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Palladium(II) complexes of hybrid phosphine—phosphine oxide ligands

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Abstract—Complexes of the type [L_2PdCl_2], where L = $Ph_2PCH_2P(O)Ph_2$ (dppmO), $Ph_2P(CH_2)_2P(O)Ph_2$ (dppeO), $Ph_2P(CH_2)_3P(O)Ph_2$ (dpppO), $Ph_2P(CH_2)_4P(O)Ph_2$ (dppbO), and $Ph_2PC_5H_4FeC_5H_4P(O)Ph_2$ (dppfcO), were prepared in high yield from $Na_2[PdCl_4]$ and 2 equiv. of the corresponding L in dichloromethane-methanol. All complexes, except for [$(dppfcO)_2PdCl_2$], can exist as the *cis* and *trans* isomers, or mixtures of both, with the *cis*/*trans* ratio decreasing in media of low polarity. The ferrocene containing complex, [$(dppfcO)_2PdCl_2$], appeared to be exclusively *trans* in both the solid state and solution, as established by single crystal X-ray diffraction of its 1 : 3 benzene solvate. The ion exchange extraction of dichloromethane solutions of [$(dppmO)_2PdCl_2$] and [$(dppeO)_2PdCl_2$] with aqueous $NaBF_4$ furnished the corresponding cationic *P*,*O*-chelates, *cis*-[$(dppmO)_2Pd]^{2+}$ $(BF_4^-)_2$ and *cis*-[$(dppeO)_2Pd]^{2+}$ $(BF_4^-)_2$. Alternatively, these cations can be generated by the reaction between the chloro complexes, [$(dppmO)_2PdCl_2$] and [$(dppeO)_2PdCl_2$], with Ag^+. Single crystal X-ray diffraction of *cis*-[$(dppeO)_2Pd]^{2+}$ $(BF_4^-)_2$ revealed distinct conformations (a puckered chair and a distorted sofa) for the two chelate rings situated around each Pd atom. A polymeric, poorly soluble material, $\{[(dpppO)_2Pd]^{2+} (BF_4^-)_2\}_n$, was isolated from the reaction between [$(dppO)_2PdCl_2$] and $AgNO_3$/$NaBF_4$, with both coordinated and free phosphoryl groups being present in the product (IR). In dilute solutions of the $\{[(dpppO)_2Pd]^{2+} (BF_4^-)_2\}_n$, depolymerization occurred, giving rise to the monomeric cationic chelate, *cis*-[$(dpppO)_2Pd]^{2+}$ $(BF_4^-)_2$. © 1998 Published by Elsevier Science Ltd. All rights reserved

Keywords: bis-phosphine mono-oxides; palladium; chelates.

The coordination chemistry of bis-phosphine monoxides (BPMOs) of the general formula $R_2P\text{-}X\text{-}P(O)R_2$, where X = any divalent group, e.g. $(CH_2)_n$, is still insufficiently explored. Although some BPMO complexes with various metals have been reported [1–15], very little is known about palladium derivatives of BPMOs. Only two BPMO complexes of Pd have been described in the literature. One of them, [$(dppeO)_2PdCl_2$] (dppeO = $Ph_2P(CH_2)_2P(O)Ph_2$), has been successfully used in catalyst [10]. However, no experimental procedure for the synthesis of this complex has been communicated. The other complex, [$(dppmO)_2PdCl_2$] (dppmO = $Ph_2PCH_2P(O)Ph_2$), has been reported [6,13] but not characterized by any spectral or structural means. It is worth noting that studying solution behavior of such complexes is important because of their intriguing catalytic activity [10] and potential use in synthesis [13]. In the present paper we report, for the first time, the detailed preparation, full characterization, and some chemical reactions of a series of palladium complexes containing monoxides of bis(diphenylphosphino)methane (dppmO), 1,2-bis(diphenylphosphino)ethane (dppeO), 1,3-bis(diphenylphosphino)propane (dpppO), 1,4-bis(diphenylphosphino)butane (dppbO), and 1,1′-bis(diphenylphosphino)ferrocene (dppfcO).

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RESULTS AND DISCUSSION

Synthesis of $[L_2PdCl_2]$ (L = dppmO, dppeO, dpppO, dppbO, *and* dppfcO)

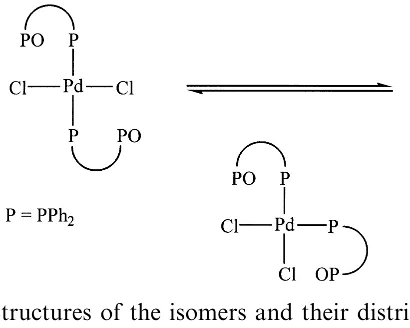
Adding methanolic $Na_2[PdCl_4]$ to a dichloromethane solution of a BPMO, L, (ca 2.1 equiv.) resulted in the formation of the corresponding $[L_2PdCl_2]$ in nearly quantitative yield (eqn (1)). The isolation and purification (if necessary) of the complexes is described in the Experimental Section.

$$Na_2[PdCl_4] + 2L \longrightarrow \underset{94\text{-}99\%}{[L_2PdCl_2]} + 2NaCl \qquad (1)$$

All five compounds are stable crystalline solids which can be stored at room temperature in air for months with no sign of decomposition. All of them are soluble in dichloromethane and chloroform, slightly soluble in benzene, and insoluble in ether and alkanes. The complexes of dppmO and dppeO are soluble in methanol, whereas those containing dpppO and dppbO are only sparingly soluble in this solvent. The dppfcO complex was found to be insoluble in alcohols.

Solution behavior of $[L_2PdCl_2]$ (L = dppmO, dppeO, dpppO, dppbO, *and* dppfcO)

Like many square-planar Pd^{II} compounds of the general formula $[L_2PdCl_2]$ [16], complexes with L = dppmO, dppeO, dpppO, and dppbO exist in solution as mixtures of *cis* and *trans* isomers (eqn (2), Table 1). At room temperature, the isomers seem to equilibrate much more readily (seconds) than their monodentate tertiary phosphine counterparts. This remarkably facile *cis–trans* isomerization is likely due to the presence of the phosphoryl groups, whose oxygen atoms are capable of intramolecularly coordinating to the metal center. Clearly, this effect is similar to the free-ligand catalysis in the *cis–trans* isomerization reactions of Pd(II) and Pt(II) complexes [16]. As described below, firm evidence was obtained for such weak and reversible Pd—O interactions.



(2)

Structures of the isomers and their distribution in various solvents were studied by ^1H and ^{31}P NMR techniques. To assure reliable ^{31}P NMR integration measurements, the spectra of the first few samples were run with delay times D_1 = 1, 3, and 5 s. Since no changes in the integration ratios were noticed, the rest of the spectra were obtained with D_1 = 1 s. As anticipated [16], the *cis*/*trans* ratio for the equilibrated mixtures increased with solvent polarity (see Table 1).

$[(dppmO)_2PdCl_2]$. No NMR spectral characterization of this complex has appeared in the literature. According to our ^{31}P NMR data (Table 1), $[(dppmO)_2PdCl_2]$ in benzene is exclusively *trans*, whereas in methanol it is mostly *cis*, with the *cis–trans* ratio being 95 : 5. The resonances of both isomers are clearly seen in the ^{31}P NMR spectra obtained in CH_2Cl_2 and $CHCl_3$, solvents of intermediate polarity in comparison with benzene and MeOH. The small ^{31}P–^{31}P coupling constants did not allow us to immediately assign the observed resonances to the corresponding isomers. However, the proper assignment of the lines is easily made by comparison of the spectra of $[(dppmO)_2PdCl_2]$ with those of its dppeO analogue (see Table 1 and text below). In line with this assignment of the ^{31}P resonances are the patterns observed in the ^1H NMR spectra of the dppmO complex. The ^1H NMR spectrum of the $[(dppmO)_2PdCl_2]$ in $CDCl_3$, where the complex is 90% *trans* according to the ^{31}P NMR data, contains a doublet of virtual triplets ($J_{P\text{–}H}$ = 11.4 Hz; $^2J_{P\text{–}H}+^4J_{P\text{–}H}$ = 7.4 Hz) at 3.9 ppm and a shoulder at 3.8 ppm due to the minor amount of the *cis* isomer. In methanol-d_4, the *cis* geometry prevails (ca 95%) and the resonance from the methylene protons appears at 4.3 ppm as a doublet of doublets with $J_{P\text{–}H}$ = 13.5 and 10.5 Hz. This pattern was observed only for the freshly prepared sample, since the acidic CH_2 protons of the complex were found to undergo facile H/D exchange with the CD_3OD solvent. As a result, the methylene resonance soon began to diminish in intensity while transforming into a complex multiplet, and eventually disappeared altogether after a few days. As the H/D exchange occurred, a number of isotopomers (30.3–30.9 ppm) of varying intensities were observed for the P—Pd resonance in the ^{31}P NMR spectrum, due to the molecules containing the CH_2, CHD, and CD_2 groups.

$[(dppeO)_2PdCl_2]$. The ^{31}P NMR spectrum of a solid formulated as $[(dppeO)_2PdCl_2]\cdot 2H_2O$ was reported [3] to exhibit one singlet at 34.45 ppm. In another paper [10], two resonances (20.14 and 33.09 ppm) were observed in the ^{31}P NMR spectrum of $[(dppeO)_2PdCl_2]$ in chloroform-*d*, but no information was provided on the multiplicity of these signals. We found that solutions of $[(dppeO)_2PdCl_2]$ in chloroform-*d* contain both the *cis* and *trans* isomers, as can be clearly seen from the ^{31}P NMR spectrum. The *trans* isomer exhibits a doublet of doublets at 19.9 ppm for the P atom coordinated to the metal with $^3J_{P\text{–}P}$ = 28.4 Hz and $^5J_{P\text{–}P}$ = 25.9 Hz, and a virtual triplet at 33.2 ppm for the phosphoryl group with $^3J_{P\text{–}P}+^5J_{P\text{–}P}$ = 54.0 Hz. This spectral pattern exhibiting the remarkable long-range coupling is perfectly consistent with the *trans* geometry. Two doublets at 30.4 and 32.8 ppm ($J_{P\text{–}P}$ = 56.1 Hz) were also found in the spectrum, obviously due to the *cis* isomer. Essentially the same pattern was observed for solutions of [(dppe-

Table 1. ^{31}P NMR data for palladium complexes of the type [L_2PdCl_2] in different solvents

L	Solvent	Geometry	^{31}P NMR, δ		*trans* : *cis*
			P—Pd	P═O	
dppmO	Benzene	*trans*	11.8	26.6	100 : 0
		cis	None	None	
	Chloroform	*trans*	11.8	24.4	90 : 10
		cis	22.5	24.9	
	Dichloromethane	*trans*	11.8	24.2	65 : 35
		cis	21.5	25.0	
	Methanol	*trans*	12.0	44.1	5 : 95
		cis	30.6	44.1	
dppeO	Benzene	*trans*	19.9	29.7	100 : 0
		cis	None	None	
	Chloroform	*trans*	19.9	33.2	85 : 15
		cis	30.4	32.8	
	Dichloromethane	*trans*	19.7	31.5	85 : 15
		cis	29.3	31.2	
	Methanol	*trans*	20.3	37.5	60 : 40
		cis	31.0	38.0	
dpppO	Benzene	*trans*	Insoluble		—
		cis	in benzene		
	Chloroform	*trans*	16.3	32.2	85 : 15
		cis	30.7	32.4	
	Dichloromethane	*trans*	16.2	30.8	80 : 20
		cis	28.5	30.7	
	Methanol	*trans*	16.9	37.6	55 : 45
		cis	30.7	38.0	
dppbO	Benzene	*trans*	16.8	28.4	100 : 0
		cis	None	None	
	Chloroform	*trans*	16.7	32.5	85 : 15
		cis	28.4	32.2	
	Dichloromethane	*trans*	16.7	30.9	80 : 20
		cis	27.6	30.9	
	Chloroform/methanol 1 : 10	*trans*	17.8	37.2	45 : 55
		cis	29.6	37.5	
dppfcO	Benzene	*trans*	15.2	25.5	—
		cis	None	None	
	Chloroform	*trans*	15.1	28.4	—
		cis	None	None	
	Dichloromethane	*trans*	15.3	27.4	—
		cis	None	None	
	Methanol	*trans*	Insoluble		—
		cis	in methanol		

O)$_2$PdCl$_2$] in dichloromethane. It is worth noting that the coupling constant measured for the *cis* isomer is close to the values of 47.3–48.1 Hz obtained for the free ligand [17]. As anticipated, only the *trans* isomer was found in benzene solutions of the complex, whereas both the *cis* and *trans* isomers were present when methanol was used as the solvent (Table 1). The portionwise addition of water to the methanol solution lead to a noticeable increase in the *cis–trans* ratio.

[(dpppO)$_2$PdCl$_2$] ***and*** **[(dppbO)$_2$PdCl$_2$].** As the number of methylene groups separating the P^{III} and P^{V} atoms increases, the spectral behavior of the corresponding Pd complexes becomes less distinct. In fact, the ^{31}P NMR spectral patterns for the [(dpppO)$_2$PdCl$_2$] and [(dppbO)$_2$PdCl$_2$] are very similar, displaying almost identical parameters (Table 1). The chemical shift values provide information for the easy and unambiguous assignment of the resonances. Because of poor solubility no ^{31}P NMR spectra were obtained for solutions of [(dpppO)$_2$PdCl$_2$] in benzene and [(dppO)$_2$PdCl$_2$] in methanol. However, both isomers of [(dppbO)$_2$PdCl$_2$] in approximately equal quantities were observed in a 1 : 10 chloroform–methanol solution of the complex.

[(dppfcO)$_2$PdCl$_2$]. Like the two preceding complexes, [(dppfcO)$_2$PdCl$_2$] is a new compound. The ^{31}P NMR spectra of this complex suggest that in benzene, chloroform, and dichloromethane it exists as only one isomer. In line with this is the ^{1}H NMR spectrum of the complex (see Experimental Section). Virtual insolubility of the [(dppfcO)$_2$PdCl$_2$] in polar media, methanol included, prevented its characterization by NMR in such solvents.

As clearly seen from the above data, for the complexes [L$_2$PdCl$_2$], where L = dppmO, dppeO, dpppO, and dppbO, the existence of both *cis* and *trans* isomers was reliably established by ^{31}P and ^{1}H NMR techniques. This was not the case, however, with the dppfcO complex, for which only one isomer was found to exist in various solvents. Due to the steric bulk of dppfcO ligand the *trans* geometry for the [(dppfcO)$_2$ PdCl$_2$] seemed to be more plausible. This conjecture was examined by X-ray analysis of the compound.

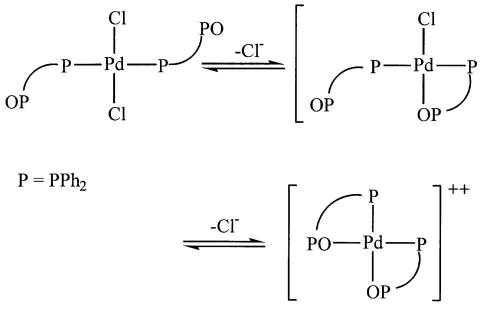
Single crystal X-ray diffraction study of [(dppfcO)$_2$ PdCl$_2$]

As a new compound [18], the dppfcO ligand has been characterized by elemental analysis and NMR spectral data [19]. Although we had attempted a single crystal X-ray diffraction study of dppfcO twice, crystallographic disorder did not allow us to obtain accurate molecular parameters of the ligand. X-ray quality crystals of [(dppfcO)$_2$PdCl$_2$] were obtained by diluting its saturated dichloromethane solution with benzene which caused slow precipitation of the complex as a 1 : 3 benzene solvate. Crystallographic parameters, data collection, and structure refinement summary are presented in Table 2. Table 3 lists the most important bond lengths and bond angles for the complex. As anticipated, the complex has a centrosymmetric *trans*-structure (Fig. 1) with almost ideal square-planar configuration around the Pd atom. One of the solvate benzene molecules occupies a general position in the crystal, whereas the second one lies on the center of symmetry. Both disubstituted ferrocene units possess slightly twisted conformation, often called "skew rings", which is dictated by steric requirements of diphenylphosphino and diphenylphosphoryl groups. The pseudo torsion angle P(1)–ring 1(center)–ring 2(center)–P(2) is equal to 133.7°, whereas at the ideal eclipsed conformation of the rings in ferrocene this angle is 144°. Both P(1) and P(2) slightly deviate from the mean planes of the corresponding 5-membered rings by 0.036 and 0.022 Å, respectively. The interplanar angle between the rings is 4.1°.

Although the dppfcO ligand is certainly bulkier than dppeO or PPh$_3$, the Pd—Cl and the Pd—P bond distances in [(dppfcO)$_2$PdCl$_2$] are only slightly longer than those of *trans*-[(dppeO)$_2$PdCl$_2$]^{11} and *trans*-[(Ph$_3$P)$_2$PdCl$_2$ [21,22]. Thus, the Pd—Cl bond length of 2.306 (1) Å was found in [(dppfcO)$_2$PdCl$_2$], whereas the values of 2.292(1) Å [11] and 2.281–2.296(1) [21,22] have been reported for the dppeO [11] and triphenylphosphine [21,22] counterparts. The Pd—P bond in the dppfcO complex (2.347(1) Å) is ca 0.01 and 0.02 Å longer than those in the *trans*-[L$_2$PdCl$_2$], where L = PPh$_3$ [21,22] and dppeO [11], respectively. This elongation may be due to the presence of the electron-rich, bulky ferrocene substituents on the coordinated phosphorus atoms. Among other features of the molecular geometry of the [(dppfcO)$_2$ PdCl$_2$]·3C$_6$H$_6$ it is worth noting the small difference between the C—P (phosphine) and C—P (phosphoryl) bond lengths of 1.804–1.837(5) and 1.795–1.815(5) Å, respectively. No shortened intramolecular or intermolecular contacts were found in the structure of the complex.

Cationic palladium bis-chelates, [(BPMO)$_2$Pd]$^{2+}$

The literature [10–12] data and the data described above provide no firm evidence for any coordination of the phosphoryl group oxygen atoms to the metal center in complexes of the general formula [(BPMO)$_2$PdCl$_2$] in the solid state or in solution. It was proposed [10] that such interactions between the phosphoryl oxygen atoms and the metal center might be responsible for the unique regioselectivity observed in the hydroxycarbonylation reaction of olefins catalyzed by [(dppeO)$_2$PdCl$_2$]. Higgins, Shaw, and Taylor [6] demonstrated that [(dppmO)$_2$PdCl$_2$] can be forced to lose the chloro ligands when treated with 2 equiv. of AgNO$_3$. According to their ^{31}P NMR data, the resulting cationic complex, [(dppmO)$_2$Pd]$^{2+}$, is a *cis*-chelate with both oxygens of the phosphoryl groups coordinated to the metal [6]. Because of the ability of Ag$^+$ to trap Cl$^-$ efficiently this result should not be regarded as evidence for the existence of equilibrium 3, either.



(3)

First evidence for equilibrium 3 was found in our work. Washing a dichloromethane solution of [(dppmO)$_2$PdCl$_2$] with a few portions of 40% aqueous NaBF$_4$ at room temperature lead to the quantitative (^{31}P NMR) formation of [(dppmO)$_2$Pd] (BF$_4$)$_2$ which was subsequently isolated in 74% yield. The ^{31}P NMR characterises of this complex were identical to those described for the cationic species obtained by the reaction between [(dppmO)$_2$PdCl$_2$] and AgNO$_3$ [6]. The synthesis of [(dppeO)$_2$Pd] (BF$_4$)$_2$ from the corresponding neutral dichloride and NaBF$_4$ was carried out in the same manner, furnishing the cationic complex in 96% isolated yield (eqn (4)).

Table 2. Crystallographic data for $[(dppfcO)_2PdCl_2]\cdot 3C_6H_6$ and $[(dppeO)_2Pd]\ (BF_4)_2$

	$[(dppfcO)_2PdCl_2]\cdot 3C_6H_6$	$[(dppeO)_2Pd]\ (BF_4)_2$
Empirical formula	$C_{86}H_{74}Cl_2Fe_2O_2P_4Pd$	$C_{52}H_{48}B_2F_8O_2P_4Pd$
Formula weight	1552.3	1108.8
Temperature (K)	153(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P=2_1/c$	$P2_1/c$
a (Å)	13.710(3)	19.187(8)
b (Å)	10.566(2)	13.549(5)
c (Å)	25.170(6)	20.125(8)
β (°)	95.29(2)	93.72(5)
Z	2	4
V (Å^3)	3630(1)	5221(4)
D_{calcd} (g/cm^3)	1.420	1.411
Absorption coefficient	0.85 min^{-1}	0.545 mm^{-1}
F(000)	1596	2256
Crystal size (mm)	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.2
Θ range (°)	2.09–25.9	4.0–21.9
Reflections collected	6728	5878
Independent reflections	6420 ($R_{int}=0.056$)	5668 ($R_{int}=0.121$)
Refinement method	Full-matrix L.S. on F^2	Full-matrix L.S. on F^2
Data/restrains/parameters	6389/0/439	5076/0/620
Goodness of fit on F^2	1.061	1.146
Final R indices ($I>2\sigma(I)$)	$R_1=0.051$; $wR_2=0.097$	$R_1=0.118$; $wR_2=0.263$

Table 3. Selected bond lengths (Å) and angles (°) in the crystal structure of $[(dppfcO)_2PdCl_2]\cdot 3C_6H_6$

Pd(1)—Cl(1)	2.306(1)	Pd(1)—P(1)	2.347(1)
Fe(1)—C(1)	2.044(5)	Fe(1)—C(2)	2.051(5)
Fe(1)—C(3)	2.060(5)	Fe(1)—C(4)	2.061(5)
Fe(1)—C(5)	2.033(5)	Fe(1)—C(6)	2.069(5)
Fe(1)—C(7)	2.046(5)	Fe(1)—C(8)	2.041(4)
Fe(1)—C(9)	2.027(5)	Fe(1)—C(10)	2.057(5)
P(1)—C(1)	1.804(5)	P(1)—C(11)	1.822(5)
P(1)—C(17)	1.837(5)	P(2)—O(1)	1.487(3)
P(2)—C(8)	1.795(5)	P(2)—C(23)	1.815(5)
P(2)—C(29)	1.807(5)	C(1)—C(2)	1.439(6)
C(1)—C(5)	1.446(7)	C(2)—C(3)	1.412(7)
C(3)—C(4)	1.419(7)	C(4)—C(5)	1.426(7)
C(6)—C(7)	1.431(7)	C(6)—C(10)	1.411(7)
C(7)—C(8)	1.443(7)	C(8)—C(9)	1.431(6)
C(9)—C(10)	1.418(6)		
Cl(1)—Pd(1)—P(1)	93.17(5)	Cl(1)—Pd(1)—P(1)	86.83(5)
C(1)—P(1)—C(11)	105.8(2)	C(1)—P(1)—C(17)	101.2(2)
C(11)—P(1)—C(17)	103.5(2)	C(1)—P(1)—Pd(1)	115.8(2)
C(11)—P(1)—Pd(1)	106.3(2)	C(17)—P(1)—Pd(1)	122.5(2)
O(1)—P(2)—C(8)	116.0(2)	O(1)—P(2)—C(29)	113.2(2)
C(8)—P(2)—C(29)	103.9(2)	O(1)—P(2)—C(23)	110.8(2)
C(8)—P(2)—C(23)	104.5(2)	C(29)—P(2)—C(23)	107.7(2)
C(2)—C(1)—C(5)	107.3(4)	C(2)—C(1)—P(1)	126.2(4)
C(5)—C(1)—P(1)	126.4(4)	C(3)—C(2)—C(1)	107.6(4)
C(2)—C(3)—C(4)	109.4(4)	C(3)—C(4)—C(5)	107.7(4)
C(4)—C(5)—C(1)	107.8(4)	C(10)—C(6)—C(7)	107.9(4)
C(6)—C(7)—C(8)	107.7(4)	C(9)—C(8)—C(7)	107.3(4)
C(9)—C(8)—P(2)	126.9(4)	C(7)—C(8)—P(2)	125.8(4)
C(10)—C(9)—C(8)	108.0(4)	C(6)—C(10)—C(9)	109.1(4)

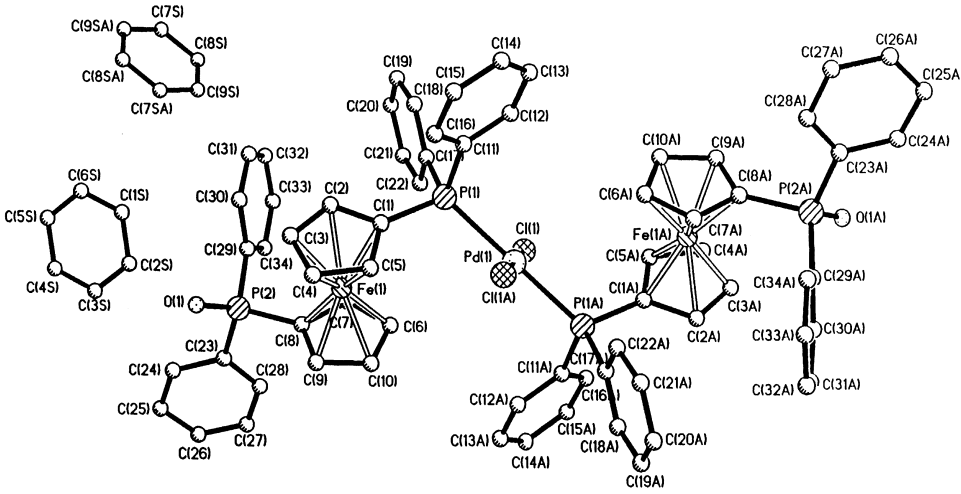
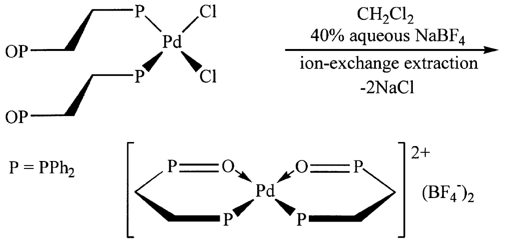


Fig. 1. Molecular structure of *trans*-[$(dppfcO)_2PdCl_2$] with adopted numbering scheme. Hydrogen atoms are omitted for clarity.



(4)

Both tetrafluoroborates, [$(dppeO)_2Pd$] $(BF_4)_2$ and [$(dppmO)_2Pd$] $(BF_4)_2$, are air-stable crystalline compounds soluble in dichloromethane and acetone, slightly soluble in chloroform, but insoluble in water, ether, and hydrocarbon solvents. Taking into account the poor affinity of the tetrafluoroborate anion for palladium(II) [23], it is reasonable to conclude that an intramolecular replacement of the chloro ligands by an oxygen of the coordinated BPMO takes place, followed by Cl^-/BF_4^- ion exchange.

The structure of the cationic bis-chelate, [$(dppeO)_2Pd$] $(BF_4)_2$, was established by a single crystal X-ray diffraction study. Selected crystallographic data obtained, including experimental and structure refinement details, are given in Table 2. Some molecular geometry parameters are summarized in Table 4 and a general view of the dication is presented in Fig. 2. Although crystal disorder of the BF_4^- anions and the single crystal's insufficient quality lowered accuracy of the structural results, the *cis* structure of the cation, [$(dppeO)_2Pd$]$^{2+}$, in the solid state was established beyond any doubt. The Pd atom and the four atoms constituting the first coordination sphere (P(1), P(2), O(1), and O(2)) are coplanar within 0.018 Å. However, a noticeable distortion from the ideal square-planar configuration is observed in the crystal structure, the O—Pd—O and P—Pd—P bond angles being 84.4(4)° and 97.3(2)°, respectively. It is remarkable that the two six-membered metallacycles appear to be in different conformations in the crystal state. For the PdP(1)C(49,50)P(2)O(1) ring a puckered chair conformation was established; the metal, oxygen, and both carbon atoms were coplanar within 0.011 Å, whereas P(1) and P(2) deviated from the plane by +0.84 and −0.70 Å, respectively. A distorted sofa conformation was observed for the other ring, PdP(3)C(51,52)P(4)O(2), with C(51) deviating by 0.77 Å from the mean plane formed by the other five atoms which are coplanar within 0.06 Å. It is worth noting the significant difference in the Pd—O—P bond angles, 124.1(6)° for Pd—O(1)—P(2) and 143.9(6)° for Pd—O(2)—P(4). Interestingly, the Pd—O bond distances (2.088(12) and 2.119(10) Å) are either comparable with or substantially shorter than the values reported for the Pd—O bond lengths in various palladium complexes containing hydroxo (2.07–2.28 Å) [24] and carboxylato (2.12–2.17 Å) [25] ligands. This suggests that the Pd—O coordination bonds are of considerable strength, despite the fact that they are *trans* to phosphine ligand whose *trans*-influence is normally significant. The Pd—P bond distances (2.240(4) and 2.247(5) Å) in the chelate are similar to those in *cis*-[$(dmpmO)_2PdCl_2$] (2.254(1) and 2.248(1) Å) [12] but shorter by 0.08–0.09 Å than the Pd—P bond length in *trans*-[$(dppeO)_2PdCl_2$] (2.327(1) Å) [11]. The Pd—P and Pd—O bond lengths measured suggest that the dication [$(dppeO)_2Pd$]$^{2+}$ is remarkably stable.

Among other structural characteristics of the chelate are shortened (3.27–3.28 Å) intramolecular C···C contacts due to the stacking interaction between the almost parallel C(1)—C(6) and C(31)—C(36) phenyl rings. Also, strong distortions are observed in the tetrahedral environment of P(1) and P(3), due to steric hindrance. Thus, Pd—P(1)—C(1) and Pd—P(3)—

Table 4. Selected bond lengths (Å) and angles (°) in the crystal structure of [(dppeO)$_2$Pd] (BF$_4^-$)$_2$

Pd—O(2)	2.088(12)	Pd—O(1)	2.119(10)
Pd—P(3)	2.240(4)	Pd—P(1)	2.247(5)
P(1)—C(7)	1.79(2)	P(1)—C(1)	1.79(2)
P(1)—C(49)	1.86(2)	P(2)—O(1)	1.509(11)
P(2)—C(50)	1.77(2)	P(2)—C(13)	1.79(2)
P(2)—C(19)	1.83(2)	P(3)—C(51)	1.80(2)
P(3)—C(25)	1.81(2)	P(3)—C(31)	1.86(2)
P(4)—O(2)	1.537(12)	P(4)—C(37)	1.77(2)
P(4)—C(43)	1.80(2)	P(4)—C(52)	1.81(2)
C(49)—C(50)	1.53(2)	C(51)—C(52)	1.55(3)
O(2)—Pd—O(1)	84.4(4)	O(2)—Pd—P(3)	88.8(3)
O(1)—Pd—P(3)	173.1(3)	O(2)—Pd—P(1)	173.8(3)
O(1)—Pd—P(1)	89.6(3)	P(3)—Pd—P(1)	97.3(2)
C(7)—P(1)—C(1)	109.1(8)	C(7)—P(1)—C(49)	105.7(8)
C(1)—P(1)—C(49)	98.1(8)	C(7)—P(1)—Pd	108.9(6)
C(1)—P(1)—Pd	122.7(6)	C(49)—P(1)—Pd	110.9(6)
O(1)—P(2)—C(50)	112.1(7)	O(1)—P(2)—C(13)	110.6(7)
C(50)—P(2)—C(13)	108.2(9)	O(1)—P(2)—C(19)	109.3(7)
C(50)—P(2)—C(19)	109.4(9)	C(13)—P(2)—C(19)	107.1(8)
C(51)—P(3)—C(25)	105.9(9)	C(51)—P(3)—C(31)	103.5(9)
C(25)—P(3)—C(31)	106.2(9)	C(51)—P(3)—Pd	109.6(6)
C(25)—P(3)—Pd	110.5(6)	C(31)—P(3)—Pd	120.1(7)
O(2)—P(4)—C(37)	110.2(8)	O(2)—P(4)—C(43)	108.0(7)
C(37)—P(4)—C(43)	107.7(8)	O(2)—P(4)—C(52)	111.6(8)
C(37)—P(4)—C(52)	108.2(8)	C(43)—P(4)—C(52)	111.2(8)
P(2)—O(1)—Pd	124.1(6)	P(4)—O(2)—Pd	143.9(6)
C(50)—C(49)—P(1)	118.1(12)	C(49)—C(50)—P(2)	112.9(12)
C(52)—C(51)—P(3)	118.0(13)	C(51)—C(52)—P(4)	112.6(13)

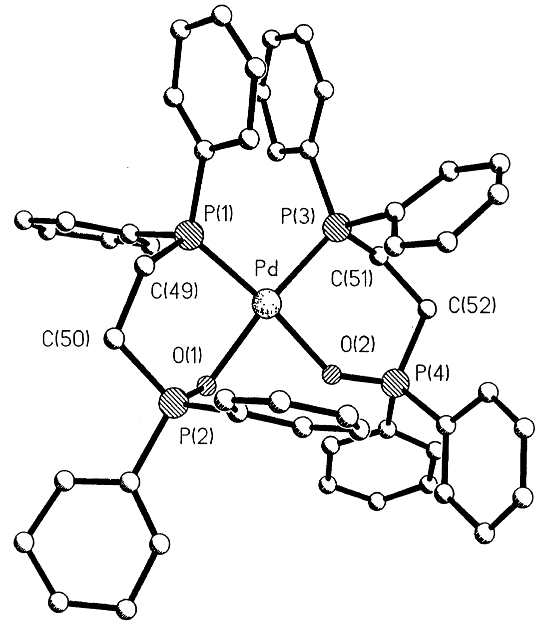


Fig. 2. Molecular structure of *cis*-[(dppeO)$_2$Pd]$^{2+}$ with adopted numbering scheme for the metallacycle atoms. Hydrogen atoms are omitted for clarity.

C(31) bond angles are increased to 122.7(6) and 120.1(7) degrees, whereas adjacent C(1)—P(1)—C(49) and C(25)—P(3)—C(31) bond angles are diminished to 98.1(8) and 103.5(8) degrees, respectively. On the contrary, P(2) and P(4) of the phosphoryl groups form tetrahedral bond angles of the almost ideal value, varying in the range of 107.1(8) to 112.1(7)°.

According to the room temperature ^{31}P NMR data, the [(dppeO)$_2$Pd] (BF$_4$)$_2$ remains *cis* in dichloromethane or methanol solutions, with both chelate rings undergoing conformational changes which are fast on the NMR time scale. Two sharp doublets of doublets at 36.5 and 48.2 ppm with $J_{P\text{–}P} = 10$ and 3 Hz were observed in the ^{31}P NMR spectrum of [(dppeO)$_2$Pd]$^{2+}$ in aqueous methanol, indicating that the geometry around the metal center is *cis*.

The dpppO counterpart of [(dppeO)$_2$Pd]$^{2+}$ and [(dppmO)$_2$Pd]$^{2+}$ was prepared by the reaction between [(dpppO)$_2$PdCl$_2$] and AgNO$_3$ in dichloromethane/water, followed by the treatment of the reaction mixture with 40% NaBF$_4$ in water. Two broadened singlet resonances were observed in the ^{31}P NMR spectrum of the organic phase, with the chemical shifts of 30 ($\Delta\nu_{1/2} = 40$ Hz) and 55 ($\Delta\nu_{1/2} = 100$ Hz) ppm being indicative of a *P*,*O*-coordination mode for the dpppO ligands, as expected.

However, once precipitated by adding ether to the organic layer of the reaction mixture, the $[(dpppO)_2Pd]$ $(BF_4)_2$ appeared to be very poorly soluble in common organic solvents, dichloromethane and acetone included. In spite of this remarkably low solubility of the isolated crystalline compound, its ^{31}P NMR spectrum in CH_2Cl_2 was measured, exhibiting two *sharp doublets* ($J_{P-P} = 7$ Hz) with virtually the same chemical shifts (30.4 and 55.6 ppm) as those observed before the complex was isolated. It is conceivable that in the concentrated solution formed upon reacting $[(dpppO)_2PdCl_2]$ with Ag^+ and then BF_4^-, the structure of the species obtained is somewhat different from that of the complex which has been isolated and consequently redissolved. The identical ^{31}P NMR chemical shifts suggest that both the P and O centers participate in coordinative interactions with the metal [6,14]. On the other hand, intermolecular Pd—O interactions of the type Pd—P—CH_2—CH_2—CH_2—PO—Pd might be pictured for the concentrated solution of the complex, resulting in the formation of oligometric/polymeric chains (Fig. 3). Facile ligand exchange in the oligomer is likely to be responsible for the line broadening in the ^{31}P NMR spectrum of the concentrated solution. It is noteworthy that the PO—Pd resonance was noticeably broader than the P—Pd signal, suggesting that the exchange processes involving the oxygen centers may be faster than those resulting in the cleavage and formation of the P—Pd bonds. In contrast, dilute solutions of the isolated complex contain the monomeric cation, $[(dpppO)_2Pd]^{2+}$, as indicated by the ^{31}P NMR data (see above).

Clearly, intramolecular vs intermolecular O—Pd coordination modes in the $[(dpppO)_2Pd]^{2+}$ system are strongly influenced by concentration effects which were not observed for the $[(dppmO)_2Pd]^{2+}$ and $[(dppeO)_2]^{2+}$ complexes. Furthermore, in the solid state both $[(dppmO)_2Pd]^{2+}$ and $[(dppeO)_2Pd]^{2+}$ are monomeric chelates, according to the solubility, X-ray, and also IR data. The IR spectra (KBr) of their tetrafluoroborate salts exhibited strong bands at 1102–1129 cm^{-1} due to the coordinated phosphoryl oxygens and no peaks in the range of 1180–1200 cm^{-1} where "free" phosphoryl P=O bonds normally absorb [6,14,15]. At the same time, two groups of bands were observed in the IR spectrum of the solid $[(dpppO)_2Pd]$ $(BF_4)_2$, at 1123–1105 cm^{-1} and 1195–1175 cm^{-1}. The former was obviously due to PO groups coordinated with the metal, whereas the latter pointed to the presence of free phosphoryls in the sample. It is clear that in order to contain both types of the phosphoryl groups while retaining square-planar geometry at the Pd centers, the solid $[(dpppO)_2Pd]$ $(BF_4)_2$ must possess polymeric or macrocyclic structure and should rather be formulated as $\{[(dpppO)_2Pd]\ (BF_4)_2\}_n$. This is consistent with the ^{31}P NMR data obtained for the concentrated solution of oligomeric $[(dpppO)_2Pd]$ $(BF_4)_2$, prepared upon the exhaustive dechlorination of the $[(dpppO)_2PdCl_2]$ with Ag^+ (see above). The remarkable difference in the structure and behaviour of the three cationic complexes is definitely due to the substantial decrease in the magnitude of the chelate effect when going from the 5- and 6-membered metallacyles ($[(dppmO)_2Pd]^{2+}$ and $[(dppeO)_2Pd]^{2+}$, respectively) to the analogous, but much less stable, 7-membered rings ($[(dpppO)_2Pd]^{2+}$ [26]. For the same reason, the "silverless" synthesis of $[(dpppO)_2Pd]$ $(BF_4)_2$ from the corresponding dichloride requires many more ion-exchange extractions with aqueous $NaBF_4$, as compared with the above described similar preparation of $[(dppmO)_2Pd]$ $(BF_4)_2$ and $[(dppeO)_2Pd]$ $(BF_4)_2$. For instance, after a dichloromethane solution of $[(dpppO)_2PdCl_2]$ had been thoroughly washed with 40% aqueous $NaBF_4$ 12 times, the conversion to $[(dpppO)_2Pd]$ $(BF_4)_2$ was still incomplete (^{31}P NMR).

Attempted syntheses of $[(dppfcO)_2Pd]^{2+}$ and $[(dppbO)_2Pd]^{2+}$ from the corresponding dichloro complexes and aqueous $NaBF_4$ or $AgNO_3/NaBF_4$ were unsuccessful, and a complex mixture of unidentified products was obtained in both cases (^{31}P NMR). The metallacycles formed by the dppbO and dppfcO ligands are apparently too large in size to be

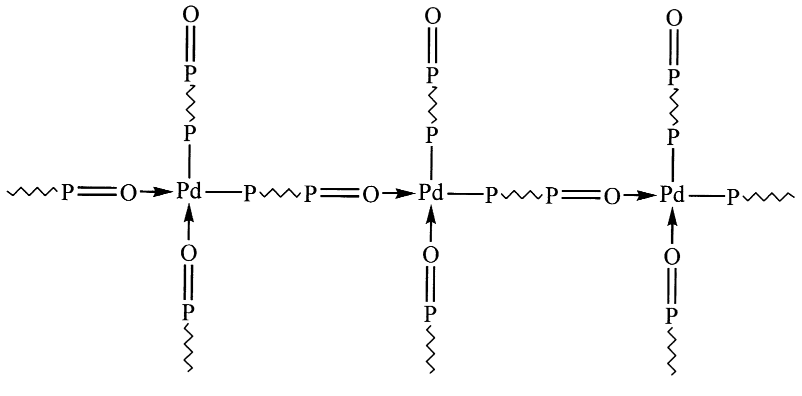


Fig. 3. Proposed structure for the $\{[(dpppO)_2Pd]^{2+}\}_n$ oligomer containing both coordinated and free phosphoryl groups.

sufficiently stable for successful isolation and characterization of the corresponding Pd chelates. Most likely, the generated compounds exist as mixtures of oligomeric species.

EXPERIMENTAL

NMR spectra were recorded on a Varian VXR-200 spectrometer. Chemical shifts are reported relative to TMS (^1H) and 85% H_3PO_4 (^{31}P). The BPMO ligands may be synthesized by the procedures reported in the literature [1b,3,6,27]. The phosphorus ligands, dppmO, dppeO, dpppO, dppbO, and dppfcO used in this work were prepared by the selective catalytic mono-oxidation of the corresponding bis-phosphines [18]. All other chemicals were purchased from Organometallics, Aldrich, and Strem and used as received. The synthesis, isolation, and purification of all complexes were conducted in air.

[(dppmO)$_2$PdCl$_2$]

A solution of $Na_2[PdCl_4]$ obtained by dissolving $PdCl_2$ (265 mg; 1.50 mmol) and NaCl (180 mg; 3.10 mmol) in hot methanol (20 ml) was added dropwise to a vigorously stirred solution of dppmO (1.459 g; 3.65 mmol) in CH_2Cl_2 (20 ml). The mixture was taken to dryness (rotary evaporation) and the residue was extracted with CH_2Cl_2 (30 ml). The dichloromethane solution was filtered, reduced in volume to ca 15 ml, diluted with ether (portionwise, 4 × 15 ml), and left at $-15°C$ overnight. The yellow precipitate was separated, washed with ether, and dried under vacuum. The yield of [(dppmO)$_2$PdCl$_2$] was 1.460 g (99%). The ^{31}P and ^1H NMR spectra of this complex in both chloroform-*d* and methanol-d_4 are described in the text and Table 1. In the ^1H NMR spectra, aromatic protons of the complex resonate as multiplets at 6.9–8.0 ppm and 7.0—8.0 ppm in $CDCl_3$ and CD_3OD, respectively.

[(dppeO)$_2$PdCl$_2$]

A solution of $Na_2[PdCl_4]$ obtained by dissolving $PdCl_2$ (498 mg; 2.81 mmol) and NaCl (361 mg; 6.22 mmol) in warm methanol (50 ml) was added dropwise to a vigorously stirred solution of dppeO (2.614 g; 6.23 mmol) in CH_2Cl_2 (30 ml). The mixture was evaporated to dryness and the residue was extracted with CH_2Cl_2. The combined dichloromethane extracts were filtered, reduced in volume, and treated with ether. The yellow precipitate was separated, washed with ether, and dried under vacuum. The yield of [(dppeO)$_2$PdCl$_2$] was 2.677 g (95%). ^1H NMR ($CDCl_3$), δ: 2.6 (m, 8H, CH_2); 7.0–7.9 (m, 40H, C_6H_5).

[(dpppO)$_2$PdCl$_2$]

A solution of $Na_2[PdCl_4]$ obtained by dissolving $PdCl_2$ (520 mg; 2.94 mmol) and NaCl (385 mg; 6.64 mmol) in hot methanol (40 ml) was added dropwise to a vigorously stirred solution of dpppO (2.779 g; 6.49 mmol) in CH_2Cl_2 (30 ml). The mixture was taken to dryness (rotary evaporation) and the residue was extracted with CH_2Cl_2 (200 ml; the complex is only moderately soluble in dichloromethane [28]). The combined dichloromethane extracts were filtered, reduced in volume, and treated with ether to give a yellow microcrystalline solid which was separated, washed with ether, and dried under vacuum. The yield of [(dpppO)$_2$PdCl$_2$]·H_2O was 3.057 g (98%). Anal: Calcd for $C_{54}H_{54}Cl_2O_3P_4Pd(C_{54}H_{52}Cl_2O_2P_4Pd \cdot H_2O)$: C, 61.6; H, 5.2. Found: C, 61.7; H, 4.9. ^1H NMR ($CDCl_3$), δ: 1.8 (m, 4H, CCH_2C); 2.4 (m, 4H, CH_2PPd); 2.6 (m, 4H, CH_2PO); 7.0–7.8 (m, 40H, C_6H_5).

[(dppbO)$_2$PdCl$_2$]

A solution obtained by dissolving $PdCl_2$ (213 mg; 1.20 mmol) and NaCl (130 mg; 2.24 mmol) in hot methanol (50 ml) was added dropwise to a vigorously stirred solution of dppbO (1.216 g; 2.75 mmol) in CH_2Cl_2 (30 ml) [28]. Evaporation of the mixture gave a yellow oil which was dissolved in CH_2Cl_2 and the resulting solution was filtered, reduced in volume to ca 5 ml, and treated with ether (20 ml) to precipitate the complex. The crude solid product thus obtained (contaminated with ca 5% dppbO; ^{31}P NMR) was dissolved in dichloromethane (10 ml), the mixture was diluted with benzene (ca 30 ml), and the resulting yellow solution was slowly reduced in volume to ca 10 ml (rotary evaporation at room temperature). Upon standing for a few hours, yellow crystals of analytically and spectroscopically pure [(dppbO)$_2$PdCl$_2$]·2C_6H_6 precipitated, which was separated, washed with small quantities of benzene, and dried. The yield was 1.443 g (98%). Anal: Calcd for $C_{68}H_{68}Cl_2O_2P_4Pd$ ($C_{56}H_{56}Cl_2O_2P_4Pd \cdot 2C_6H_6$): C, 67.0; H, 5.6. Found: C, 67.4; H, 5.7. ^1H NMR ($CDCl_3$), δ: 1.6 (m, 8H, $C(CH_2)_2C$); 2.2 (m, 4H, CH_2PPd); 2.4 (m, 4H, CH_2PO); 7.1–7.8 (m, 40H + 12H, $C_6H_5 + C_6H_6$); an intense singlet at 7.3 ppm was observed due to the benzene present in the solid.

trans-[(dppfcO)$_2$PdCl$_2$]

A mixture of $PdCl_2$ (207 mg; 1.17 mmol) and NaCl (139 mg; 2.39 mmol) was stirred with methanol (40 ml) at ca 50°C until the solids dissolved. The resulting brown solution of $Na_2[PdCl_4]$ was added dropwise to a stirring solution of dppfoO [18,19] (1.477 g; 2.6 mmol) in CH_2Cl_2 (20 ml). After the dark red mixture was evaporated to dryness the residue was extracted with CH_2Cl_2 (first 20 ml, then 4 × 5 ml), and the combined extracts were filtered, reduced in volume to ca 10 ml, and diluted with ether (portionwise, 4 × 5 ml). The orange-red crystals were separated, washed with ether, and dried. The yield of the *trans*-[(dppfcO)$_2$ PdCl$_2$]·CH$_2$Cl$_2$ was 1.544 g (94%). Anal: Calcd for $C_{69}H_{58}Cl_4Fe_2O_2P_4Pd$ ($C_{68}H_{56}Cl_2Fe_2O_2P_4Pd \cdot CH_2Cl_2$): C, 59.1; H, 4.2. Found: C, 59.6; H, 4.2. ^{1}H NMR (CDCl$_3$), δ: 4.3 (s, 2H, C_5H_4); 4.4 (s, 2H, C_5H_4); 4.6 (s, 2H, C_5H_4); 4.9 (s, 2H, C_5H_4); 7.2–7.8 (m, 40H, C_6H_5).

cis-[(dppmO)$_2$Pd] (BF$_4$)$_2$

A solution of [(dppmO)$_2$PdCl$_2$] (202 mg; 0.21 mmol) in CH_2Cl_2 (5 ml) was vigorously stirred with 40% aqueous $NaBF_4$ (10 ml) for 15 min. The aqueous layer was separated by a pipette, another 10 ml of 40% $NaBF_4$ were added to the dichloromethane solution, and the mixture was stirred for another 15 min. This procedure was repeated five times. The organic phase was separated, filtered through cotton, and evaporated. The solid residue was recrystallized twice from CH_2Cl_2/ether to give 166 mg (74%) of white *cis*-[(dppmO)$_2$Pd] (BF$_4$)·H$_2$O. Anal: Calcd for $C_{50}H_{46}B_2F_8O_3P_4Pd$ ($C_{50}H_{44}B_2F_8O_2P_4Pd \cdot H_2O$): C, 54.7; H, 4.2. Found: C, 54.9; H, 4.2. ^{1}H NMR (acetone-d_6), δ: 4.8 (dd, 4H, $J_{P\text{–}H}$ = 9.8 and 13.8 Hz, CH$_2$); 7.2–8.0 (m, 40H, C_6H_5). ^{31}P NMR (acetone-d_6), δ: 36.2 (d, 2P, $J_{P\text{–}P}$ = 5.3 Hz, PPd); 59.7 (d, 2P, $J_{P\text{–}P}$ = 5.3 Hz, POPd). IR (KBr), cm^{-1}: 1129, 1102 (PO).

cis-[(dppeO)$_2$Pd] (BF$_4$)$_2$

A solution of [(dppeO)$_2$PdCl$_2$] (204 mg; 0.21 mmol) in CH_2Cl_2 (5 ml) was vigorously stirred with 40% aqueous $NaBF_4$ (10 ml) for 15 min. The aqueous layer was separated by a pipette, another 10 ml of 40% $NaBF_4$, were added to the dichloromethane solution, and the mixture was stirred for another 15 min. This procedure was repeated five times. The organic phase was separated, filtered through cotton, and evaporated. The solid residue was recrystallized from CH_2Cl_2/ether (twice) and dried under vacuum to give 215 mg (96%) of pale-yellow *cis*-[(dppeO)$_2$Pd] (BF$_4$)$_2$. Anal: Calcd for $C_{52}H_{48}B_2F_8O_2P_4Pd$: C, 56.3; H, 4.4. Found: C, 56.1; H, 4.3. ^{1}H NMR (acetone-d_6), δ: 3.2 (m, 8H, CH$_2$); 7.2–8.2 (m, 40H, C_6H_5). ^{31}P NMR (MeOH), δ: 36.5 (dd, 2P, $J_{P\text{–}P}$ = 10.0 Hz and 3.0 Hz, PPd); 48.2 (dd, 2P, $J_{P\text{–}P}$ = 10.0 Hz and 3.0 Hz, POPd). ^{31}P NMR (acetone-d_6), δ: 37.8 (dd, 2P, $J_{P\text{–}P}$ = 8.5 Hz and 4.6 Hz, PPd); 47.9 (dd, 2P, $J_{P\text{–}P}$ = 8.5 H and 4.6 Hz, POPd). IR (KBr), cm^{-1}: 1125, 1103 (PO).

[(dpppO)$_2$Pd] (BF$_4$)$_2$

A solution of $AgNO_3$ (0.43 g; 2.5 mmol) in water (2 ml) was added to a vigorously stirred suspension of [(dpppO)$_2$PdCl$_2$] (1.00 g; 0.97 mmol) in CH_2Cl_2 (8 ml), causing an immediate precipitation of AgCl. Water (5 ml) and CH_2Cl_2 (7 ml) were added, and the mixture was stirred for another 5 min. The organic phase was separated, and the aqueous suspension of AgCl was washed with CH_2Cl_2 several times. The combined dichloromethane solutions were vigorously stirred with 40% $NaBF_4$ (2 × 20 ml, 30 min each), separated, filtered, reduced in volume, and treated with ether. The light-yellow precipitate was washed with ether and dried under vacuum. The yield of the cationic complex was 0.84 g (76%). Anal: Calcd for $C_{54}H_{52}B_2F_8O_2P_4Pd$: C, 57.0; H, 4.6. Found: C, 56.5; H, 4.6. ^{1}H NMR (acetone-d_6), δ: 2.8 (m, 4H, CH$_2$); 3.0 (m, 4H, CH$_2$); 3.2 (m, 4H, CH$_2$); 7.1–7.9 (m, 40H, C_6H_5). ^{31}P NMR (CH$_2$Cl$_2$), δ: 30.4 (d, 2P, $J_{P\text{–}P}$ = 7.0 Hz, PPd); 55.6 (d, 2P, $J_{P\text{–}P}$ = 7.0 Hz, POPd). IR (KBr), cm^{-1}: 1195, 1188, 1175, 1123, 1105 (PO).

X-ray diffraction studies

X-ray diffraction data were obtained with a Siemens P3/PC four-circle diffractometer with Mo–K$_\alpha$-radiation and a graphite monochromator ($\theta/2\theta$ scan method) at 153 K and room temperature for single crystals of *trans*-[(dppfcO)$_2$PdCl$_2$] and *cis*-[(dppeO)$_2$ Pd] (BF$_4$)$_2$, respectively. The diffraction quality of all examined crystal samples of the cationic complex was rather poor, displaying broad reflection peaks and irregular twinning. As all attempts to cool the samples led to an increase in the diffraction profiles, data collection was performed at room temperature. An empirical absorption correction was applied for the *trans*-[(dppfcO)$_2$PdCl$_2$], but not for the [(dppeO)$_2$Pd] (BF$_4$)$_2$ because of insufficient diffraction data quality. The structures were solved by direct methods and refined by the least squares techniques in the anisotropic (isotropic for disordered BF_4^- anions) approximation. All H atoms were placed in geometrically calculated positions and included into refinement using a riding motion model. A PC SHELX PLUS program package was used for all calculations. Rotational disorder of the BF_4^- anions was detected in the difference Fourier maps for the cationic chelate, and therefore additional orientations of these anions were taken into account in the final refinement.

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Supporting information available—Full details of the X-ray diffraction studies of *trans*-[(dppfcO)$_2$PdCl$_2$] and *cis*-[(dppeO)$_2$Pd] (BF$_4$)$_2$, including crystallographic data, data collection, structure solution and refinement, ORTEP drawings, full tables of non-hydrogen atom coordinates with isotropic displacement parameters, full tables of bond lengths and bond angles, hydrogen atom coordinates, tables of anisotropic displacement parameters (22 pages), and two X-ray structure files in the CIF format. Ordering information is given on any current masthead page.

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19. (a) Spectral and analytical data for dppfcO: ^{1}H NMR (CDCl$_3$, 20°C), δ: 4.0 (m, 2H, Cp); 4.2 (m, 2H, Cp); 4.4 (m, 2H, Cp); 4.6 (m, 2H, Cp); 7.1–7.7 (m, 20H, Ph). ^{13}C NMR (CDCl$_3$, 20°C), δ: 72.9 (s, C$_5$H$_4$); 73.0 (s, C$_5$H$_4$); 73.1 (s, C$_5$H$_4$); 73.2 (s, C$_5$H$_4$); 73.3 (d, $J_{\text{P–C}} = 1.7$ Hz, C$_5$H$_4$); 73.5 (d, $J_{\text{P–C}} = 1.7$ Hz, C$_5$H$_4$); 128.2 (d, $J_{\text{P–C}} = 11.0$ Hz, m-C$_6$H$_5$PCp); 128.4 (d, $J_{\text{P–C}} = 16.7$ Hz, m-C$_6$H$_5$P(O)Cp); 131.3 (s, p-C$_6$H$_5$PCp); 131.4 (s, p-C$_6$H$_5$P(O)Cp); 131.4 (d, $J_{\text{P–C}} = 9.7$ Hz, o-C$_6$H$_5$PCp); 133.4 (d, $J_{\text{P–C}} = 19.7$ Hz, o-C$_6$H$_5$P(O)Cp); 134.5 (d, $J_{\text{P–C}} = 105.6$ Hz, q-C$_6$H$_5$PCp); 138.8 (d, $J_{\text{P–C}} = 10.8$ Hz, q-C$_6$H$_5$P(O)Cp). ^{31}P NMR (CDCl$_3$, 20°C), δ: -16.7 (s, 1P, CpPPh$_2$); 28.5 (s, 1P, CpP(O)Ph$_2$). Anal: Calcd for $C_{68}H_{58}Fe_2O_3P_4$ ($C_{34}H_{28}FeOP_2 \cdot 0.5H_2O$): C, 70.5; H, 5.0. Found: C, 70.7; H, 5.0; (b) Although dppfcO itself is a new compound, its rhenium [19c] and tungsten [19d] complexes have been reported and structurally characterized. The Re and W complexes were obtained by the oxidation of the corresponding dppfc metal derivatives with H$_2$O$_2$; (c) Hor, T. S. A., Chan, H. S. O., Tan, K.-L., Phang, L.-T., Yan, Y. K., Liu, L.-K. and Wen, L.-K., *Polyhedron*, 1991, **10,** 2437; (d) Hsu, S. C. N., Yeh, W.-Y. and Chiang, M. Y., *J. Organomet. Chem.*, 1995, **492,** 121.
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28. It is worth noting that the solubility of dpppO in CH_2Cl_2 and $CHCl_3$ is much higher than that of dppbO, whereas the solubility of $[(dpppO)_2PdCl_2]$ in these solvents is noticeably lower than that of $[(dppbO)_2PdCl_2]$.