl₂] was recrystallized directly from 2-methoxyethanol and collected as above.

trans-[Pt(ligand)Cl₂]. 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(C₂H₄)Cl₃] (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-

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Table I. Elemental Analyses and Molecular Weight Data for the Complexes *cis*-[Pt(Ph₂P(CH₂)_nPPh₂)Cl₂]

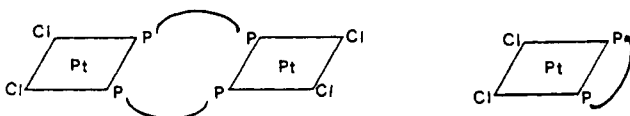
complex	% C	% H ^a	% Cl ^a	mol wt (obsd) ^b	mol wt (calcd) ^d
Pt(dpe)Cl ₂	45.8 (45.7) ^a	3.9 (3.8)	10.9 (10.4)	<i>c</i>	
Pt(dph)Cl ₂	49.2 (50.0)	4.8 (4.4)	9.6 (9.9)	<i>c</i>	
Pt(dphp)Cl ₂	51.2 (50.7)	5.0 (4.6)	9.8 (9.7)	<i>c</i>	
Pt(dpo)Cl ₂	51.4 (51.3)	4.9 (4.8)	9.9 (9.5)	1490 (748) ^e	1496
Pt(dpn)Cl 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)	<i>c</i>	
Pt(dpu)Cl ₂	53.4 (53.2)	5.2 (5.3)	9.5 (9.0)	1368 (790) ^e	1359
Pt(dpdod)Cl ₂	53.6 (53.7)	5.5 (5.5)	9.2 (8.8)	<i>c</i>	
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(Ph₂P(CH₂)_nPPh₂)Cl₂]

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

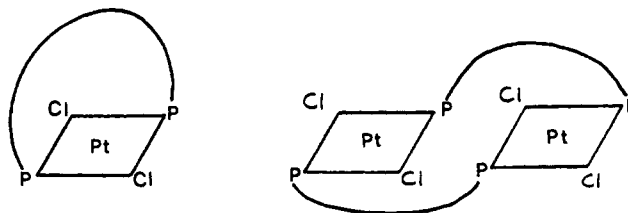
**Figure 1.** Structures of the *cis* dimer and the *cis* monomer.

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)Cl₂, 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(PR₃)₂X₂] 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

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

good for the assignment of molecular geometries in complexes where X = Cl⁻, Br⁻, and I⁻, it gives ambiguous results when X = NO₂⁻²² and R₂S.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 ¹⁹⁵Pt: the central portion of the spectrum is that which is not coupled to ¹⁹⁵Pt, 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 A₂X system and can be analyzed by first-order methods.^{7,8} Complexes of the type *cis*-[Pt(PR₃)₂Cl₂] normally have ¹J_{Pt-P} = ca. 3500 Hz, whereas those of the type *trans*-[Pt(PR₃)₂Cl₂] 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 MP₂Cl₂ donor set should give rise to one band (B_u) for D_{2h} symmetry (*trans* chlorine atoms) and to two bands (A₁ and B₂) for C_{2v} symmetry (*cis* chlorine

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Table III. Phosphorus-31 NMR and Infrared Data for the Complexes *cis*-[Pt(Ph₂P(CH₂)_nPPh₂)Cl₂]

complex	$\delta(^{31}\text{P})^a$	$^1J_{\text{Pt-P}}^b$	% composition	$\nu(\text{Pt-Cl})^c$
<i>cis</i> -[Pt(dpe)Cl ₂]	-41.0 (monomer)	3617	low sol	294, 315
	-7.8 (dimer)	3654		
<i>cis</i> -[Pt(dph)Cl ₂]	-7.4	3655	295, 320	294, 321
<i>cis</i> -[Pt(dphp)Cl ₂]	-7.4 (monomer)			
	-7.1			
<i>cis</i> -[Pt(dpo)Cl ₂]	-7.1 (dimer)	3649	100	292, 320
<i>cis</i> -[Pt(dpn)Cl ₂]	-7.4 (monomer)	3654	39	291, 321
	-7.1 (dimer)	3639	58	
	-13.0 (trans)	2570	3	
<i>cis</i> -[Pt(dpd)Cl ₂]	-7.3 (monomer)	3648	50	294, 320
	-7.1 (dimer)	3650	50	
<i>cis</i> -[Pt(dpu)Cl ₂]	-7.5 (monomer)	3657	68	295, 320
	-7.1 (dimer)	3654	28	
	-13.0 (trans)	2564	4	
<i>cis</i> -[Pt(dpdod)Cl ₂]	-7.1 (dimer)	3649	100	294, 320
<i>cis</i> -[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% H₃PO₄ external standard with CDCl₃ 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(Ph₂P(CH₂)_nPPh₂)Cl₂]

complex	$\delta(^{31}\text{P})^a$	$^1J_{\text{Pt-P}}^b$	% composition	$\nu(\text{Pt-Cl})^c$
<i>trans</i> -[Pt(dpe)Cl ₂]	-47.3	2359	low sol	340
<i>trans</i> -[Pt(dph)Cl ₂]	-12.4	2548	low sol	340
<i>trans</i> -[Pt(dphp)Cl ₂]	-17.5 (monomer)	2544	12	340
	-12.4 (dimer)	2548	82	
	-13.4	2573		
	-6.9 (cis)	3648	6	
<i>trans</i> -[Pt(dpo)Cl ₂]	-16.0 (monomer)	2587	54	338
	-12.4 (dimer)	2550	48	
	-12.8	2562		
<i>trans</i> -[Pt(dpn)Cl ₂]	-15.9 (monomer)	2595	51	340
	-12.5 (dimer)	2550	45	
	-13.3	2569		
	-7.0 (cis)	3644	4	
<i>trans</i> -[Pt(dpd)Cl ₂]	-15.5 (monomer)	2595	67	340
	-12.5 (dimer)	2550	33	
	-12.9	2563		
<i>trans</i> -[Pt(dpu)Cl ₂]	-14.2 (monomer)	2585	62	340
	-12.5 (dimer)	2549	25	
	-13.1	2564		
	-7.1 (cis)	3648	13	
<i>trans</i> -[Pt(dpdod)Cl ₂]	-13.5 (monomer)	2579	87	340
	-12.5 (dimer)	2580	13	
	-12.9	2569		
<i>trans</i> -[Pt(dphd)Cl ₂]	-12.6 (dimer)	2566	92	338
	-7.0 (cis)	3648	8	

^a Measured relative to 85% H₃PO₄ external standard with CDCl₃ 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 $^1J_{\text{Pt-P}}$.

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% H₃PO₄ 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)Cl₂ 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 $^1J_{\text{Pt-P}}$ = ca. 3600 Hz could be assigned immediately as a *cis* impurity due to both the value of $^1J_{\text{Pt-P}}$ 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. Shaw⁷ noted that the reaction of (*t*-Bu)₂P(CH₂)₆P(*t*-Bu)₂ with [PtCl₂(NCPPh)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 ^1H NMR spectrum ("virtual coupling") which could only arise if the two phosphorus nuclei were equivalent. Similarly the mononuclear *trans*-PdCl₂[(*t*-Bu)₂P(CH₂)₁₀P(*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 ^1H 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 ($^1J_{\text{Pt-P}}$ = 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 ($^1J_{\text{Pt-P}}$ = 2563–2575 Hz) with the exception of *trans*-[Pt(dphd)Cl₂], for which only one conformer was observed ($\delta(^{31}\text{P})$ = 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 $\delta(^{31}\text{P})$ = -47.3 and $^1J_{\text{Pt-P}}$ = 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)

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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	<i>e</i>	<i>e</i>	<i>e</i>
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	<i>e</i>	<i>e</i>	<i>e</i>
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.

results in the formation of the expected *cis*-chelated monomer with δ (^{31}P) = -41.0 and $^1J_{\text{Pt-P}}$ = 3617 Hz in agreement with literature reports³⁰⁻³² and also a species at -7.8 ppm with $^1J_{\text{Pt-P}}$ = 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 phenomenon³⁰⁻³³ 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 diamines,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*-BuPh $_2$ 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

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	<i>e</i>	<i>e</i>	<i>e</i>

^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.

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*-[Pt(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 $^1J_{\text{Pt-P}}$ 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

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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)Cl₂] 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)Cl₂] 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.

Registry No. *cis*-Pt(dpe)Cl₂, 14647-25-7; *cis*-Pt(dph)Cl₂, 83095-87-8; *cis*-Pt(dphp)Cl₂, 83095-88-9; *cis*-[Pt(dpo)Cl₂]₂, 83095-89-0; *cis*-Pt(dpn)Cl₂, 83095-90-3; *cis*-Pt(dpd)Cl₂, 83095-91-4; *cis*-Pt(dpu)Cl₂, 83095-92-5; *cis*-[Pt(dpdod)Cl₂]₂, 83151-17-1; *cis*-Pt(dphd)Cl₂, 83095-93-6; *cis*-[Pt(dpe)Cl₂]₂, 83095-94-7; *cis*-[Pt(dpn)Cl₂]₂, 83095-95-8; *cis*-[Pt(dpd)Cl₂]₂, 83095-96-9; *cis*-[Pt(dpu)Cl₂]₂, 83095-97-0; *cis*-[Pt(dphd)Cl₂]₂, 83095-98-1; *trans*-[Pt(dpe)Cl₂]₂, 83095-84-5; *trans*-[Pt(dph)Cl₂]₂, 83095-86-7; *trans*-Pt(dphp)Cl₂, 83149-21-7; *trans*-Pt(dpo)-Cl₂, 83095-99-2; *trans*-Pt(dpn)Cl₂, 83149-22-8; *trans*-Pt(dpd)Cl₂, 83149-23-9; *trans*-Pt(dpu)Cl₂, 83149-24-0; *trans*-Pt(dpdod)Cl₂, 83096-00-8; *trans*-[Pt(dphd)Cl₂]₂, 83149-25-1; *trans*-[Pt(dphp)Cl₂]₂, 83096-01-9; *trans*-[Pt(dpo)Cl₂]₂, 83149-26-2; *trans*-[Pt(dpn)Cl₂]₂, 83149-27-3; *trans*-[Pt(dpd)Cl₂]₂, 83149-28-4; *trans*-[Pt(dpu)Cl₂]₂, 83149-29-5; *trans*-[Pt(dpdod)Cl₂]₂, 83096-02-0; K₂[PtCl₄], 10025-99-7; K[Pt(C₂H₄)Cl₃], 12012-50-9.

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

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Abstract: Near-UV irradiation of $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_3\text{R}$ ($\text{R}' = \text{H, Me; M} = \text{Mo, W; R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-pentyl}$) results in efficient ($\Phi_{366} > 0.1$) 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 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$, that is, a relaxed structure. Upon warming, $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2\text{R}$ reacts with CO or added PPh₃ to regenerate starting material or form $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2(\text{PPh}_3)\text{R}$, respectively. In the case where R contains β -hydrogens, warming in the absence of ligand results in β -hydrogen transfer to form *trans*- $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2(\text{alkene})(\text{H})$. For the R groups having β -hydrogens, optical and infrared spectroscopy give evidence for a second $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2\text{R}$ 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 PPh₃ at 195 K as do the $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2\text{CH}_3$ complexes. The activation energy ΔG^\ddagger for the conversion of all such 16-valence-electron species to an alkene-hydride is 10 ± 2 kcal/mol, and the C₂H₅ and C₂D₅ species react at the same rate. Irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CD}_2\text{CH}_3$ gives a mixture of *trans*- $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{C}_2\text{H}_5\text{D})(\text{D})$ and *trans*- $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{C}_2\text{H}_2\text{D}_2)(\text{H})$ 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. $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2(\text{alkene})(\text{H})$ reacts with PPh₃ at 298 K to form $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2(\text{PPh}_3)(\text{alkyl})$. For $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{C}_5\text{H}_{10})(\text{H})$ the reaction rate is proportional to PPh₃ 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 PPh₃ reacting with the dicarbonyl-alkyl. The rate constant for the conversion of the pentene-hydride to the dicarbonyl-pentyl is determined to be $1.7 \times 10^{-3} \text{ s}^{-1}$ at 298 K. In the case of $\text{M} = \text{Mo}$, $\text{R} = \text{C}_2\text{H}_5$, 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

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