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Synthesis and characterization of $[Pd_2X_2(\mu\text{-}X)_2\{Ph_2P(CH_2CH_2O)_n\text{-}CH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3, 5, X = Cl, I) dimetallacrown ethers and the related dinuclear $[Pd_2Cl_2(\mu\text{-}Cl)_2\{Ph_2P(CH_2)_{12}PPh_2\text{-}P,P'\}]_m$ and $[Pd_2X_2(\mu\text{-}X_2)\{Ph_2P(CH_2CH_2O)_2CH_2CH_3\text{-}P)_2\}]$ (X = Cl, I) complexes

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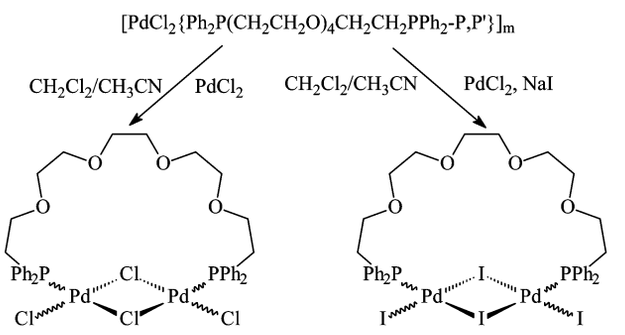
Received 31st March 2003, Accepted 23rd May 2003
First published as an Advance Article on the web 13th June 2003

Reactions of the metallacrown ethers, $[PdCl_2\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3, 5), with $PdCl_2$ or $Pd(PhCN)_2Cl_2$ yield the new dimetallacrown ethers, $[Pd_2Cl_2(\mu\text{-}Cl)_2\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3 (**3**), n = 5 (**4**)). Similar reactions of $[PdCl_2\{PPh_2(CH_2)_{12}PPh_2\text{-}P,P'\}]_m$ and $[PdCl_2\{PPh_2(CH_2CH_2O)_2CH_2CH_3\text{-}P\}_2]$ with $PdCl_2$ or $Pd(PhCN)_2Cl_2$ yield $[Pd_2Cl_2(\mu\text{-}Cl_2)\{PPh_2(CH_2)_{12}PPh_2\text{-}P,P'\}]_m$ (**5**) and $[Pd_2Cl_2(\mu\text{-}Cl)_2\{PPh_2(CH_2CH_2O)_2\text{-}CH_2CH_3\text{-}P\}_2]$ (**6**), respectively. The chloride-bridged dimetallacrown ethers, **3** and **4**, are cleanly converted into the iodide-bridged dimetallacrown ethers, $[Pd_2I_2(\mu\text{-}I)_2\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3 (**7**), n = 5 (**8**)) by reaction with excess NaI. In solution, **3** and **4** exist as mixtures of *syn* monomers and cyclic oligomers while **7** and **8** exist as mixtures of both *syn* and *anti* monomers and cyclic oligomers. The solid state structures of *syn*-$[Pd_2I_2(\mu\text{-}I)_2\text{-}\{PPh_2(CH_2CH_2O)_3CH_2CH_2PPh_2\text{-}P,P'\}]$ (*syn*-**7**) and of *anti*-$[Pd_2I_2(\mu\text{-}I)_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_3)_2\text{-}P\}_2\}$ (*anti*-**9**) have been determined. These structures are consistent with the major species present in the solutions. They also suggest that *syn*-**7** experiences ring-strain, which is consistent with the results from the $^{31}P\{^1H\}$ NMR studies.

Introduction

Molecules with multiple receptor sites have received considerable attention because they can exhibit unusual catalytic properties[1] or act as highly selective sensors.[2] Metallacrown ethers, formed by chelation of α,ω-bis(phosphorus-donor)polyether ligands to transition metals, are one such class of molecules and have an unusual combination of receptors.[3,4] The transition metal center in these complexes can bind a variety of small molecules such as carbon monoxide while the metallacrown ether oxygens, like those in the traditional crown ethers,[5,6] can bind hard metal cations.

Recently we reported that the $[PdCl_2\{PPh_2(CH_2CH_2O)_4\text{-}CH_2CH_2PPh_2\text{-}P,P'\}]_m$ metallacrown ether can also serve as a receptor for PdX_2 (X = Cl, I) *via* a ring expansion reaction to form the dimetallacrown ethers, $[Pd_2X_2(\mu\text{-}X)_2\{PPh_2(CH_2\text{-}CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]_m$ (X = Cl (**1**), I (**2**)) as shown in Fig. 1.[7] This type of receptor behavior does not occur with traditional crown ethers and suggests that the independent exchange the cations and anions of the salt in the dimetallacrown ethers may be possible.



1 (81 % *syn*:19 % oligomer) **2** (60 % *anti*:35 % *syn*:5 % oligomer)

Fig. 1 Synthetic routes to the $[Pd_2X_2(\mu\text{-}X)_2\{PPh_2(CH_2CH_2O)_4\text{-}CH_2CH_2PPh_2\text{-}P,P'\}]_m$ (X = Cl (**1**), I (**2**)) dimetallacrown ethers. Ratios of isomers are given for 0.350 M solutions of **1** in chloroform-*d* and of **2** in 1 : 1 chloroform-*d*–dichloromethane-d_2.

Our preliminary study raised a number of questions in addition to the possibility of independent exchange of anions and cations. Among these are (1) how does the length of the polyether tether and the presence of ether function groups in the α,ω-bis(phosphorus-donor)polyether ligands affect the geometrical and monomer–oligomer equilibria in solutions of dimetallacrown ethers and (2) how stable is the μ-chloro bridge in the dimetallacrown ethers? To answer these questions, we have synthesized and characterized a number of $[Pd_2X_2\text{-}(\mu\text{-}X)_2\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ dimetallacrown ethers (X = Cl, I; n = 3, 5) with both shorter (n = 3) and longer (n = 5) α,ω-bis(phosphorus donor)-polyether ligands. We have also synthesized and characterized the related complexes, $[Pd_2Cl_2(\mu\text{-}Cl)_2\{Ph_2P(CH_2)_{12}PPh_2\text{-}P,P'\}]_m$ and $[Pd_2X_2(\mu\text{-}X)_2\text{-}\{Ph_2P(CH_2CH_2O)_2CH_2CH_3\text{-}P\}_2]$ (X = Cl, I) to allow the effects of the polyether groups and the chelate ring on the various equilibria to be determined. The stabilities of the μ-chloro bridges have been evaluated by ^{31}P NMR spectroscopic studies of the reactions of the dimetallacrown ethers with pyridine. Finally, X-ray crystal structures of two of the complexes have been determined to allow the solution and solid state conformations of the complexes to be compared.

Experimental

General procedures

Dichloromethane and acetonitrile were distilled from calcium hydride before use. All other reagents were used as provided. All free ligands and solvents were manipulated under a dry nitrogen atmosphere using standard Schlenk techniques. The palladium complexes are air stable, and no special handling precautions were taken. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker ARX300 FT-NMR spectrometer. The $^{31}P\{^1H\}$ chemical shifts were referenced to external 85%

DOI: 10.1039/b303584k

phosphoric acid (capillary) in chloroform-*d*. The ^{1}H chemical shifts were referenced to internal tetramethylsilane. The precursor complexes, [$PdCl_2${$Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$-*P*,*P*′}]$_m$,[4] [$PdCl_2${$Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$-*P*,*P*′}]$_m$,[4] [$PdCl_2${$Ph_2P(CH_2CH_2O)_2CH_2CH_3)_2$-*P*}],[4] [$PdCl_2${$Ph_2P(CH_2)_{12}PPh_2$-*P*,*P*′}]$_m$,[4] and $Pd(PhCN)_2Cl_2$,[8] and the dimetallacrown ethers, [Pd_2X_2(μ-X)$_2${$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}]$_m$ (X = Cl (**1**), I (**2**)),[7] were prepared by previously published methods.

Synthesis of [Pd_2Cl_2(μ-Cl)$_2${$Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$-*P*,*P*′}]$_m$, 3. A mixture of 0.102 g (0.144 mmol) of [$PdCl_2${$Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$-*P*,*P*′}]$_m$, and 0.0560 g (0.144 mmol) of $Pd(PhCN)_2Cl_2$ in 15 mL of dichloromethane was stirred at room temperature for 24 h and then filtered. The filtrate was poured into 400 mL of hexanes, and the orange–yellow precipitate was collected. The powder was triturated with diethyl ether and then dried *in vacuo* (0.02 mm at 60 °C) for 48 h yielding 0.0926 g (77.5%) of analytically pure **3**·H_2O. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*, ppm): 2.4–2.9 (m, 4H, P–CH_2), 3.3–4.5 (m, 12H O–CH_2), 7.2–7.9 (m, 20H, C_6H_5–P). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*, ppm): 28.6–27.8 (all s, cyclic oligomers), 32.9 (s, monomer, *syn*-**3**). Anal. Calcd for $C_{32}H_{38}O_4P_2Cl_4Pd_2$: C, 42.54; H, 4.20; Cl, 15.70. Found: C, 42.52; H, 4.20; Cl, 15.60%.

Synthesis of [Pd_2Cl_2(μ-Cl)$_2${$Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$-*P*,*P*′}]$_m$, 4. Using the procedure for **3**, 0.149 g (0.187 mmol) of [$PdCl_2${$Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$-*P*,*P*′}]$_m$ and 0.0710 g (0.187 mmol) of $Pd(PhCN)_2Cl_2$ yielded 0.152 g (83.1%) of analytically pure **4**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*): 3.6–3.9 (m, 4H, P–CH_2), 3.4–4.5 (m, 18H O–CH_2), 7.2–7.9 (m, 20H, C_6H_5–P). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*): 28.1–27.8 (all s, cyclic oligomers), 29.7 (s, monomer, *syn*-**4**). Anal. Calcd for $C_{36}H_{44}O_5P_2Cl_4Pd_2$: C, 44.42; H, 4.56; Cl, 14.57. Found: C, 44.23; H, 4.64; Cl, 14.75%.

Synthesis of [Pd_2Cl_2(μ-Cl)$_2${$Ph_2P(CH_2)_{12}PPh_2$-*P*,*P*′}]$_m$, 5. Using the procedure for **3**, 0.101 g (0.141 mmol) of [$PdCl_2${$Ph_2P(CH_2)_{12}PPh_2$-*P*,*P*′}]$_m$ and 0.0540 g (0.141 mmol) of $Pd(PhCN)_2Cl_2$ yielded 0.112 g (89.0%) of analytically pure **5**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*): 2.1–2.5 (m, 4H, P–CH_2), 1.0–1.8 (m, 20H –CH_2), 7.3–7.8 (m, 20H, C_6H_5–P). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*, ppm): 31.6 (s, cyclic oligomers), 33.8 (s, monomer, *syn*-**5**). Anal. Calcd for $C_{36}H_{44}P_2Cl_4Pd_2$: C, 48.40; H, 4.96; Cl, 15.87. Found: C, 48.52; H, 5.02; Cl, 15.99%.

Synthesis of *anti*-[Pd_2Cl_2(μ-Cl)$_2${$Ph_2P(CH_2CH_2O)_2CH_2CH_3$-*P*}$_2$], *anti*-6. Using the procedure for **3**, 0.101 g (0.133 mmol) of [$PdCl_2${$Ph_2P(CH_2CH_2O)_2CH_2CH_3$-*P*}$_2$] and 0.0511 g (0.133 mmol) of $Pd(PhCN)_2Cl_2$ yielded 0.108 g (84.2%) of analytically pure *anti*-**6**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*, ppm): 1.1–1.2 (t, 6H, CH_3), 2.7–2.8 (m, 4H, P–CH_2), 3.4–3.8 (m, 16H O–CH_2), 7.3–7.8 (m, 20H, C_6H_5–P). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*, ppm): 27.5 (s). Anal. Calcd for $C_{36}H_{46}O_4P_2Cl_4Pd_2$: C, 45.07; H, 4.83; Cl, 14.78. Found: C, 45.15; H, 4.81; Cl, 14.87%.

Synthesis of [Pd_2I_2(μ-I)$_2${$Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$-*P*,*P*′}]$_n$, 7. A mixture of 0.107 g (0.121 mmol) of **3** and 0.300 g (2.00 mmol) of finely ground NaI in 30 mL of dichloromethane was stirred at room temperature for 48 h and then filtered. The filtrate was evaporated to dryness (21 mm at 45 °C), and the deep red residue was recrystallized from a dichloromethane–hexanes mixture to yield 0.120 g (79.2%) of analytically pure **7**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*, ppm): 2.7–3.4 (m, 4H, P–CH_2), 3.6–4.6 (m, 12H O–CH_2), 7.1–7.8 (m, 20H, C_6H_5–P). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*, ppm): 30.6 (s, cyclic oligomers), 34.2 (s, monomer, *anti*-**7**), 37.8 (s, monomer, *syn*-**7**). Anal. Calcd for $C_{32}H_{36}O_3P_2I_4Pd_2$: C, 30.72; H, 2.90; I, 40.58. Found: C, 30.65; H, 2.87; I, 40.75%.

Synthesis of [Pd_2I_2(μ-I)$_2${$Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$-*P*,*P*′}]$_n$, 8. Using the procedure for **7**, 0.089 g (0.091 mmol) of **4** and 0.295 g (1.96 mmol) of NaI yielded 0.104 g (84.7%) of analytically pure **8**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*, ppm): 3.0–3.3 (m, 4H, P–CH_2), 3.5–4.4 (m, 20H, O–CH_2), 7.2–7.7 (m, 20H, C_6H_5–P). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*, ppm): 29.9 to 29.1 (all s, cyclic oligomers), 31.4 (s, monomer, *anti*-**8**), 36.5 (s, monomer, *syn*-**8**). Anal. Calcd for $C_{36}H_{44}O_5P_2I_4Pd_2$: C, 32.29; H, 3.31; I, 37.91. Found: C, 32.18; H, 3.37; I, 37.78%.

Synthesis of [Pd_2I_2(μ-I)$_2${$Ph_2P(CH_2CH_2O)_2CH_2CH_3$-*P*}$_2$], 9. A mixture of 0.101 g (0.134 mmol) of [$PdCl_2${$Ph_2P(CH_2CH_2O)_2CH_2CH_3$-*P*}$_2$], 0.0510 g (0.134 mmol) of $Pd(PhCN)_2Cl_2$ and 0.325 g (2.18 mmol) of finely ground NaI was stirred at room temperature for 48 h and then filtered. The filtrate was evaporated to dryness (21 mm at 45 °C), and the deep red residue was recrystallized from a dichloromethane—hexanes mixture to yield 0.160 g (90.4%) of analytically pure **9**. ^{1}H NMR (chloroform-*d*, 300 MHz, *δ*, ppm): 1.2 (t, 6H, CH_3), 3.1 (m, 4H, P–CH_2), 3.3–4.3 (m, 16H, O–CH_2), 7.2–7.8 (m, 20H, C_6H_5–P). ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*, ppm): 30.01 (s, *anti*-**9**), 33.85 (s, *syn*-**9**). Anal. Calcd for $C_{36}H_{46}O_4P_2I_4Pd_2$: C, 32.63; H, 3.50; I, 38.30. Found: C, 32.71; H, 3.52; I, 38.43%.

Reaction of [Pd_2Cl_2(μ-Cl)$_2${($Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′)}]$_n$, 1, with pyridine. A solution of 0.0105 mmol of **1** in 0.600 mL of chloroform-*d* (0.0175 M) was treated with 0.1 mL (1 mmol) of pyridine, and then the ^{31}P{^{1}H} NMR spectrum of the solution was recorded. The resonances for *syn*-[Pd_2Cl_2(μ-Cl_2){($Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′)}] (*syn*-**1**) and a new complex, **10**, were observed in a 1.00 : 20.0 ratio. ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*, ppm): 19.79 (s, **10**).

Reactions of [Pd_2I_2(μ-I)$_2${($Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′)}]$_n$, 2, with pyridine. A solution of 0.0105 mmol of **2** in 0.600 mL of chloroform-*d* (0.0175 M) was treated with 0.1 mL (1 mmol) of pyridine, and then the ^{31}P{^{1}H} spectrum of solution was recorded. The resonances for **2** and that of a new complex (**11**) were observed in a 1.00 : 12.5 ratio. ^{31}P{^{1}H} NMR (chloroform-*d*, 121.5 MHz, *δ*, ppm): 14.16 s (s, **11**).

Collection, solution and refinement of X-ray diffraction data. The X-ray crystal structures of *syn*-**7** and *anti*-**9** have been determined. All crystals in this study were grown by slow evaporation of dichloromethane–hexanes solutions of the complexes. Suitable X-ray quality single crystals of each compound were sealed into thin-walled glass capillaries under aerobic conditions. Each crystal was then mounted and aligned upon an Enraf Nonius CAD4 single crystal diffractometer with κ-geometry (graphite monochromated Mo Kα radiation, λ = 0.71073 Å). Details of the data collections are collected in Table 1. All data were corrected for the effects of absorption and for Lorentz and polarization effects. All crystallographic calculations were performed with the Siemens SHELXTL-PC program package. The positional and anisotropic thermal parameters for all non-hydrogen atoms were refined. All hydrogen atoms were placed in calculated positions with the appropriate molecular geometry and the δ(C–H) = 0.96 Å. The isotropic thermal parameter associated with each hydrogen atom was fixed equal to the U_{eq} of the carbon atom to which it was bound.

CCDC reference numbers 207336 and 211031.

See http://www.rsc.org/suppdata/dt/b3/b303584k/ for crystallographic data in CIF or other electronic format.

Table 1 Data collection, structure solution and refinement parameters for *syn*-**7** and *anti*-**9**

	syn-**7**	*anti*-**9**
Formula	$C_{32}H_{35}I_4O_3P_2Pd_2$	$C_{36}H_{46}I_4O_4P_2Pd_2$
MW	1250.9	1325.1
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/n$
a/Å	16.5945(31)	10.5171(14)
b/Å	24.7338(27)	10.7549(12)
c/Å	9.3914(10)	19.5756(14)
β/°	—	97.973(8)
V/Å^3	3855.0(20)	2192.8(11)
Z	4	2
Abs. coeff./mm^{-1}	4.249	3.742
Temp./K	298	298
Collected reflections	9809	5898
Independent reflections	2580	2865
Observed reflections ($F > 0.3\sigma(F)$)	2580	2865
R^b, wR^c (obs. data, %)	4.52, 5.24	4.74, 4.51
R^b, wR^c (all data, %)	4.52, 5.24	4.74, 4.51

[a] $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [c] $R = \Sigma w(|F_o| - |F_c|)^2/\Sigma(|F_o|^2))^{0.5}$. [d] GOF $= [\Sigma w(|F_o| - |F_c|)^2/n - m]^{0.5}$.

^{31}P{^{1}H} NMR spectroscopic studies. Quantitative ^{31}P{^{1}H} spectra were acquired using an inverse-gated 30° pulse sequence, to eliminate NOE,[9] and a 30 s delay time. 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. Empirically, a thirty second delay was found to be satisfactory for accurate measurement of species concentration *via* integration of the resonances. Accurate ^{31}P{^{1}H} NMR integrations were calculated from the ^{31}P{^{1}H} NMR spectra. The signal to noise ratio was at least 100 : 1 relative to the most intense resonance for each quantitative ^{31}P{^{1}H} NMR spectrum.

Results and discussion

Syntheses of dinuclear palladium complexes

We have previously reported that the metallacrown ether, $[PdCl_2\{PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]_m$, reacts with either $[Pd(PhCN)_2Cl_2]$ or $PdCl_2$ to form $[Pd_2Cl_2(\mu\text{-}Cl)_2\{PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]_m$ (**1**), the first example of a dimetallacrown ether (Fig. 1).[7] We have now carried out similar reactions with the metallacrown ethers, $[PdCl_2\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3, 5), the closely related bis(phosphine) complex, $[PdCl_2\{Ph_2P(CH_2)_{12}PPh_2\text{-}P,P'\}]_m$, and the monodentate phosphine complex, $[PdCl_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_3\text{-}P\}_2]$ to form the dimetallacrown ethers, $[Pd_2Cl_2(\mu\text{-}Cl)_2\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3 (**3**), 5, (**4**)), and the related chloride-bridged dipalladium complexes, $[Pd_2Cl_2(\mu\text{-}Cl)_2\{PPh_2(CH_2)_{12}PPh_2\text{-}P,P'\}]_m$ (**5**) and $[Pd_2Cl_2(\mu\text{-}Cl)_2\{Ph_2P(CH_2CH_2O)_2CH_2CH_3\}_2\text{-}P\}_2]$ (**6**). All of these reactions are rapid if the Pd precursors are soluble in the reaction solvent (*i.e.* $PdCl_2(NCPh)_2$ in dichloromethane or $PdCl_2$ in acetonitrile) but are slow if the Pd precursors are insoluble (solid $PdCl_2$ in dichloromethane).

We have also previously demonstrated that the iodide-bridged dimetallacrown ether, $[Pd_2I_2(\mu\text{-}I)_2\{PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]_m$ (**2**), is obtained in quantitative yield when the reaction of $[PdCl_2\{PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]_m$ and $PdCl_2$ is carried out in the presence of a five-fold excess of NaI in a 1 : 1 dichloromethane–acetonitrile mixture (Fig. 1).[7] This result suggested that it might be possible to exchange the anion in the dimetallacrown ethers without exchanging the cation. To determine if this is the case, the reactions of the dimetallacrown ethers with finely ground NaI in dichloromethane (Fig. 2) have been studied. In all cases, the corresponding iodide-bridged dimetallacrown ethers, $[Pd_2I_2(\mu\text{-}I)_2\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$, ($n$ = 3, (**7**), n = 4 (**2**), n = 5, (**8**)) are obtained in quantitative crude yields. It is

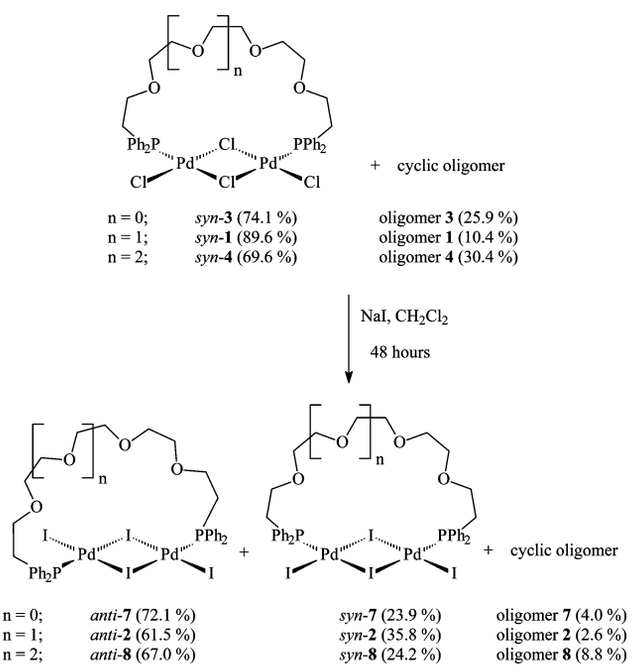


Fig. 2 Anion exchange reactions of the $[Pd_2Cl_2(\mu\text{-}Cl)_2\{PPh_2(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ dimetallacrown ethers. Ratios of isomers are given for 0.175 M solutions of chloro-dimetallacrown ethers in chloroform-*d* and of the iodo-dimetallacrown ethers in 1 : 1 chloroform-*d*–dichloromethane-d_2 at 295 K.

interesting that the reactions of $[Pd_2Cl_2(\mu\text{-}Cl)_2\{PPh_2(CH_2)_{12}PPh_2\text{-}P,P'\}]_m$ (**5**) and $[Pd_2Cl_2(\mu\text{-}Cl)_2\{(Ph_2P(CH_2CH_2O)_2CH_2CH_3)_2\text{-}P\}_2]$ (**6**) with finely ground NaI under similar reaction conditions do not cleanly yield the corresponding iodide complexes. The $[Pd_2I_2(\mu\text{-}I)_2\{(Ph_2P(CH_2CH_2O)_2CH_2CH_3)_2\text{-}P\}_2]$ (**9**) complex can instead be prepared by the reaction of $[PdCl_2\{(Ph_2P(CH_2CH_2O)_2CH_2CH_3)_2\text{-}P\}_2]$, $PdCl_2$ and NaI in a 1 : 1 dichloromethane–acetonitrile mixture. This suggests that the binding of the NaI by the dimetallacrown ether ring is necessary for clean halide exchange reactions.

^{31}P{^{1}H} spectroscopic studies of monomer–oligomer and *syn*–*anti* equilibria. In our earlier report, we noted that **1** exists as a mixture of the *syn* monomer and cyclic oligomers, while **2** exists as a mixture of *syn* and *anti* monomers and oligomers. However, our preliminary study provided no insight into the factors that affect the monomer–oligomer and *syn*–*anti* equilibria in solutions of these complexes. To better understand these

Table 2 Percentages of *syn* monomers and cyclic oligomers in solutions of complexes **1**,[7] **3**, **4** and **5** in chloroform-*d* at 295 K

	0.0175 M $[Pd_2Cl_2(\mu\text{-}Cl)_2\{L\sim L\}]_m$		0.0350 M $[Pd_2Cl_2(\mu\text{-}Cl)_2\{L\sim L\}]_m$	
	Monomer	Oligomer	Monomer	Oligomer
3	74.1	25.9	55.1	44.9
4	69.6	30.4	51.8	48.2
5	29.6	70.4	16.9	83.1
1	89.6	10.4	81.3	18.7

factors, we have studied these equilibria using $^{31}P\{^1H\}$ NMR spectroscopy (Table 2).

The $^{31}P\{^1H\}$ NMR spectra of the complexes with the monodentate ligand, $Ph_2P(CH_2CH_2O)_2CH_2CH_3$ (**6** and **9**) are simplest because no monomer–oligomer equilibria occur with monodentate phosphines. The spectrum of **6** contains a single resonance that is assigned to the *anti* isomer while the spectrum of **9** contains two resonances that are assigned to *syn* (downfield) and *anti* (upfield) monomers. These assignments are based on the similarity of the $^{31}P\{^1H\}$ NMR chemical shift of **6** with those of other *syn*-$[Pd_2Cl_2(\mu\text{-}Cl_2)L_2]$ (L = monodentate phosphine) complexes[10] and on the similarities of the chemical shifts of the resonances of **9** and those of **2**, which were previously assigned on the basis of the effects of changes in solvent polarity.[7]

The $^{31}P\{^1H\}$ spectra of **3**, **4**, and **5** are similar to that of **1**[7] and each contains a more intense downfield resonance and a cluster of less intense upfield resonances. For each complex, the intensity of the downfield resonance decreases and those of the upfield resonances increase with increasing concentration. This is consistent with the existence of a reversible equilibrium between monomeric and cyclic oligomeric complexes in all of the solutions.[11] The monomeric complexes all appear to have *syn* configurations based on the similarities of their NMR chemical shifts to those of **6** and other *syn*-$[Pd_2Cl_2(\mu\text{-}Cl_2)L_2]$ (L = monodentate phosphine) complexes.[10]

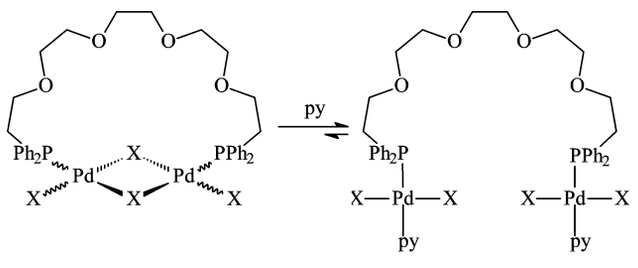
The length of the polyether chain has a dramatic effect on the monomer–oligomer equilibria in solutions of the $[Pd_2Cl_2(\mu\text{-}Cl)_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3 (**3**), 4 (**1**), 5 (**4**)) dimetallacrown ethers. For all concentrations, **1** has the highest and **4** has the lowest monomer to oligomer ratio. This suggests that the $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$ ligand has an optimal chain length to bridge the $Pd_2(\mu\text{-}Cl)_2$ center. This behavior is very different from that which occurs in solutions of $[PdCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3, 4, 5) metallacrown ethers. In these solutions, the monomer to oligomer ratio increases as the chain length of the ligand increases.[4]

The presence of ether oxygens in the ligand backbone also has a dramatic effect on the monomer–oligomer equilibria. The $[Pd_2Cl_2(\mu\text{-}Cl)_2\{Ph_2P(CH_2)_{12}PPh_2\text{-}P,P'\}]_m$ (**5**) complex has a much lower monomer to oligomer ratio than either **3** or **1** although the bridging group of **5** is intermediate in length (12 atoms) between those of **3** (11 atoms) and **1** (14 atoms). This suggests that the presence of the ethers strongly favors the monomeric species. We have previously observed similar behavior solutions of $[PdCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\text{-}P,P'\}]_m$ (n = 3, 4, 5) metallacrown ethers and demonstrated that this behavior is due to the ability of the ether oxygens to serve as hemilabile ligands.[4]

The $^{31}P\{^1H\}$ NMR spectra of **7** and **8** are similar to that of **2**, and each contains two major resonances (both singlets) and a cluster of minor resonances.[7] In each spectrum, the major downfield resonance is assigned to the *syn* monomer, the major upfield resonance is assigned to the *anti* monomer, and the cluster of small resonances are assigned to cyclic oligomers. These assignments are based in the changes in the intensities of the resonances as both the concentrations and polarities of the solvent are varied with high concentrations favoring the oligomers and high polarities favoring the *syn* monomers (Table 3).[7]

The monomer to oligomer ratios of the iodide-bridged dimetallacrown ethers also depend on the length of the bridging polyether chain with **2** having the highest monomer to oligomer ratio and **8** having the lowest monomer to oligomer ratio. This trend parallels that observed for the chloride-bridged dimetallacrown ethers and indicates that the coordination geometry (*syn versus anti*) has little effect on the monomer–oligomer equilibrium.

Reactions of bridging chloro and iodo complexes with pyridine. The reactions of the dimetallacrown ethers, $[Pd_2Cl_2(\mu\text{-}Cl)_2\{(Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P')\}]_m$ (**1**) and $[Pd_2I_2(\mu\text{-}I)_2\{(Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P')\}]_m$ (**2**), with pyridine have been studied to evaluate the stabilities of the μ-halide bridges. The $^{31}P\{^1H\}$ NMR spectrum of each reaction mixture indicated that a single, new complex was formed. Surprisingly, the reactions did not go to completion, even in the presence of a large excess of pyridine, suggesting that the bridging $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$ ligand stabilizes the dimetallacrown ethers. Although these equilibria prevented pure products from being isolated, the products are assigned as $[\{trans\text{-}PdCl_2(py)\}_2\{\mu\text{-}Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]$ (**10**) and $[\{trans\text{-}PdI_2(py)\}_2\{\mu\text{-}Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]$ (**11**) as shown in Fig. 3. This assignment is based on the fact that pyridine reacts with closely related $Pd_2(\mu\text{-}X)_2X_2$-



X = Cl (**1**), I (**2**) X = Cl (**10**), I (**11**)

Fig. 3 Proposed reactions of the $[Pd_2X_2(\mu\text{-}X)_2\{PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]_m$ dimetallacrown ethers with pyridine.

Table 3 Percentages of monomers and cyclic oligomers in solutions of **7**, **8**, **9** and **2** in chloroform-*d* and in 1 : 1 dichloromethane–chloroform-*d* at 295 K

	0.0175 M $[Pd_2I_2(\mu\text{-}I)_2\{L\sim L\}]_m$			0.0350 M $[Pd_2I_2(\mu\text{-}I)_2\{L\sim L\}]_m$		
	syn-Monomer	*anti*-Monomer	Oligomer	*syn*-Monomer	*anti*-Monomer	Oligomer
7[b]	23.9	72.1	4.0	23.5	70.5	6.0
8[b]	24.2	67.0	8.8	22.6	59.6	17.8
8[a]	—	—	—	16.3	68.6	15.1
9[a]	11.2	88.8		11.3	88.7	
2[b]	35.8	61.5	2.6	35.5	59.1	5.2
2[a]	28.4	69.4	2.2	—	—	—

[a] Chloroform-*d* solution. [b] 1 : 1 dichloromethane–chloroform-*d* solution.

Table 4 Selected bond lengths (Å) for *syn*-**7**, *syn*-**2** and *anti*-**9**

syn-**7**		*syn*-**2**		*anti*-**9**	
I1–Pd1	2.582(1)	I2–Pd1	2.602(1)	I1A–Pd1	2.601(1)
I1–Pd1A	2.582(1)	I2–Pd1A	2.602(1)	I1A–Pd1A	2.661(1)
I2–Pd1	2.672(1)	I1–Pd1	2.667(1)	I1–Pd1	2.661(1)
I2–Pd1A	2.672(1)	I1–Pd1A	2.667(1)	I1–Pd1A	2.601(1)
I3–Pd1	2.600(1)	I3–Pd1	2.598(1)	I2–Pd1	2.601(1)
Pd1–P1	2.260(2)	Pd1–P1	2.264(2)	Pd1–P1	2.256(2)

Table 5 Selected bond angles (°) for *syn*-**7**, *syn*-**2** and *anti*-**9**

syn-**7**		*syn*-**2**		*anti*-**9**	
Pd1–I1–Pd1A	97.0(1)	Pd1–I2–Pd1A	97.4(1)	Pd1–I1–Pd1A	95.4(1)
Pd1–I2–Pd1A	92.8(1)	Pd1–I1–Pd1A	94.3(1)	Pd1–I2–Pd1A	95.4(1)
I1–Pd1–I2	84.7(1)	I1–Pd1–I2	84.0(1)	I1–Pd1–I1A	84.6(1)
I1–Pd1–I3	176.7(1)	I2–Pd1–I3	173.9(1)	I2–Pd1–I1A	174.0(1)
I2–Pd1–I3	92.1(1)	I1–Pd1–I3	91.3(1)	I1–Pd1–I2	90.9(1)
I1–Pd1–P1	93.1(1)	I2–Pd1–P1	94.7(1)	P1–Pd1–I1A	96.2(1)
I2–Pd1–P1	177.8(1)	I1–Pd1–P1	177.4(1)	I1–Pd1–P1	178.5(1)
I3–Pd1–P1	90.1(1)	I3–Pd1–P1	90.1(1)	I2–Pd1–P1	88.4(1)

(phosphine)$_2$ complexes to yield *trans*-PdX_2(py)(phosphine) complexes as the only products.[12]

Solid state structures of *syn*-[$Pd_2I_2(\mu\text{-}I)_2${$PPh_2(CH_2CH_2O)_3CH_2CH_2PPh_2$-*P*,*P*′}] (*syn*-7), and *anti*-[$Pd_2I_2(\mu\text{-}I)_2(PPh_2(CH_2CH_2O)_2CH_2CH_3)_2$] (*anti*-9). The X-ray crystal structures of *syn*-**7** and *anti*-**9** have been determined, and the data collection, structure solution and refinement parameters are given in Table 1. ORTEP drawings of *syn*-**7** and *anti*-**9** are shown in Figs. 4 and 5. Selected bond distances and bond angles for *syn*-**7** and *anti*-**9** as well as those for the *syn*-[$Pd_2I_2(\mu\text{-}I)_2${$PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}] dimetallacrown ether (*syn*-**2**), which we have previously reported,[7] are given in Tables 4 and 5. The ORTEP atom labeling scheme for *syn*-**7** and *anti*-**9** are somewhat different, and the data in Tables 4 and 5 has been arranged to allow comparison of related bonds and angles.

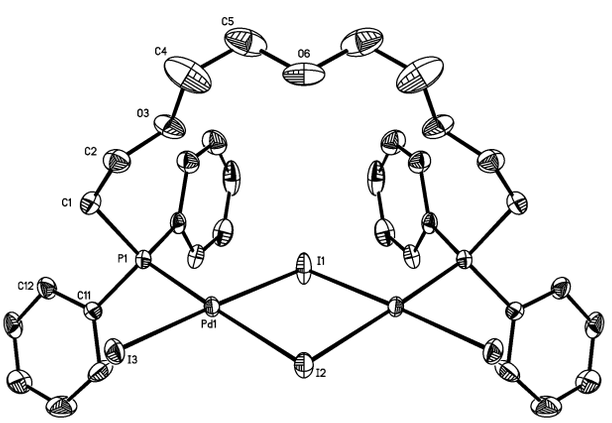


Fig. 4 ORTEP drawing of the molecular structure of *syn*-**7**. Thermal ellipsoids are drawn at the 25% probability level, and hydrogen atoms are omitted for clarity.

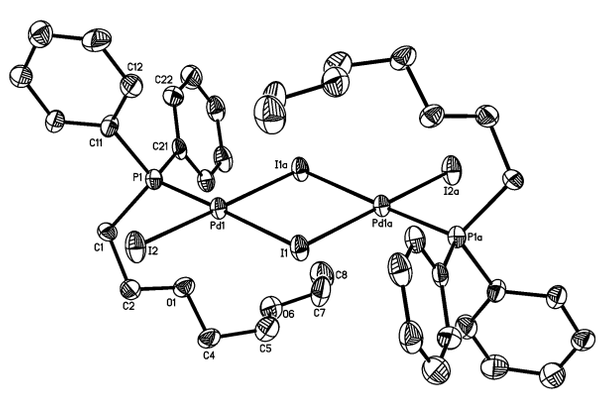


Fig. 5 ORTEP drawing of the molecular structure of *anti*-**9**. Thermal ellipsoids are drawn at the 25% probability level, and hydrogen atoms are omitted for clarity.

The coordination geometries of the palladium metal centers in *syn*-**2**, *syn*-**7** and *anti*-**9** are distorted square-planes differing primarily in the arrangement of the phosphine and iodo ligands. The palladium–phosphorus bond lengths for *syn*-**2**, *syn*-**7** and *anti*-**9** are nearly identical, and similar to palladium–phosphorus bond lengths found for other palladium(II) complexes.[13] In contrast, the palladium–iodine bond lengths in *syn*-**7**, *anti*-**9** and *syn*-**2** depend on the atom that is *trans* to the iodine. When the iodine is *trans* to a phosphorus, the palladium–iodine bond is longer than when the iodine is *trans* to another iodine. This phenomenon can be explained by the greater σ donor ability of the phosphorus relative to that of the iodine.[14]

There is also some evidence of ring strain in these complexes. The palladium–iodine bond trans to phosphorus in *syn*-**7** is slightly longer than that in *syn*-**2**, likewise the palladium–iodine bond trans to iodine in *syn*-**7** is shorter than that in *syn*-**2**. The presence of ring strain in *syn*-**7** is consistent with the fact that the monomer to oligomer ratio for *syn*-**7** is lower than that for *syn*-**2**.

The orientations of the ligands in the two complexes are quite different, in part due to the different coordination geometries of the Pd centers. In *syn*-**2**, the metallacrown ether ring wraps around the $Pd_2(\mu\text{-}I)_2$ center such that O6 is nearly directly over I1. This is shown by the fact that the O6–I1 distance (4.640 Å) is nearly identical to the distance between O6 and the least squares plane through Pd1, I1 and I2 (4.619 Å). In *anti*-**9**, the $CH_2CH_2OCH_2CH_3$ group has a planar configuration (deviation from least squares plane (Å): C4, −0.0571; C5, −0.0490; O6, 0.0705; C7, −0.0613; C8, −0.0017) and is nearly coplanar with the $Pd_2(\mu\text{-}I)_2$ center (interplanar angle: 12.5°). The distance between the least squares plane through the $Pd_2(\mu\text{-}I)_2$ center and the $CH_2CH_2OCH_2CH_3$ group varies from 3.994 Å for C4 to 4.633 Å for C8.

Conclusions

The chloride-bridged [$Pd_2Cl_2(\mu\text{-}Cl)_2${$(Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-*P*,*P*′)}]$_m$ (n = 3, 4, 5) dimetallacrown ethers can be readily prepared in high yields by the reactions of the [$PdCl_2$-{$Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-*P*,*P*′}]$_m$ (n = 3, 4, 5) metallacrown ethers with $PdCl_2$ or $PdCl_2(NCPh)_2$. The chloride-bridged dimetallacrown ethers can be quantitatively converted into the iodide-bridged [$Pd_2I_2(\mu\text{-}I)_2${$(Ph_2P(CH_2CH_2O)_4CH_2$-

CH_2PPh_2-*P*,*P*′)}]$_m$ dimetallacrown ethers by reaction with solid NaI demonstrating that selective exchange of the anions in the dimetallacrown ethers is possible. The chloride-bridged dimetallacrown ethers exist as mixtures of *syn*-monomers and cyclic oligomers while the iodide-bridged dimetallacrown ethers exist as mixtures of *syn*- and *anti*-monomers and cyclic oligomers. The monomer–cyclic oligomer equilibria are highly sensitive to the nature of the bis(phosphorus-donor)polyether ligand with the $n = 4$ dimetallacrown ethers exhibiting the highest monomer : cyclic oligomer ratios. The bis(phosphorus-donor)-polyether ligands in the dimetallacrown ethers also appears to stabilize the μ-halide bridges as indicated by the incomplete reactions of the dimetallacrown ethers with pyridine even when a large excess of pyridine is used.

Acknowledgements

Support of this work by the University of Alabama at Birmingham and the Petroleum Research Fund of the American Chemical Society (35349-AC3) is gratefully acknowledged. DCS, Jr. also thanks the Graduate School at UAB for a graduate fellowship.

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