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Oligomerization and *cis-trans* isomerization equilibria in dichloropalladium(II) metallacrown ethers and a dichloropalladium(II) complex of 1,12-bis(diphenylphosphino)-dodecane

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Quantitative $^{31}P\{^1H\}$ NMR spectroscopic studies of monomer–oligomer and *cis-trans* equilibria in chloroform-*d* solutions of $PdCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}_n$ (n = 3, 4, 5) metallacrown ethers and of $PdCl_2\{Ph_2P\text{-}(CH_2)_{12}PPh_2\text{-}P,P'\}$ are reported. The NMR data for all of the complexes can be adequately modeled using a single *cis-trans* isomerization equilibrium and two step-polymerization (dimerization, oligomerization) equilibria. As expected, both the dimerization and oligomerization equilibrium constants for the metallacrown ethers increase as n increases. However, the dimerization equilibrium constants of the metallacrown ethers are much smaller than are the oligomerization equilibrium constants. In contrast, the dimerization and oligomerization equilibrium constants for $PdCl_2\{Ph_2P(CH_2)_{12}PPh_2\text{-}P,P'\}$ are nearly identical and are significantly larger than are those of the metallacrown ethers. Kinetic studies of monomer–oligomer and *cis-trans* equilibria in solutions of *cis*-$PdCl_2\{Ph_2P(CH_2CH_2O)_3\text{-}CH_2CH_2PPh_2\text{-}P,P'\}$ indicate that the *trans* monomer and *trans* oligomers are formed at approximately the same rates and that the reactions follow reversible first-order kinetics. The very different dimerization constants for the metallacrown ethers and $PdCl_2\{Ph_2P(CH_2)_{12}PPh_2\text{-}P,P'\}$and the similar rates of formation for the *trans* monomer and *trans* oligomers suggest that the isomerization and dimerization reactions have a common rate-determining step that involves cleavage of a palladium–phosphorus bond.

Introduction

Metallacrown ethers, a class of polyfunctional molecular receptors,[1,2] are formed when $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ {n = 3, (**1**); 4, (**2**); 5, (**3**)} ligands chelate to transition metals.[3] When the transition metal is inert to phosphine exchange and has a *cis* coordination geometry, monomeric metallacrown ethers that can bind alkali metal cations and small molecules are obtained.[4] In contrast, when the transition metal is labile to phosphine exchange, as is the case in the $[PdCl_2\{Ph_2P(CH_2CH_2O)_n\text{-}CH_2CH_2PPh_2\text{-}P,P'\}]$ {n = 3, (**4**); 4, (**5**); 5, (**6**)} metallacrown ethers, complex mixtures of monomeric and cyclic oligomeric metallacrown ethers are observed.[5,6]

Monomeric and cyclic oligomeric metallacrown ethers should have quite different receptor properties, and thus it is important to understand factors that affect the monomer–oligomer and *cis-trans* equilibria in solutions of these complexes. Preliminary $^{31}P\{^1H\}$ NMR spectroscopic studies of solutions of **5**[6] led to the development of a model for the monomer–oligomer and *cis-trans* equilibria based on the thermodynamics of *cis-trans* isomerization[7] and reversible step-polymerization equilibria.[8,9] Surprisingly, the equilibrium constant calculated for the dimerization reaction was one-tenth of that calculated for the higher oligomerization reactions. This means that only monomeric metallacrown ethers will be present in dilute solutions of **5**.

Our preliminary study demonstrated that monomer–oligomer and *cis-trans* equilibria in solutions of complexes with long-chain bis(phosphine)polyether ligands can be accurately modeled. However, this study provided no insight into the effects of the length and functionality of the bridging group on these equilibria because only one complex, **5**, was examined. In this paper, the effect of the length of the bridging group is determined by comparing the equilibria in solutions of three metallacrown ethers with three, **4**, four, **5**, and five, **6**, ethylene oxides in the bridging group. The effect of the ether functionality is determined by comparing the equilibria in solutions of the metallacrown ethers to those in solutions of $[PdCl_2(Ph_2P\text{-}(CH_2)_{12}PPh_2\text{-}P,P'\}]_n$, **7**. Kinetic studies of monomer–oligomer and *cis-trans* equilibria in solutions of *cis*-**4** provide insight into the reaction mechanisms. The thermodynamic and kinetic studies in this paper provide the first quantitative assessment of the factors that affect the *cis-trans* and monomer–oligomer equilibria in labile transition metal complexes with long-chain bis(phosphine) ligands.

Experimental

General procedures

All starting materials, free ligands and deuterated solvents were handled under a dry nitrogen atmosphere using standard Schlenk techniques. The palladium complexes were air stable and required no special handling precautions. Tetrahydrofuran was distilled from sodium–benzophenone, and both dichloromethane and acetonitrile were distilled from calcium hydride before use. The ligands, $Ph_2P(CH_2CH_2O)_3CH_2CH_2\text{-}PPh_2$ (**1**), $Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$ (**3**) and $Ph_2P(CH_2)_{12}\text{-}PPh_2$ (**8**) were prepared by modifications of literature methods in which commercially available $KPPh_2$ was substituted for $LiPPh_2$.[10,11]

Multinuclear ($^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H) NMR spectra were recorded on a Bruker ARX300 FT-NMR spectrometer. The ^1H NMR and $^{13}C\{^1H\}$ chemical shifts were referenced to internal tetramethylsilane (TMS), and the $^{31}P\{^1H\}$ NMR chemical shifts were referenced to external 85% phosphoric acid (capillary) in chloroform-*d*. Variable temperature measurements are ±1 K as recorded with an external thermocouple

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calibrated with ethylene glycol using standard procedures.[12] Atlantic Microlabs of Norcross, Georgia performed elemental analyses.

[$PdCl_2${$Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$-*P*,*P*′}]$_n$, 4. A mixture of 0.177 g (1.00 mmol) of palladium chloride and 0.530 g (1.00 mmol) of **1** in 15 mL of a 1:2 acetonitrile–dichloromethane mixture was stirred at ambient temperature for 24 h, and then was filtered through a medium frit covered with silica gel. The filtrate was evaporated to dryness (21 mmHg at 315 K), and the residue was dried *in vacuo* (0.02 mmHg at 298 K) for 48 h yielding 0.560 g (79.2%) of **4**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*): 2.18–2.92 (P-CH_2, m, 4H), 3.42–4.23 (O-CH_2, m, 12H), 7.09–7.79 (C_6H_5-P, m, 20H). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*): 12.36–12.64 (*trans*-oligomers (**4a**), all s), 14.77 (*trans*-monomer (**4b**), s), 24.37–24.51 (*cis*-oligomers (**4c**), all s), 25.55 (*cis*-monomer (**4d**), s). Anal. Calc. for $C_{32}H_{36}O_3P_2Cl_2Pd$: C, 54.32; H, 5.08; Cl, 10.02. Found: C, 54.20; H, 5.15; Cl, 10.13%.

***cis*-[$PdCl_2${$Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$-*P*,*P*′}], 4d.** A mixture of 0.434 g (2.45 mmol) of palladium chloride and 1.30 g (2.45 mmol) of $Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$ in 25 mL of a 2:1 acetonitrile–tetrahydrofuran mixture was stirred for 18 h at ambient temperature. Then, the pale yellow precipitate was collected, washed with acetonitrile (3 × 50 mL) and dried *in vacuo* (0.02 mmHg at 298 K) for 48 h yielding 1.21 g (69.8%) of **4d**. The filtrate was evaporated to dryness (21 mmHg at 315 K), and the orange oily residue was purified by column chromatography on silica gel with ethyl acetate as the eluent (R_f = 0.35) to yield 0.450 g (26.0%) of an equilibrium mixture of **4**. ^{1}H NMR of **4d** (chloroform-*d*, 300 MHz, *δ*): 2.18–2.92 (m, 4H, P-CH_2), 3.42–4.23 (m, 12H O-CH_2), 7.79–7.09 (m, 20H, C_6H_5-P). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*): 25.55 (s). Anal. Calc. for $C_{32}H_{36}O_3P_2Cl_2Pd$: C, 54.32; H, 5.08; Cl, 10.02. Found: C, 54.18; H, 5.19; Cl 9.94%.

[$PdCl_2${$Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$-*P*,*P*′}]$_n$, 6. A mixture of 0.364 g (2.05 mmol) of palladium chloride and 1.27 g (2.05 mmol) of **3** in 55 mL of acetonitrile was stirred at ambient temperature for 24 h. The mixture was then evaporated to dryness (21 mmHg at 315 K) to yield a yellow-orange oil. The oil was dissolved in dichloromethane, and the solution was filtered through a medium frit. The filtrate was evaporated to dryness (21 mmHg at 315 K), and the residue was triturated with hexanes to yield a yellow powder. The powder was dried *in vacuo* (0.02 mmHg at 298 K) for 48 h to yield 1.57 g (96.8%) of **6**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*): 2.42–2.75 (P-CH_2, m, 4H), 3.29–4.06 (O-CH_2, m, 20H), 7.00–7.71 (C_6H_5-P, m, 20H). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*): 12.26–12.52 (*trans*-oligomers, (**6a**), all s), 13.56 (*trans*-monomer, (**6b**), s), 24.54–24.71 (*cis*-oligomers (**6c**) and *cis*-monomer (**6d**), all s). Anal. Calc. for $C_{36}H_{44}O_5P_2Cl_2Pd$: C, 54.82; H, 5.57; Cl, 8.91. Found: C, 54.58; H, 5.52; Cl, 8.74%.

[$PdCl_2${$Ph_2P(CH_2)_{12}PPh_2$-*P*,*P*′}]$_n$, 7. This complex was prepared by a modification of a previously published method.[10] A mixture of 0.319 g (1.80 mmol) of palladium chloride and 0.970 g (1.80 mmol) of **8** in 35 mL of a 1:2 acetonitrile–dichloromethane mixture was stirred at ambient temperature for 24 h. The mixture was then filtered through a medium frit, and the filtrate was evaporated to dryness (21 mmHg at 315 K). The residue was triturated with hexanes to yield a yellow-orange powder. The powder was dried *in vacuo* (0.02 mmHg at 298 K) for 48 h to yield 1.24 g (96.3%) of **7**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*): 0.90–1.46 (CH_2, m, 20 H), 2.05–3.10 (P-CH_2, m, 4H), 7.00–7.83 (C_6H_5-P, m, 20H). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*): 16.99–16.90 (*trans*-oligomers (**7a**), all s), 17.42 (*trans*-monomer (**7b**), 27.64–27.15 (*cis*-oligomers (**7c**) and *cis*-monomer (**7d**), all s). Anal. Calc. for $C_{36}H_{44}P_2Cl_2Pd$: C, 60.38; H, 6.15; Cl, 9.90. Found: C, 60.04; H, 6.31; Cl 9.94%.

^{31}P{^{1}H} NMR spectroscopic studies of the dynamic equilibria in solutions of 4, 6 and 7

Chloroform-*d* solutions of **4**, **6** and **7** with concentrations ranging from 0.17 to 0.020 M were used in the equilibrium studies. A stock solution was first prepared, and then the NMR solutions were prepared by pipetting appropriate amounts of the stock solution into 5 mm, screw cap NMR tubes and diluting to 0.7 mL with chloroform-*d*. The NMR tubes were then capped, and the caps were sealed with TEFLON tape. The NMR tubes were stored in an oil bath whose temperature was regulated to ±1 K. Each NMR tube was placed in the preheated NMR probe 30 minutes before acquisition of the ^{31}P{^{1}H} NMR spectra to insure that the solution was at equilibrium when the spectrum was acquired. Quantitative ^{31}P{^{1}H} NMR spectra were acquired using an inverse-gated 30° pulse sequence with a 20 s pulse delay and 4.5 s acquisition time. The inverse-gated pulse sequence was employed to remove NOE.[13] The delay time necessary for quantitative spectra was determined directly by measuring the change in ^{31}P{^{1}H} integral area as a function of delay time in seconds. Accurate ^{31}P{^{1}H} NMR integrations were calculated from the ^{31}P{^{1}H} NMR spectra using Bruker's UXNMR software. All quantitative ^{31}P{^{1}H} NMR spectra had a signal to noise ratio greater than 200:1 for the most intense peak. No solvent loss was observed in any sample during the course of the measurements. As previously described, a routine written with MATHCAD software was employed in the non-linear approximations of the equilibrium constants.[6]

Results

Syntheses of the palladium complexes

Equilibrium mixtures of the metallacrown ethers, [$PdCl_2$-{$Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-*P*,*P*′}]$_n$ (*n* = 3 (**4**), 5 (**6**)), and [$PdCl_2${$Ph_2P(CH_2)_{12}PPh_2$-*P*,*P*′}]$_n$, **7**, were prepared at ambient temperature by reactions of equimolar amounts of solid palladium dichloride and the ligand in either a 1:2 acetonitrile–dichloromethane mixture (**4**, **7**) or pure acetonitrile (**6**). However, when the reaction of $PdCl_2$ and $Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$ was carried out in a 2:1 acetonitrile–THF mixture, solid *cis*-[$PdCl_2${$Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$-*P*,*P*′}], **4d**, precipitated from the solution. This suggests that monomeric, *cis*-metallacrown ethers such as **4d** are the kinetic products of the reactions. The equilibrium mixtures of the metallacrown ethers are slightly to moderately soluble in acetonitrile, methanol and acetone, but very soluble (>0.160 M) in tetrahydrofuran, dioxane, dichloromethane and chloroform.

NMR spectra of the palladium complexes

^{31}P{^{1}H} NMR spectra. The ^{31}P{^{1}H} spectra of **4**, **6** and **7** are quite similar and exhibit a number of resonances due to monomers and cyclic oligomers with both *cis* and *trans* palladium centers. Fig. 1 and 2 show the ^{31}P{^{1}H} spectra of **4** and **7**, respectively, at varying concentrations. In the spectra of **4**, **6** and **7**, the upfield resonances (**4a**, **6a**, **7a**) are due to *trans*-oligomers, a single resonance (**4b**, **6b**, **7b**) slightly downfield of these is due to the *trans*-monomer, and the downfield resonances are due to both the *cis*-oligomers (**4c, 6c**, **7c**) and *cis*-monomer (**4d**, **6d**, **7d**).[6] The resonances of the *cis*-oligomers and *cis*-monomer of **6** and **7**, like those of **5**, are nearly superimposed while those of **4**, labeled **4c** and **4d**, are well separated. The fact that ^{31}P NMR resonances of the *trans*-monomer and *trans*-oligomers are well separated for all of the complexes while the ^{31}P NMR chemical shifts of the *cis*-monomer and *cis*-oligomers are well separated only for **4** is consistent with the

Table 1 Aliphatic $^{13}C\{^1H\}$ NMR chemical shifts for selected complexes[a]

Compound	C1 $\delta(^{13}C)$	C1 $J(PC)/Hz$[b]	C2 $\delta(^{13}C)$	C2 $J(PC)/Hz$[c]	$\delta(^{13}C)$ C3 C4 C5 C6
4b	26.97 aq	31	67.21 aq	5	71.99s, 70.70s
4d	28.92 aq	33	68.46 aq	4	71.63s, 70.70s
5a[d]	25.82 aq	30	66.60 bs		[e]
5b[d]	26.69 aq	30	67.02 aq	16	71.36s, 71.11s, 70.25s
6a	25.78 aq	28	66.47 bs		69.85s, 70.28s, 70.33s, 70.38s
6b	26.48 aq	29	66.78 bs		70.81s, 70.73s, 70.38 bs, 70.36 bs
7a	25.84 aq	30	66.55 aq	12	69.95s, 69.60s, 66.49s, 15.31s

[a] b = broad, s = singlet, aq = apparent quintet. [b] $|^1J(PC) + {}^3J(PC)|$. [c] $|^2J(PC) + {}^4J(PC)|$. [d] Data from reference 6. [e] Ambiguous.

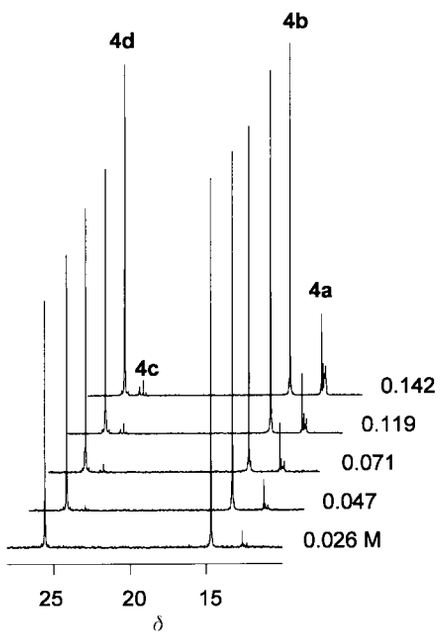


Fig. 1 Selected quantitative $^{31}P\{^1H\}$ NMR spectra of **4** at 308 K. The resonances of the *trans*-oligomers are **4a**, the resonance of the *trans*-monomer is **4b**, the resonances of the *cis*-oligomers are **4c** and the resonances of the *cis*-monomer are **4d**.

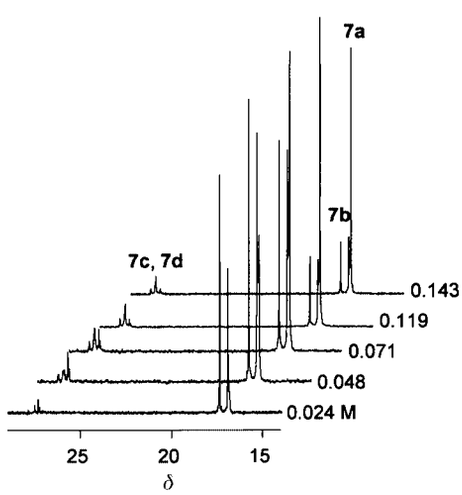


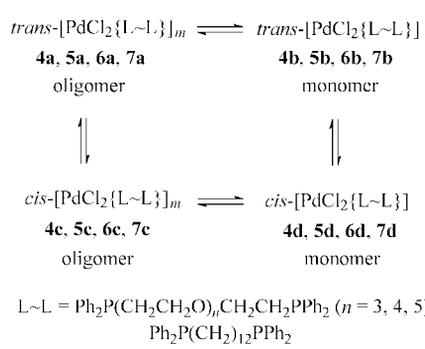
Fig. 2 Selected quantitative $^{31}P\{^1H\}$ NMR spectra of **7** at 308 K. The resonances of the *trans*-oligomers are **7a** and the resonance of *trans*-monomer is **7b**. The resonances of the *cis*-oligomers and *cis*-monomer, **7c** and **7d**, are overlapped.

greater ring strain in the *trans*-monomers. As is the case for **5**,[6] no $^{31}P\{^1H\}$ NMR resonances associated with free Ph_2P groups are observed in solution. Given the low degrees of polymerization in these solutions, this indicates that all of the oligomers are cyclic.

$^{13}C\{^1H\}$ NMR spectra. The assignments for the ^{13}C NMR resonances of the methylene carbons of the metallacrown ethers are given in Table 1. Only the resonances of the methylene one (C1) and two (C2) bonds from the phosphines can be assigned with certainty due to their unique ^{13}C NMR chemical shifts. All of these resonances are either A portions of AXX′ spin systems or broad singlets.[14] Assignment of these resonances for the cyclic *trans*-oligomers, **6a** and **7a**, is straightforward because the *trans*-oligomers are the predominant species in solution at high concentrations, and the chemical shifts and coupling constants for all of the *trans*-oligomers are very similar. Assignment of the C1 and C2 methylene $^{13}C\{^1H\}$ NMR resonances for the *trans*-monomers of **6b** and **7b** is also straightforward because the *trans*-monomer is the only major species present in solutions at low concentrations.

Oligomerization–isomerization equilibria in solutions of 3, 4, 5, and 7

The effects of the length and nature of the chelate chain on the *cis-trans* and monomer–oligomer equilibria in long-chain bis(phosphine) complexes are not understood. To assist in the understanding of these phenomena, we have modeled the equilibria in solutions of **4**, **6** and **7** and compared the results to those previously obtained for solutions of **5**.[5] Our models relate the concentrations of the various species observed in solutions of these complexes, as measured by quantitative $^{31}P\{^1H\}$ NMR spectroscopy, to a *cis-trans* equilibrium and one, two or three step-polymerization equilibria, see Scheme 1. The data set for **4**



Scheme 1 Isomerization–oligomerization equilibria for **4**, **5**, **6** and **7**.

consisted of 23 spectra at 308 K and 14 spectra at 331 K of solutions at seven different concentrations. The data set for **6** consisted of 23 spectra at 308 K and 27 spectra at 331 K on solutions at seven different concentrations. The data set for **7** consisted of 15 spectra at 308 K on solutions at seven different concentrations. All the quantitative $^{31}P\{^1H\}$ NMR spectra were reproducible within the limits of the analysis.

The useful data in the $^{31}P\{^1H\}$ NMR spectra are the integral areas X_A, X_B and X_C of the resonances **a**, **b** and **c** + **d** as shown in Fig. 1. These integral areas were converted into the concentrations of the *trans*-monomer, $[M_t]$, the concentrations of

Table 2 Equilibrium constants calculated using model I

Compound	K_{ct} [a]	K_1 [a]	R [b]
308 K			
4	1.6 ± 0.1	3.3 ± 0.6	4.6×10^{-2}
5 [c]	5.2 ± 0.3	8.2 ± 1.7	1.7×10^{-1}
6	5.8 ± 0.1	14.5 ± 2.0	1.7×10^{-1}
7	6.0 ± 0.2	40.7 ± 3.1	1.5×10^{-1}
331 K			
4	2.6 ± 0.2	2.3 ± 0.2	3.6×10^{-2}
5 [c]	7.6 ± 0.6	6.2 ± 3.2	1.6×10^{-1}
6	9.5 ± 0.3	11.4 ± 1.6	1.4×10^{-1}

[a] Absolute errors are listed at 99% confidence level. [b] $R = \Sigma(|X_{obs}| - |X_{calc}|)/\Sigma(|X_{obs}|)$. [c] Data for **5** is from ref. 6.

Table 3 Equilibrium constants calculated using model II

Compound	K_{ct} [a]	K_1 [a]	K_3 [a]	R [b]
308 K				
4	1.6 ± 0.1	2.0 ± 0.1	9.3 ± 1.4	6.4×10^{-3}
5 [c]	5.2 ± 0.2	2.4 ± 0.5	19.1 ± 1.9	1.1×10^{-2}
6	5.7 ± 0.1	5.0 ± 1.2	26.1 ± 1.3	4.8×10^{-2}
7	6.0 ± 0.2	35.8 ± 8.0	40.1 ± 5.2	2.5×10^{-1}
331 K				
4	2.4 ± 0.1	1.5 ± 0.1	6.5 ± 0.2	1.7×10^{-3}
5 [c]	7.6 ± 0.2	2.0 ± 0.3	15.2 ± 1.3	5.8×10^{-2}
6	9.5 ± 0.3	4.1 ± 0.7	21.2 ± 1.6	3.4×10^{-3}

[a] Absolute errors are listed at 99% confidence level. [b] $R = \Sigma(|X_{obs}| - |X_{calc}|)/\Sigma(|X_{obs}|)$. [c] Data for **5** is from ref. 6.

trans-monomer formula units in all the *trans*-oligomers, $[W_t]$, and the concentrations of *cis*-monomer formula units in both the *cis*-monomer and -oligomers [*cis*] using eqn. (1), (2) and (3), respectively.

$$[W_t] = \frac{X_A}{X_A + X_B + X_C} \times [\text{total solute}] \quad (1)$$

$$[M_t] = \frac{X_B}{X_A + X_B + X_C} \times [\text{total solute}] \quad (2)$$

$$[cis_t] = \frac{X_C}{X_A + X_B + X_C} \times [\text{total solute}] \quad (3)$$

Equilibrium constants were calculated from these data and the isomerization and step-polymerization equilibria by minimizing the non-linear least squares error function $(\Sigma([X_{obs}] - [X_{calc}])^2)$.[6] Three models, incorporating a single isomerization equilibria, eqn. (4), and one (model I, eqn. (5)), two (model II, eqn. (6)) or three (model III, eqn. (7)) step-polymerization

$$K_{ct} = \frac{[M_t] + [W_t]}{[cis]} \quad (4)$$

$$[W_t] = \frac{2K_1[M_t]^2 - K_1^2[M_t]^3}{(K_1[M_t] - 1)^2} \quad (5)$$

$$[W_t] = \frac{K_1[M_t]^2(2 - K_3[M_t])}{(K_3[M_t] - 1)^2} \quad (6)$$

$$[W_t] = \frac{K_1[M_t]^2(2K_3^2[M_t]^2 - 2K_2[M_t]K_3 - 4K_3[M_t] + 3K_2[M_t] + 2)}{(K_3[M_t] - 1)^2} \quad (7)$$

equilibria were evaluated. In model I, a single equilibrium constant, K_1 is used for all step-polymerizations. In model II, two equilibrium constants, one for dimerization, K_1, and one for higher step-polymerizations, K_3, are used. In model III, three equilibrium constants, one for dimerization, K_1, one for trimerization, K_2, and one for higher step-polymerizations, K_3, are used.

The correlation factor R ($R = \Sigma(|X_o| - |X_c|)/\Sigma(|X_o|)$) was used as a comparative statistical measure and is reported in terms of overall total formula concentration (mol L^{-1}). The equilibrium constants for **4**, **6** and **7** and those previously reported for **5**, calculated using each of the models, are given in Tables 2, 3, and 4.[5] Fig. 3, 4 and 5 show fits of the calculated and experimental $^{31}P\{^1H\}$ NMR data for **4**, **6** and **7**. For **4**, **5** and **6**, the R factors of models II and III, are similar in magnitude and are an order of magnitude smaller than those of model I. This indicates that model II sufficiently describes the equilibria in solutions of the metallacrown ethers, **4**, **5** and **6**.

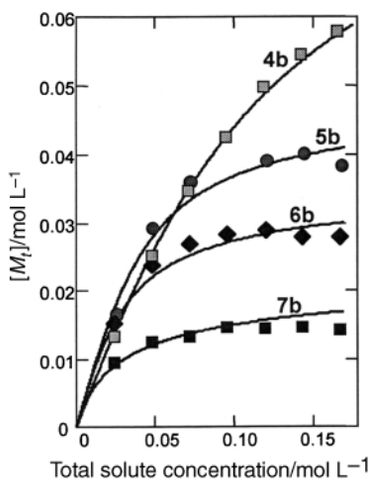


Fig. 3 Plot of the *trans*-monomer concentrations *versus* total solute concentrations in chloroform-*d* solutions at 308 K. The curves are calculated using model II for **4b**, **5b, 6b** and **7b**. The data for **5b** are from reference 6.

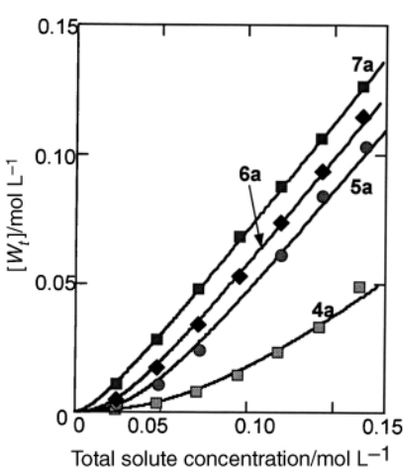


Fig. 4 Plot of the *trans*-oligomer concentrations *versus* total solute concentrations in chloroform-*d* solutions at 308 K. The curves are calculated using model II for **4a**, **5a**, **6a** and **7a**. The data for **5a** are from reference 6.

Kinetics of oligomerization–isomerization equilibria for 4d

The isolation of pure **4d** allowed the kinetics of the *cis*-*trans* and step-polymerization reactions to be studied. A 0.094 M solution of **4d** in chloroform-*d* was placed in the NMR probe at

Table 4 Equilibrium constants calculated using model III

Compound	K_{ct} [a]	K_1 [a]	K_2 [a]	K_3 [a]	R [b]
308 K					
4	1.6 ± 0.1	2.5 ± 0.1	3.8 ± 0.5	11.8 ± 4.1	7.1×10^{-3}
5 [c]	5.2 ± 0.1	3.1 ± 0.7	11.8 ± 3.4	20.0 ± 3.2	1.2×10^{-2}
6	5.8 ± 0.2	5.9 ± 1.4	21.7 ± 6.2	25.6 ± 1.7	8.1×10^{-2}
7	5.8 ± 0.3	23.3 ± 4.1	41.1 ± 8.2	52.4 ± 2.1	8.1×10^{-2}
331 K					
4	2.4 ± 0.1	1.5 ± 0.1	6.6 ± 0.3	6.2 ± 1.1	1.3×10^{-2}
5 [c]	7.6 ± 0.2	2.3 ± 0.4	10.3 ± 2.2	16.0 ± 2.3	3.3×10^{-2}
6	9.5 ± 0.2	4.9 ± 0.9	16.9 ± 4.0	20.8 ± 2.1	5.7×10^{-2}

[a] Absolute errors are listed at 99% confidence level. [b] $R = \Sigma(|X_{obs}| - |X_{calc}|)/\Sigma(|X_{obs}|)$. [c] Data for **5** is from ref. 6.

Table 5 Ring contributions ($\Delta\Delta_R$)[a] to $^{31}P\{^1H\}$ NMR and $^{13}C\{^1H\}$ NMR chemical shifts of the *trans*-monomers and -oligomers

Compound	= P $\Delta\Delta_R$	C1 $\Delta\Delta_R$	C2 $\Delta\Delta_R$
4b	+2.38	+1.13	+0.66
5b [b]	+1.24	+0.85	+0.47
6b	+0.69	+0.64	+0.23
5a [b]	+0.32 to −0.04	−0.02	+0.05
6a	+0.20 to −0.04	−0.06	+0.08

[a] The ring contributions were calculated by subtracting the coordination chemical shifts of these resonances from those of similar resonances in $[PdCl_2\{(PPh_2CH_2CH_2O)_2CH_2CH_3\}_2]$,[5] which has monodentate ligands and thus no ring strain. [b] Data for **5a** and **5b** are from ref. 6.

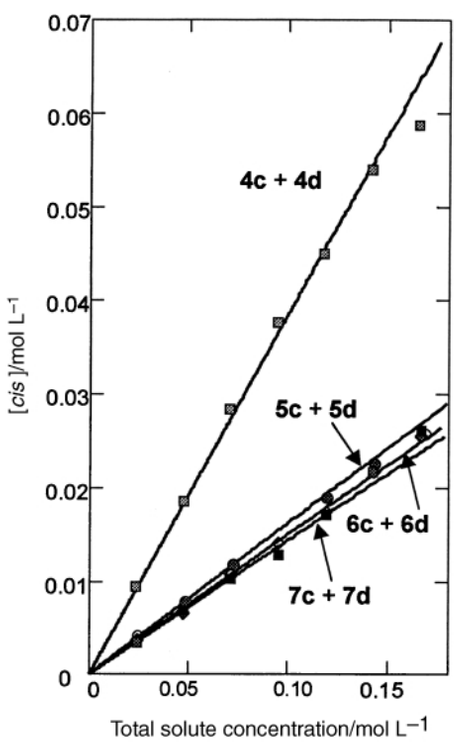


Fig. 5 Plot of the *cis*-monomer plus *cis*-oligomer concentrations *versus* total solute concentrations in chloroform-*d* solutions at 308 K. The curves are calculated using model II for **4**, **5, 6** and **7**. The data for **5** are from reference 6.

331 K, and the *cis-trans* and oligomerization reactions followed by quantitative $^{31}P\{^1H\}$ NMR spectroscopy. Representative spectra are shown in Fig. 6. Relative concentrations of the *cis* and *trans* isomers were measured by integration of the resonances for **4d** and for **4a** + **4b**, respectively. Analysis according to reversible first-order kinetics gave an excellent fit of the experimental data as shown in Fig. 7 (correlation coefficient = 0.998)

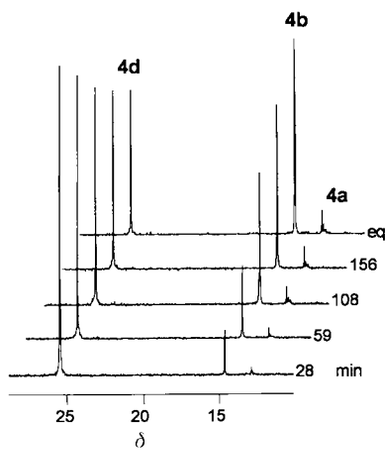


Fig. 6 Selected $^{31}P\{^1H\}$ spectra of the isomerization of a 0.094 M solution of **4d** to **4b** and **4a** at 331 K.

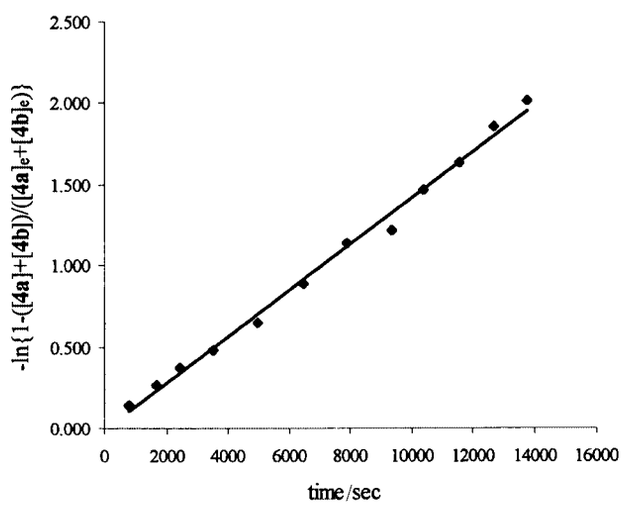


Fig. 7 Kinetics plot of the isomerization of **4d** (0.094 M in chloroform-*d*) at 331K.

with $k_{ct} = 1.0 \pm 0.1 \times 10^{-4}$ s^{-1} and $k_{tc} = 4.2 \pm 0.5 \times 10^{-5}$ s^{-1} (the errors are three standard deviations which are approximately significant at the 99.7% level). This excellent fit suggests that the rate determining step is the same for the formation of **4a** and **4b**.

Discussion

cis-trans Isomerization equilibria

The *cis-trans* isomerization equilibria in solutions of **4, 6** and **7** are consistent with those observed in solutions of **5**.[6] As shown in Table 3, the magnitudes of the *cis-trans* equilibrium con-

stants, K_{ct}, of all of the complexes increase with temperature. This is due to the fact that the maximization of solute–solution disorder favors the *trans* isomers in solvents with low polarities such as chloroform-*d*.[7] The *cis*-*trans* equilibrium constants for **5**, **6**, and **7** are similar in magnitude and are significantly larger than that of **4**. This suggests that the smaller ligand in **4b** is more strained when *trans* coordinated than are the larger ligands in **5b**, **6b** and **7b**. This conclusion is supported by the comparison of the ring contributions to the chemical shifts, $\Delta\Delta_R$,[15] for the $^{31}P\{^1H\}$ NMR and methylene C1 and C2 $^{13}C\{^1H\}$-NMR resonances of both the *trans*-monomers and -oligomers of **4**, **5** and **6** (Table 5). For the *trans*-monomers, the $\Delta\Delta_R$ values are largest for **4** and smallest for **6**. In contrast, the $\Delta\Delta_R$ values for all of the *trans*-oligomers are very small. These results are consistent with those reported for other palladium(II) complexes with long chain bis(phosphine) ligands.[15,16]

The *cis*-*trans* equilibrium constants for **5**, **6**, and **7** are somewhat larger than those reported for other dichlorobis(phosphine)palladium(II) complexes in chloroform-*d* (phosphine = $P(C_6H_4$-*p*-Cl)Me_2, 1.41; $PhPMe_2$, 0.67; $P(C_6H_4$-*p*-Me)Me_2, 0.42; $P(C_6H_4$-*p*-Cl)$_2Me$, 2.56; PPh_2Me, 2.06; $P(C_6H_4$-*p*-Me)$_2Me$, 3.31).[7] This suggests that the larger chelate rings favor the *trans* isomer, most likely due to steric crowding when the phosphines are *cis*-coordinated. These results are consistent with our recent report that the metallacrown ether rings in both *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$-*P*,*P*'} and *cis*-$PtCl_2\{Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$-*P*,*P*'} exhibit conformational isomers at low temperatures.[17]

Oligomerization equilibria

Comparison of the equilibrium constants for the reversible oligomerization equilibria in **4**, **5**, **6** and **7**, calculated using model II, allows the effects of temperature, chelate ring size and chelate ring functionality to be evaluated. As expected, higher temperatures result in higher monomer concentrations and lower average degrees of polymerization for all of the complexes.[6] For the metallacrown ether complexes, **4**, **5**, and **6**, the magnitudes of the equilibrium constants for the dimerization and oligomerization reactions increase dramatically as the number of ethylene oxide units in the metallacrown ether increases. This behavior is consistent with the fact that as the chain length increases, the probability that both phosphines will chelate to the same metal decreases because the phosphines are further apart, on the average.

The most interesting and unexpected result of this study is that both the absolute and relative magnitudes of the dimerization and oligomerization constants of the metallacrown ethers, **4**, **5** and **6**, are quite different from those of **7**. The dimerization constants for the metallacrown ethers are much smaller than the oligomerization constants (10–20%) while the dimerization and the oligomerization constants for **7** are very similar (95%). In addition, the oligomerization constants for the metallacrown ethers are significantly smaller (25–65%) than the oligomerization constant of **7**. These differences indicate that both dimerization and oligomerization are more favorable with alkylene chains than with polyether chains.

Because the bis(phosphine) chelate ring in **7** is larger than that in **4** and smaller than that in **5**, the significant differences in the magnitudes of the dimerization and oligomerization constants of the metallacrown ethers, **4**, **5**, **6**, and those of **7** cannot be due to the size of the chelate rings in the complexes. Nor does it seem likely that the differences are due to different conformational preferences of the chelate chains because both are conformationally mobile. Instead, these differences appear to be due to the ability of the ether oxygens in the metallacrown rings to serve as hemilabile ligands for the palladium. The hemilabile coordination of an ether oxygen upon phosphine dissociation from the *trans*-monomer would hold the free phosphine in the proximity of the palladium and favor coordination of the phosphine to this palladium, to reform the monomer, rather than coordination to another palladium, to form an oligomer.

The ability of the ether oxygens to function as hemilabile ligands and affect the oligomerization equilibria depends on both the nature of the oligomer and the number of ethylene oxide units in the metallacrown ether. This is most clearly demonstrated by the variation in the trimerization constants, K_2 from model III, with the number of ethylene oxide units in the metallacrown ether ring. The trimerization constant for **4**, with three ethylene oxide units, is very similar in magnitude to the dimerization constant, K_1, suggesting that hemilabile coordination of an ether oxygen also strongly affects the trimerization equilibrium in **4**. In contrast, the trimerization constant for **6**, with five ethylene oxide units in the metallacrown ether ring, is similar in magnitude to the oligomerization constant, K_3, suggesting that hemilabile ether coordination does not strongly affect the trimerization equilibrium in **6**. As might be expected, the trimerization constant of **5** is intermediate in magnitude between the dimerization and oligomerization constants.

Kinetics of isomerization and oligomerization equilibria

Additional insight into the mechanism proposed for the oligomerization equilibria is provided by the study of the kinetics of isomerization and oligomerization equilibria of **4d**. When **4d** is dissolved in chloroform-*d* at 331 K, the *cis*-*trans* isomerization reactions and oligomerization reactions occur simultaneously, and the reaction obeys reversible first-order kinetics. This behavior suggests that the rate-determining step for both isomerization and oligomerization is the same and thus must involve cleavage of a palladium–phosphorus bond. This proposal is supported by the results from studies of *cis*-*trans* isomerism in $Pd(X)(R)(PPh_3)_2$ by Casado and Espinet[18] and in $PdCl_2(PPr^n{}_3)_2$ by Traverso and co-workers[19] but is inconsistent with the absence of phosphine exchange during *cis*-*trans* isomerizations of mixtures of $PdCl_2(PR_3)_2$ (R = Et, ^{n}Pr).[20] These differences may be due to competing pathways that involved cleavage of either palladium–phosphine or palladium–chloride bonds.[21]

The *cis*-*trans* and monomer–oligomer reactions of **4d** are surprisingly slow with equilibrium concentrations being observed only after 5 h at 331 K in chloroform-*d* solution. In contrast, Nelson and co-workers have reported that the *cis*-*trans* isomerization of $PdCl_2(PPh_{3-n}Me_n)_2$ (n = 1, 2) complexes is so rapid that the equilibrium is reestablished within a few seconds of changing temperature.[7c] Because the Ph_2PMe ligands in Nelson's complexes are electronically similar to the Ph_2PCH_2– groups in **4d**, the metallacrown ether ring in **4d** must be inhibiting the *cis*-*trans* isomerization and monomer–oligomer reactions. This could be a steric effect as Cooper and Powell have reported that slow *cis*-*trans* isomerization occurs in $PdCl_2\{Me_2$(*o*-tolyl)P$\}_2$.[7d] It is also possible that the low reaction rates are due to coordination of the ether oxygens to the axial coordination sites of the palladium because coordinating solvents have been demonstrated to decrease the rates of *cis*-*trans* isomerization of *cis*-$PtCl_2(^nBu_3P)_2$.[22] However, the reactions of the platinum complex are catalyzed by excess phosphine, and thus may have a quite different mechanism for the *cis*-*trans* isomerization reaction.

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