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Bis-phosphine monoxide platinum(II) and palladium(II) cationic complexes as Lewis acid catalysts in Diels–Alder and sulfoxidation reactions

Paolo Sgarbossa [a], Erika Pizzo [a], Alessandro Scarso [b], Silvia Mazzega Sbovata [a],
Rino A. Michelin [a,*], Mirto Mozzon [a], Giorgio Strukul [b,*], Franco Benetollo [c]

[a] *Dipartimento di Processi Chimici, dell'Ingegneria, Università di Padova, Via F. Marzolo 9, 35131 Padua, Italy*
[b] *Dipartimento di Chimica, Università Cà Foscari di Venezia, Dorsoduro 2137, 30123 Venice, Italy*
[c] *ICIS – C.N.R., Corso Stati Uniti 4, 35127 Padua, Italy*

Abstract

A series of bis-phosphine monoxide (BPMO) palladium(II) and platinum(II) cationic complexes of the type $[M(BPMO\text{-}\kappa^2\text{-}P,O)_2][X]_2$ (M = Pd, Pt; BPMO = $Ph_2P–(CH_2)_n–P(O)Ph_2$ with $n = 1$ (dppmO), 2 (dppeO), 3 (dpppO); X = BF_4, TfO) were prepared from the corresponding chlorides $[MCl_2(BPMO\text{-}\kappa^1\text{-}P)_2]$ upon treatment with 2 equiv. of AgX in wet acetone/CH_2Cl_2 or MeOH solutions. They were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies and, in the case of the complex $[Pt(dppeO\text{-}\kappa^2\text{-}P,O)_2][BF_4]_2$, also by X-ray crystallography. These complexes were tested as catalysts in some Diels–Alder and oxidation reactions with different substrates. In the latter reaction Pt(II) complexes showed moderate activity, while for the former one, both classes of complexes were active in the C–C coupling, in particular the Pt(II) species showed interesting high *endo/exo* diasteroselectivity depending on the counteranion.
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1. Introduction

Bis-phosphine monoxides (BPMO) of general formula $R^1R^2P\text{-}Y–P(O)R^3R^4$, where Y is a divalent spacer and R an alkyl/aryl group, constitute an important class of hemilabile ligands [1], able to supply easily accessible coordination sites at the metal center, which for softer metal ions such as Pd(II) and Pt(II), will likely result from the dissociation of the M–O bond (Scheme 1).

The availability of a vacant coordination site provides the system with low activation energy paths to ligand exchange, oxidative addition, migratory insertion, and reductive elimination, which are key transformations in organometallic chemistry and transition metal homoge-

neous catalysis. Examples of the latter are, for instance, the carbonylation of methanol to acetic acid as in the Monsanto process [2], the carbonylation of esters to carboxylic anhydrides [3] and the isomerization of methyl formate to acetic acid [4] using some complexes of rhodium of the type $[(dppeO\text{-}\kappa^2\text{-}P,O)Rh(CO)Cl]$ (dppeO = $Ph_2P–CH_2CH_2–P(O)Ph_2$). Complexes Rh–BPMO have been known for a long time also as catalysts in the hydroformylation of olefins [5] and Gladiali and co-workers have recently reported the first examples of hydroformylation of styrene with BINAP(O)–Rh [6] and Pt–Sn [7] catalysts (BINAP(O) = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl mono-oxide). Systems such as Pd–BPMO are known to catalyze the hydrocarboxylation of olefins [8]. The complexes Co–BPMO (especially with BPMO = dppmO, $Ph_2P–CH_2–P(O)Ph_2$) are instead active in the hydroformylation of epoxides. BPMOs have been successfully used in
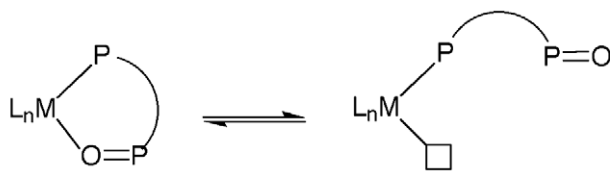
Scheme 1.

the Ni and Pd-catalyzed oligomerization of ethylene [9] and alternating copolymerization [9] and co-oligomerization of ethylene and CO with Pd [9,10] and Rh [11] catalysts. Finally, over the past six years, Faller and co-workers have published a series of papers [12] describing the synthesis of chiral BPMO–Ru and Os complexes and their use as Lewis acid catalysts in asymmetric Diels–Alder reactions of cyclopentadiene with substituted acroleins.

Our interest in developing homogeneous catalysts containing transition metals behaving as Lewis acids with free or easily accessible coordination sites at the metal center led us to report a number of catalytic processes such as the epoxidation of olefins with diluted H_2O_2 [13], the Baeyer–Villiger oxidation of ketones to give lactones [14], the cyclopropanation of olefins [15,16b], the coupling of carbenes to give olefins [16] and the insertion of carbenes into the O–H bond of alcohols to afford esters [16b]. Recently, some of us have investigated the activity of chiral and achiral complexes of the type [(P–P)M(solv)$_2$][X]$_2$, [(P–P)M(η^2-X)][X], and [(P–P)M(μ-Cl)]$_2$[X]$_2$ (where P–P = various diphosphines, including chiral diphosphines; M = Pd, Pt; X = TfO, ClO$_4$, BF$_4$) in the Diels–Alder coupling of cyclopentadiene and cyclohexadiene with unsaturated aldehydes [17]. These catalysts have promoted good conversions in relatively short times under mild conditions.

Within the research area described above, we decided to explore a series of bis-phosphine monoxide palladium(II) and platinum(II) cationic complexes of the type [M(BPMO-κ^2-P,O)$_2$][X]$_2$ (M = Pd, Pt; BPMO = Ph$_2$P–(CH$_2$)$_n$–P(O)Ph$_2$ with n = 1 (dppmO), 2 (dppeO), 3

(dpppO); X = BF$_4$, TfO) as catalysts in some Diels–Alder and oxidation reactions with different substrates.
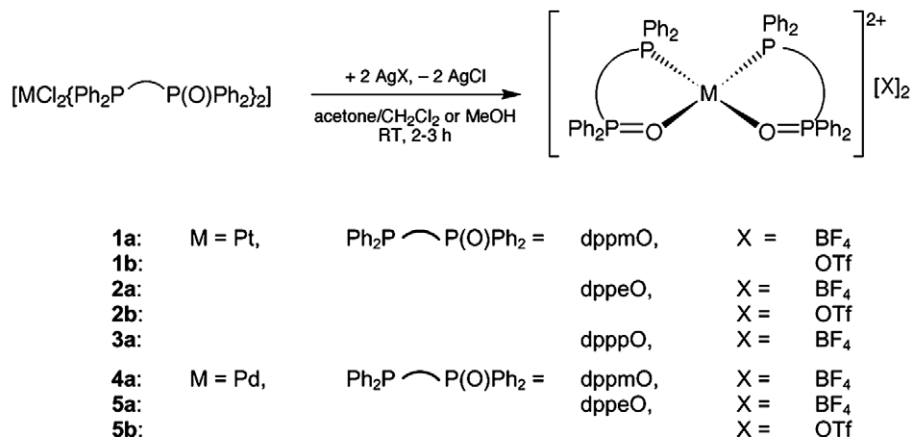
2. Results and discussion

2.1. Synthesis and characterization of the complexes

The complexes [M(BPMO-κ^2-P,O)$_2$][X]$_2$ (X = BF$_4$, TfO) were prepared according to a general method reported in the literature [18a,18b], which is illustrated in Scheme 2.

The procedure involves chloride abstraction from [MCl$_2$(BPMO-κ^1-P)$_2$] by treatment with 2 equiv. of AgX salts in wet acetone/CH$_2$Cl$_2$ or MeOH solutions; after filtration of AgCl, the BPMO complexes were isolated in high yield (>84%) upon addition of diethyl ether. The platinum compounds are white solids, while those of palladium are pale yellow.

The platinum complexes **1a**, **1b**, **2a**, **2b** and **3a** have been characterized by multinuclear NMR and elemental analysis (see Section 4). It should be noted that only **3a** is a new compound while **1a**, **1b**, **2a** and **2b** are only formally since they differ from those previously reported for the counteranions employed. Furthermore, it is worthwhile mentioning that complex **3a** is apparently stable in solution, while the corresponding Pd complex was isolated as a polymeric material of the type {[(dpppO)$_2$Pd]$^{2+}$(BF$_4^-$)$_2$}$_n$ [18b].

The ^{31}P{^{1}H} NMR data indicate that, upon chelation of the BMPO ligand, the chemical shift of the oxidized phosphorus is shifted downfield by ca. 35–40 ppm compared to the unbound species. The *cis*-structure of the cationic complexes shown in Scheme 2 is supported by X-ray structural determinations carried out for **2a** and **3a** (see below) and also in the ^{31}P{^{1}H} NMR by the $^1J_{Pt–P}$ values. The latter, are large for all the platinum complexes reported in this work and range between 3834 and 3953 Hz, as expected for P *trans* to a hard donor such as the oxygen atom [19]. At room temperature no coupling was observed between ^{195}Pt and ^{31}P=O for the complexes [Pt(dppmO-κ^2-P,O)$_2$][OTf]$_2$ (**1b**) and [Pt(dpppO-κ^2-P,O)$_2$][BF$_4$]$_2$ (**3a**),

1a:	M = Pt,	Ph$_2$P⌒P(O)Ph$_2$ =	dppmO,	X =	BF$_4$
1b:					OTf
2a:			dppeO,	X =	BF$_4$
2b:				X =	OTf
3a:			dpppO,	X =	BF$_4$
4a:	M = Pd,	Ph$_2$P⌒P(O)Ph$_2$ =	dppmO,	X =	BF$_4$
5a:			dppeO,	X =	BF$_4$
5b:				X =	OTf

Scheme 2.

although this interaction was detected for the other Pt-complexes (see Section 4). However, upon raising the temperature to 320 K, the $^2J_{Pt–P(=O)}$ coupling constant for **1b** was shown to be 73.2 Hz, while that of **3a** could not be detected even at the higher temperature. This finding is not surprising since the values of $^2J_{Pt–P(=O)}$ decrease rapidly on going from **1a** (74.2 Hz) to **2a** (23.6 Hz) and this behaviour appears to be related to the chain length of the BMPO ligand. Finally, only for dppeO-κ^2-*P,O* chelates **2a**, **2b**, **5a** and **5b**, the $^3J_{P–P(=O)}$ of ca. 5–8 Hz could be detected.

2.2. Single crystal X-ray diffraction study of [Pt(dppeO-κ^2-P,O)$_2$][BF$_4$]$_2$ (2a)

The solid-state structure of the cationic bis-chelate part of **2a** has been determined by a single-crystal X-ray diffraction study (Fig. 1) and matches closely that of the previously reported palladium derivative [(dppeO)$_2$Pd]$^{2+}$ [18b] and also that of the Pt cation [(dppmO)$_2$Pt]$^{2+}$ [18c]. Crystal data together with experimental and structure refinement details are summarized in Section 4. Relevant bond distances and angles are reported in Table 1. The Pt atom and the four atoms constituting the first coordination sphere (P(3), P(4), O(1) and O(2)) are coplanar within 0.0162(4) Å. However, a distortion from the ideal square-planar configuration is observed in the crystal structure, the bond angles O(1)–Pt–O(2) and P(3)–Pt–P(4) being 80.0(3)° and 100.2(9)°, respectively.

It is worthwhile noting that the Pt–O bond distances (2.043(6) and 2.096(6) Å) are both comparable with those found for the corresponding Pd (2.088(12) and 2.119(10) Å) and Pt (2.089(2) and 2.094(2) Å) complexes and also with the M–O (M = Pd [19a], Pt [19b]) bond

lengths in various Pd(II) and Pt(II) hydroxo and alkoxo complexes which fall in the range 1.99–2.228 Å. This suggests that the Pt–O coordination bonds are of considerable strength despite the fact that they are *trans* to P ligands whose *trans* influence is normally significant. Furthermore, also the Pt–P distances (2.226(2) and 2.221(2) Å) are comparable with those of the above-mentioned Pd (2.240(4) and 2.247(5) Å) and Pt (2.215(2) and 2.220(2) Å) complexes and also similar to those found for the corresponding dichloro Pd(II) species [(dppeO)$_2$PdCl$_2$] [18b]. The observed Pt–P and Pt–O bond lengths indicate that the bis-chelate dication [(dppeO)$_2$Pt]$^{2+}$ is remarkably stable and this structural evidence is of some relevance in explaining the chemical behaviour of these complexes (see below).

Table 1
Selected bond distances (Å) and angles (°) in the crystal structure of [(dppeO-κ^2-*P,O*)$_2$Pt][BF$_4$]$_2$ (**2a**)

Pt–O(1)	2.043(6)	Pt–O(2)	2.096(6)
Pt–P(3)	2.226(2)	Pt–P(4)	2.221(2)
P(1)–O(1)	1.517(7)	P(2)–O(2)	1.512(7)
P(1)–C(1)	1.803(9)	P(1)–C(7)	1.784(9)
P(1)–C(13)	1.803(9)	P(2)–C(27)	1.788(9)
P(2)–C(27)	1.788(9)	P(2)–C(33)	1.803(9)
P(3)–C(15)	1.800(9)	P(3)–C(21)	1.812(9)
P(3)–C(14)	1.843(9)	P(4)–C(47)	1.807(9)
P(4)–C(41)	1.810(9)	P(4)–C(40)	1.851(9)
C(13)–C(14)	1.53(1)	C(39)–C(40)	1.53(1)
O(1)–Pt–P(3)	88.9(2)	O(2)–Pt–P(4)	90.8(2)
O(1)–Pt–O(2)	80.0(3)	P(3)–Pt–P(4)	100.2(9)
O(1)–Pt–P(4)	170.8(2)	O(2)–Pt–P(3)	168.9(2)
O(1)–P(1)–C(13)	110.4(4)	O(2)–P(2)–C(39)	109.1(4)
C(14)–C(13)–P(1)	113.7(7)	C(13)–C(14)–P(3)	115.2(7)
C(40)–C(39)–P(2)	111.6(7)	C(39)–C(40)–P(4)	115.1(7)
P(1)–O(1)–Pt	145.4(4)	P(2)–O(2)–Pt	126.5(4)
C(14)–P(3)–Pt	108.4(3)	C(40)–P(4)–Pt	111.1(3)

Fig. 1. Molecular structure of the bis-chelate dication [Pt(dppeO-κ^2-*P,O*)$_2$]$^{2+}$ (**2a**) with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.
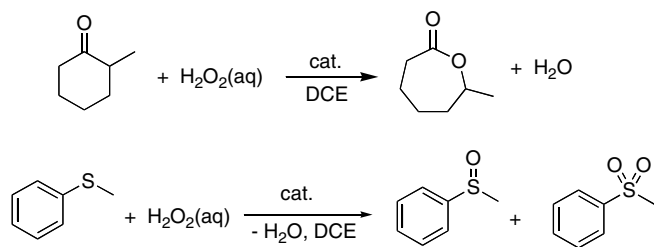
2.3. Catalytic studies

These complexes should conceivably be good Lewis acid catalysts because of (i) the 2+ charge and (ii) the ease with which the labile O donor is expectedly displaced by substrates to be transformed. We initially tested the Pt(II) and Pd(II) complexes as catalysts in two oxidation reactions where the Lewis acidity of the complex catalyst is known to be important in promoting the transformation, i.e. the Baeyer–Villiger oxidation of 2-methylcyclohexanone [13f–i] and the sulfoxidation of thioanisole [20] (Scheme 3), but the results were rather disappointing (Table 2).

The oxidation of 2-methylcyclohexanone was practically negligible, even when increasing either the amount of catalyst or the reaction temperature up to 70 °C, while the sulfoxidation of thioanisole gave poor yields. In the latter case the selectivity to sulfoxide was >99%, only traces of sulfone being observed. The reasons for this modest reactivity are probably due to the catalyst not withstanding hydrogen

peroxide, as a $^{31}P\{^{1}H\}$ analysis of the final reaction mixture clearly indicated the presence of either dppeO$_2$ or dppmO$_2$ at 36.2 and 38.2 ppm, respectively.

Tests were subsequently carried out to check the reactivity of these complexes in the Diels–Alder (DA) and hetero Diels–Alder (HDA) reactions (Scheme 4) to compare the activity observed with that of recently reported Pd(II) and Pt(II) complexes [17,21]. DA reaction led to the formation of two different stereoisomers (*exo* and *endo*) and, in the HDA, also to the formation of the so-called ene product was observed. Table 3 collects the results obtained with the different complexes and the various combinations of dienes and dienophiles.

The reaction between cyclohexadiene and acrolein (entries 1–9) was always rather productive, albeit much less than in the presence of the closely related [(diphosphine)M(solv)$_2$]$^{2+}$ complexes (M = Pd, Pt; solvent = MeCN, THF) [17] where similar reactivities could be observed at 0 °C, indicating that the P=O ligand is probably more strongly bound than MeCN or THF. However, they showed some interesting *endo/exo* selectivities particularly when BF$_4^-$ is the counteranion. The less sterically demanding *endo* product was generally favoured in these reactions and, expectedly, the presence of bulky ligands around the Lewis acidic transition metal (Fig. 1) increased the *endo/exo* ratio in catalyzed reactions. This is not so with TfO$^-$ as the counteranion (Table 3, entries 5, 6, 9): this observation may suggest that triflate is probably able to displace one of the oxygen donors in complexes thereby leading to a less sterically demanding catalytic species.
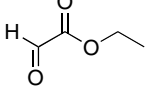
The use of methacrolein as the dienophile (Table 3, entries 10–18) resulted in lower conversions with the *endo/exo* ratio being practically the same for all catalysts. On the other hand, and despite the lower temperature (25 °C), changing the diene to the highly reactive cyclopentadiene (Table 3, entries 19–24) resulted in an appreciable catalytic effect only in the case of methacrolein as the dienophile, as can be seen by a comparison with the control experiments carried out in the absence of catalyst.

As to the hetero Diels–Alder reaction, only the cycloaddition of ethyl glyoxylate to 2,3-dimethylbutadiene was

Scheme 3.

Table 2
Oxidation of 2-methylcyclohexanone and thioanisole with hydrogen peroxide catalyzed by [Pt(BPMO-κ^2-*P,O*)$_2$][X]$_2$ derivatives

Catalyst	Substrate	Conversion (%)
1a	2-Methyl-cyclohexanone	0.8
2a		0.7
1a[a]	Thioanisole	19
2a[a]		16

Reaction conditions: catalyst 0.0083 mmol, substrate 0.83 mmol, H$_2$O$_2$ 0.91 mmol, DCE 3 ml, T = 25 °C, N$_2$ 1 atm.
[a] Catalyst 0.0166 mmol.
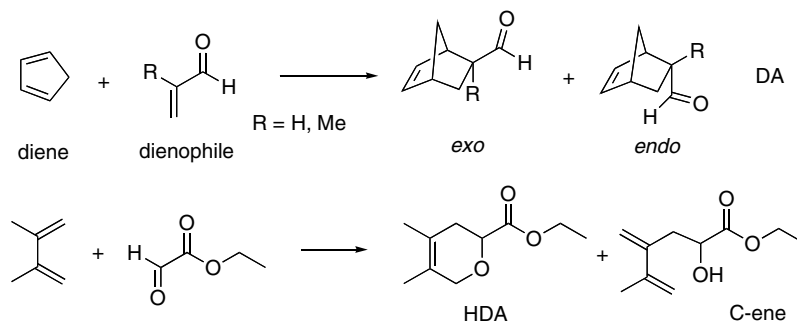
Scheme 4.

Table 3
Diels–Alder (DA) and hetero Diels–Alder (HDA) reactions catalyzed by (BPMO-κ^2-P,O)Pd(II) and -Pt(II) complexes shown in Scheme 1

Entry	Diene	Dienophile	Temperature (°C)	Catalyst	Conversion (%)	endo/exo
1			65	–	4.7	14
2				1a	98	37
3				2a	88	33
4				3a	76	14
5				1b[a]	78	8
6				2b	100	3.7
7				4a	89	41
8				5a	81	30
9				5b	96	10
10			65	–	0	
11				1a	16	2.8
12				2a	8	2.8
13				3a	4	2.7
14				1b[a]	9	2.8
15				2b	22	2.8
16				4a	5	2.9
17				5a	4	2.8
18				5b	10	2.9
19			25	–[b]	58	3.6
20				2a[b]	54	4.1
21				5a[b]	57	4.1
22			25	–	55	4.6
23				2a	81	4.5
24				5a	72	4.4
25			65	–	0	HDA/ene
26				1a	26	1
27				2a	23	1.1
28				3a	18	1
29				4a	17	1.2
30				5a	20	1.3

Reaction conditions: catalyst 0.0106 mmol, diene 0.53 mmol, dienophile 0.53 mmol, solvent 1 ml dichloroethane (DCE), reaction time 24 h.
[a] Not soluble.
[b] Reaction time 2.5 h.

found to yield moderate amounts of products but with quite a poor HDA/C-ene selectivity in keeping with the literature [22] (Table 3, entries 25–30). No reaction was observed with a common bidentate dienophile as in the case of e.g. 1,3-cyclohexadiene with phenylacryloyl-N-oxazolidinone.

3. Conclusions

A range of bis-cationic Pt(II) and Pd(II) monomeric complexes bearing two molecules of bis-phosphine monoxide ligands and different counteranions have been prepared. The *cis* coordination of the ligand was confirmed by X-ray diffraction study. Such complexes were investigated as Lewis acids in catalytic oxidation with modest results, as well as in the DA and HDA reactions with interesting results in terms of activity and more markedly of diastereoselectivity. The catalytic results here reported indicate that the new complexes synthesized are indeed Lewis acids containing hemilabile ligands.

4. Experimental

4.1. General procedures and materials

All work was carried out with the exclusion of atmospheric oxygen under a dinitrogen atmosphere using standard Schlenck techniques. Solvents were dried and purified according to standard methods. Substrates were purified by passing through neutral alumina and stored in the dark at low temperature. Hydrogen peroxide (35% Fluka) was a commercial product and used without purification. All dienes, dienophiles and substrates for oxidation reactions employed were purchased from Aldrich and used without any further purification. *cis*-[MCl$_2$(BPMO-κ^1-P)$_2$] complexes (M = Pt, BPMO = dppmO, dppeO, dpppO; M = Pd, BPMO = dppeO) were synthesized by treatment of [PtCl$_2$(COD)] and [PdCl$_2$(CH$_3$CN)$_2$] with 2 equiv. of BPMO in dichloromethane at room temperature, similarly to procedures reported in the literature [18a,18b]. Complexes 4a and 5a were prepared as reported in the literature [18b]. ^{1}H NMR

spectra were run either on a Bruker AC300 spectrometer operating at 300.13 or on a Bruker AC200 spectrometer operating at 200.13 MHz at 298 K. $^{31}P\{^1H\}$ NMR spectra were run at 298 K, unless otherwise stated, on a Bruker AC200 spectrometer operating at 81.015 MHz; δ values in ppm are relative to SiMe$_4$, 85% H$_3$PO$_4$. GLC measurement were taken on a Hewlett–Packard 5890A gas chromatograph equipped with a FID detector (gas carrier He). Identification of products was made with GLC by comparison with authentic samples. Elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padua.

4.2. Synthesis of the [M(BPMO-κ²-P,O)₂][X]₂ complexes

4.2.1. [Pt(dppmO-κ²-P,O)₂][BF₄]₂ (1a)

To a solution of cis-[PtCl₂(dppmO-κ¹-P)₂] (0.40 g, 0.38 mmol) in dichloromethane (20 ml) and acetone (20 ml) at room temperature was added 0.16 g (0.82 mmol) of AgBF₄. The reaction mixture was stirred under nitrogen for 3 h and then the solid AgCl formed was filtered off. After concentration, the solution was treated with Et₂O to give a white solid, which was filtered off and dried under vacuum. Yield: 0.42 g, 97%. Anal. Calc. for C₅₀H₄₄B₂-F₈O₂P₄Pt: C, 51.35; H, 3.79. Found: C, 51.32; H, 3.63%. ^{1}H NMR (δ (CD₃)₂CO): 7.2–8.0 (m, Ar), 4.7 (m, PCH₂P). $^{31}P\{^1H\}$ NMR (CD₂Cl₂): δ 2.8 (P, s, $^1J_{Pt-P} = 3834$ Hz), 66.7 (P=O, s, $^2J_{Pt-P(O)} = 74.2$ Hz).

4.2.2. [Pt(dppeO-κ²-P,O)₂][BF₄]₂ (2a)

To a suspension of cis-[PtCl₂(dppeO-κ¹-P)₂] (0.35 g, 0.32 mmol) in methanol (20 ml) and acetone (20 ml) at room temperature was added 0.66 ml (0.66 mmol) of 1.0 M acetone solution of AgBF₄. The reaction mixture was stirred under nitrogen for 3 h and then the solid AgCl formed was filtered off. After concentration, the solution was treated with Et₂O to give a white solid, which was filtered off and dried under vacuum. Yield: 0.34 g, 89%. Anal. Calc. for C₅₂H₄₈B₂F₈O₂P₄Pt: C, 52.15; H, 4.04. Found: C, 51.51; H, 4.07%. ^{1}H NMR (δ (CD₃)₂CO): 7.2–8.2 (m, Ar), 3.2 (m, PCH₂). $^{31}P\{^1H\}$ NMR (CD₂Cl₂): δ 3.2 (P, dd, $^1J_{Pt-P} = 3953$ Hz, $^3J_{P-PO} = 6.2$ Hz), 52.9 (P=O, dd, $^2J_{Pt-P} = 23.6$ Hz, $^3J_{P-PO} = 6.2$ Hz).

4.2.3. [Pt(dpppO-κ²-P,O)₂][BF₄]₂ (3a)

To a solution of cis-[PtCl₂(dpppO-κ¹-P)₂] (0.37 g, 0.33 mmol) in dichloromethane (15 ml) at room temperature was added 0.60 ml (0.66 mmol) of a 1.1 M acetone solution of AgBF₄. The reaction mixture was stirred under nitrogen for 2 h and then the solid AgCl formed was filtered off. After concentration, the solution was treated with Et₂O to give a white solid, which was filtered off and dried under vacuum. Yield: 0.36 g, 89%. Anal. Calc. for C₅₄H₅₂B₂F₈O₂P₄Pt: C, 52.92; H, 4.28. Found: C, 52.51; H, 4.26%. ^{1}H NMR (CDCl₃): δ 7.2–7.6 (m, 40H, Ar), 1.9 (m, 4H, C(CH₂)C), 2.7 (m, 4H, CH₂PPt), 3.2 (m, 4H, CH₂PO). $^{31}P\{^1H\}$ NMR (CDCl₃): δ −1.6 (P, s, $^1J_{Pt-P} = 3949$ Hz), 61.4 (P=O, s).

4.2.4. Synthesis of [Pt(dppmO-κ²-P,O)₂](OTf)₂ (1b)

To a suspension of cis-[PtCl₂(dppmO-κ¹-P)₂] (0.30 g, 0.28 mmol) in dichloromethane (20 ml) room temperature was added 1.46 ml (0.58 mmol) of a 0.40 M acetone solution of AgOTf. The reaction mixture was stirred under nitrogen for 3 h and then the solid AgCl formed was filtered off. After concentration, the solution was treated with n-pentane to give a white solid, which was filtered off. The solid was recrystallized from methanol/Et₂O and dried under vacuum. Yield: 0.32 g, 87%. Anal. Calc. for C₅₂H₄₄F₆O₈P₄PtS₂: C, 48.27; H, 3.43; S, 4.96. Found: C, 48.32; H, 3.13; S, 4.79%. ^{1}H NMR (CD₃)₂SO: δ 7.2–8.0 (m, Ar), 4.9 (m, PCH₂P). $^{31}P\{^1H\}$ NMR (CD₃)₂SO, 320 K: δ 3.6 (P, s, $^1J_{Pt-P} = 3878$ Hz), 66.5 (P=O, s, $^2J_{Pt-P} = 73.2$ Hz).

4.2.5. Synthesis of [Pt(dppeO-κ²-P,O)₂](OTf)₂ (2b)

To a solution of cis-[PtCl₂(dppeO-κ¹-P)₂] (0.34 g, 0.31 mmol) in dichloromethane (20 ml) at room temperature was added 1.59 ml (0.64 mmol) of a 0.40 M acetone solution of AgOTf. The reaction mixture was stirred under nitrogen for 3 h and then the solid AgCl formed was filtered off. After concentration, the solution was treated with Et₂O to give a white solid, which was filtered off and dried under vacuum. Yield: 0.34 g, 84%. Anal. Calc. for C₅₄H₄₈F₆O₈P₄PtS₂: C, 49.06; H, 3.66; S, 4.85. Found: C, 49.47; H, 3.16; S, 4.84%. ^{1}H NMR (CDCl₃): δ 7.2–8.0 (m, Ar), 3.0 (m, PCH₂). $^{31}P\{^1H\}$ NMR (CDCl₃): δ 1.6 (P, d, $^1J_{Pt-P} = 3917$ Hz, $^3J_{P-PO} = 5.5$ Hz), 52.2 (P=O, d, $^2J_{Pt-P} = 99.5$ Hz, $^3J_{P-PO} = 5.5$ Hz).

4.2.6. Synthesis of [Pd(dppeO-κ²-P,O)₂][OTf]₂ (5b)

To a orange-yellow solution of cis-[PdCl₂(dppeO-κ¹-P)₂] (0.33 g, 0.33 mmol) in dichloromethane (20 ml) at room temperature was added 1.67 ml (0.67 mmol) of a 0.40 M acetone solution of AgOTf. The reaction mixture was stirred under nitrogen for 2 h and then the solid AgCl formed was filtered off. After concentration, the solution was treated with Et₂O to give a pale yellow solid, which was filtered off and dried under vacuum. Yield: 0.37 g, 92%. Anal. Calc. for C₅₄H₄₈F₆O₈P₄PdS₂: C, 52.59; H, 3.92; S, 5.20. Found: C, 52.64; H, 3.54; S, 5.11%. ^{1}H NMR (CDCl₃): δ 7.2–7.9 (m, Ar), 2.9 (m, PCH₂). $^{31}P\{^1H\}$ NMR (CDCl₃): δ 36.5 (P, d, $^3J_{P-PO} = 7.3$ Hz, PPd), 48.5 (P=O, d, $^3J_{P-PO} = 7.3$ Hz).

4.3. X-ray diffraction studies

Crystal data for cis-[Pt(dppeO-κ²-P,O)₂][BF₄]₂ · CH₂Cl₂; C₅₃H₅₀O₂P₄B₂F₈Cl₂Pt, $M_r = 1282.47$, monoclinic, space group $P2_1/a$, with $a = 20.478(3)$ Å, $b = 25.009(3)$ Å, $c = 10.405(2)$ Å, $\beta = 90.10(3)°$, $V = 5329(1)$ Å³, $Z = 4$, $\rho_{calc} = 1.599$ Mg/m³, $F(000) = 2552$, $\lambda = 0.71073$ Å, μ (Mo Kα) = 2.922 mm^{-1}, crystal size 0.320 × 0.34 × .026 mm. A prismatic colorless crystal was centered on a four-circle Philips PW1100 (Febo System) diffractometer operating in $\theta/2\theta$ scan mode with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), following standard procedures

at room temperature. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-Polarization effects and for absorption, as described by North et al. [23]. The structure was solved by direct methods SIR-97 [24]. Refinement was carried out by full-matrix least-squares procedures using anisotropic temperature factors for all non-hydrogen atoms. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters ($1.2U$ equiv. of the parent carbon atom). For a total of 650 parameters and for 8104 reflections having ($I \geqslant 2\sigma(I)$), $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.138, \quad S = 1.344$, and conventional $R = 0.058$; minimum/maximum residual electron density $-0.964/0.674$ e Å^{-3}. Structure refinement and final geometrical calculations were carried out with SHELXL-97 [25] program, implemented in the WinGX package [26], drawings were produced using ORTEP3 [27].

4.4. Catalytic studies

4.4.1. Diels–Alder reactions

These were carried out in a 3 ml round bottomed flask fitted with a screw-capped silicone septum to allow sampling. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer. Constant temperature (20 or 65 °C) was maintained by water circulation through an external jacket connected with a thermostat. The required amount of catalyst (2% mol, 9.4 mM) was placed in solid form in the reactor, followed by 1 ml of 1,2-dichloroethane. After thermostating at the required temperature for a few minutes, the proper amount of dienophile (0.53 mmol) was added, followed by the appropriate amount of diene (0.53 mmol) and time was started. All reactions were monitored with ^{1}H NMR by periodic direct sampling of 20 μL of solution from the reaction mixtures with a microsyringe. Quenching of reaction samples was performed by dilution up to 200 times with deuterated solvent and spectra were immediately acquired. Identification of products was made with NMR by comparison with authentic samples. Products yield and diasteromeric distribution were determined by integration of the ^{1}H NMR spectra.

4.4.2. Oxidation reactions

These were carried out in a 3 ml round bottomed flask fitted with a screw-capped silicone septum to allow sampling. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer. Constant temperature (20 or 65 °C) was maintained by water circulation through an external jacket connected with a thermostat. The required amount of catalyst (2% mol, 2 mM) was placed in solid form in the reactor. To this, 3 ml of 1,2-dichloroethane were added. After thermostating at the required temperature for a few minutes, the proper amount of substrate (0.83 mmol) was added, followed by 1.1 equiv. of 35% hydrogen peroxide and time was started. All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe after quenching with triphenyl phosphine; n-decane was used as internal standard. Separation of the products was performed on a Hewlett–Packard 5890A gas chromatograph equipped with a FID detector (carrier gas He) and a 25 m HP-5 capillary. Identification of products was made with GLC and ^{1}H NMR by comparison with authentic samples.

5. Supplementary data

Crystallographic data for the structures here reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 602962. Copies of the available material can be obtained, free of charge from CCDC,12 Unino Road, Cambridge CH2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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