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Platinum(II) – phosphole complexes : synthesis and evaluation as enyne cycloisomerisation catalysts.

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Abstract

A series of Platinum(II)-monophosphole complexes have been synthesized and used in enyne cycloisomerisations in order to study the effect of the ligand on the catalytic activity and selectivity. Reactions were performed on various N- or C-tethered 1,6-enynes and in the absence or in the presence of nucleophiles. For the most efficient cationic Pt(II)-complexes, it was also evidenced that the counterion and/or the solvent could have an influence on both the efficiency and the selectivity in the competition between the 5-*exo-dig* and the 6-*endo-dig* processes.

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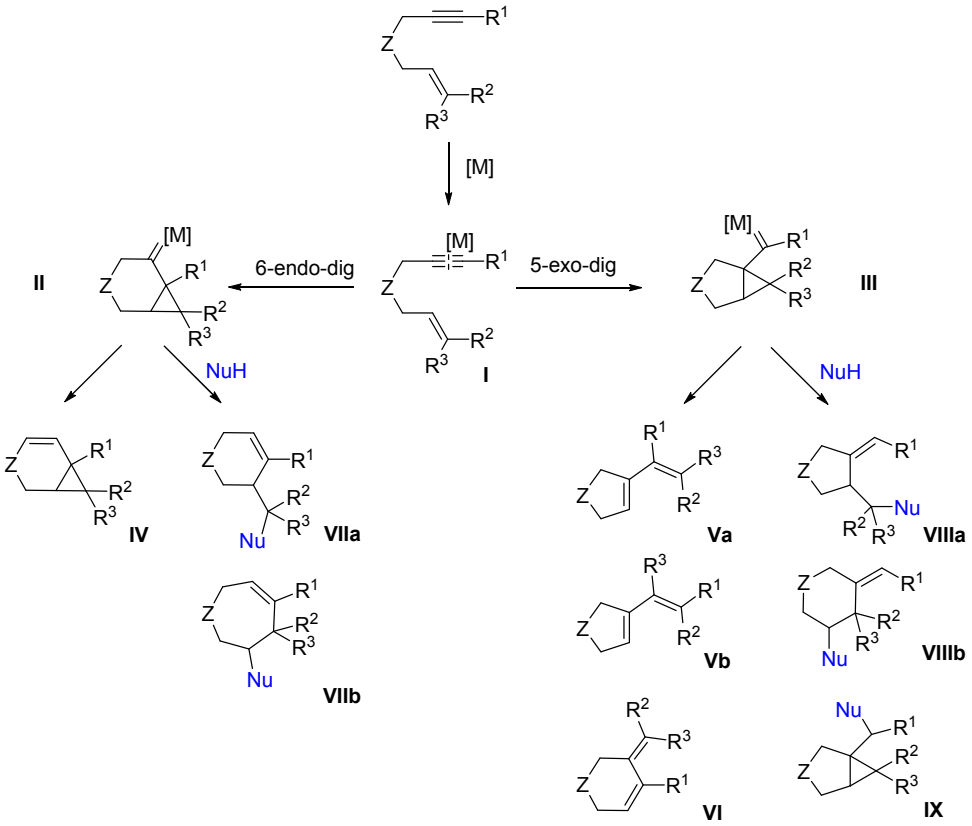
Introduction

In recent years, gold- or platinum-catalysed cycloisomerisations of 1,6-enynes have attracted considerable attention since they represent powerful synthetic tools for the construction of cyclic and heterocyclic moieties.[1]



Scheme 1: Metal-catalysed cycloisomerisations of 1,6-enynes in absence or in presence of a nucleophile.

The mechanistic pathway commonly proposed in the literature for 1,6-enyne cycloisomerisation is depicted on Scheme 1.[2] The electrophilic activation of the enyne triple bond by the metal generates its metal π-complex **I** and triggers the nucleophilic attack of the tethered alkene following a 6-*endo-dig* or a 5-*exo-dig* cyclisation mode, leading to the key

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cyclopropyl-metallocarbenoid intermediates **II** or **III** respectively. Intermediate **II** can evolve to cyclopropane **IV**[3] through an 1,2-hydrogen shift followed by a β-H elimination. On the other hand, intermediate **III** can undergo single or double-cleavage rearrangement reactions leading to 1,3-dienes **Va**[4] or **Vb**.[5] Intermediate **III** can also evolve to 1,3-endo-diene **VI** through a skeletal rearrangement.[6]

Alternatively, attack of a nucleophile NuH to intermediates **II** and **III** can give an access to a variety of 6-membered or 5-membered ring functionalised compounds **VIIa, VIIb**, **VIIIa**, **VIIIb** and **IX** respectively.[7] Various nucleophiles have been used in such reactions, including water or alcohols[8] to promote hydroxy- or alcoxycyclisations or electron-rich arenes such as indole[8g, 9] to promote hydroarylation-cyclisation tandem reactions.

$PtCl_2$-catalysed processes, first reported by Fürstner,[3] were largely studied and applied to total synthesis. Then the role of ligands in Pt(II)-complexes on the activity and/or the selectivity was demonstrated. A critical influence of CO[10] or H_2O[11] ligands was observed, albeit recently attributed to the inhibition of the chelate formation more than to the increase of Pt electrophilicity.[12] More "sophisticated" ligands surrounding the platinum center have been then designed and/or used to further improve both activity and selectivity of the catalysts in 1,6-enyne cycloisomerisations[5, 13] including chiral ligands for asymmetric reactions.[8c, 9d, 14] Notably, examples of platinum-based catalysts working efficiently at room temperature as their gold-counterparts remain scarce.[5, 13]

Given the various applications of phosphole-based ligands in homogeneous catalysis[15] and following our previous report on gold(I) phosphole complexes which are both active and selective in enyne cycloisomerisation,[16] we report herein the synthesis of a series of new platinum(II) monophosphole complexes and their evaluation in 1,6-enyne cycloisomerisations and related reactions.

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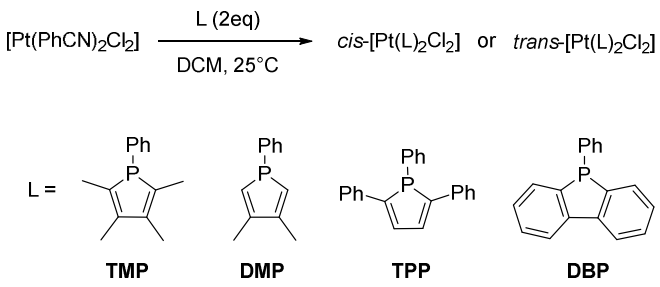
Results and Discussion

Synthesis of phosphole-based platinum complexes

Platinum(II) complexes bearing monophospholes ligands have already been reported in the literature[17] with some examples of use in catalysis, mainly in hydroformylation reaction,[18] but no example was described in the literature for an application in enyne cycloisomerisation. 1-phenyl-2,3,4,5-tetramethylphosphole (TMP),[19] 1-phenyldibenzophosphole (DBP)[20] and 1,2,5-triphenylphosphole (TPP)[21] were converted to the corresponding dichloro-diphosphole-platinum complexes $[Pt(L)_2Cl_2]$ by reaction with dichlorodibenzonitrileplatinum in dichloromethane at room temperature (Scheme 2). All the platinum (II) complexes were obtained as solids in good yields (72-84 %) after 3 hours of reaction at room temperature. This result is in contrast with the unreactive feature of sterically encumbered 2,4,6-substituted aryl-3-methylphosphole[18] which required days to be converted into their corresponding $[Pt(L)_2Cl_2]$ complexes.



Scheme 2: Synthesis of Pt(II) phosphole-complexes.

Characterisation

The platinum complexes $[Pt(TMP)_2Cl_2]$, $[Pt(DBP)_2Cl_2]$, $[Pt(TPP)_2Cl_2]$ were characterised by ^{31}P, ^{13}C and ^{1}H NMR spectroscopy, as well as mass spectrometry. The relative position of the phosphole ligands in the platinum complexes was easily determined by measuring the

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magnitude of $^{1}J_{P\text{-}Pt}$ in the ^{195}Pt isotopomer in ^{31}P NMR spectroscopy.[17a] The *cis*-arrangement of $[Pt(TMP)_2Cl_2]$ and $[Pt(DBP)_2Cl_2]$ was supported by $^{1}J_{Pt\text{-}P}$ couplings of 3330 and 3470 Hz respectively, which lie in the range (3180-3680 Hz) usually observed in platinum(II) complexes featuring two phosphole ligands in *cis* position, including $[Pt(DMP)_2Cl_2]$.[17a-d, 17f] Moreover, as depicted in Table 1, both the phosphorus-platinum coupling constant, $^{1}J(^{195}Pt,^{31}P)$, and the coordination chemical shift, $\Delta\delta(^{31}P)$, increase in the order TMP<DMP<DBP. Notably the same trend was observed in the determination of $^{1}J(^{77}Se, ^{31}P)$ in the corresponding phosphole-selenides,[16] indicating that TMP is the best σ-donor ligand of the series. By comparison, the analogous *cis*-$[Pt(PPh_3)_2Cl_2]$ complex shows a larger $^{1}J(^{195}Pt,^{31}P)$ coupling constant (3681 Hz) and a larger $\Delta\delta(^{31}P)$ (20.3 ppm),[22] which highlights a specific behaviour of phosphole ligands towards platinum coordination, that may lead to specific activities of phosphole-based complexes in catalysis as already observed in gold catalysis.[16]

Table 1: $^{31}P\{^{1}H\}$ NMR spectral data for $[Pt(L)_2Cl_2]$ phosphole complexes.

entry	Ligand L	$\Delta\delta(^{31}P)^{a}$	$^{1}J(^{195}Pt,^{31}P)$ in $[Pt(L)_2Cl_2]$	$^{1}J(^{77}Se,^{31}P)$ in L=Se[16]
1	TMP	8.9	3330	708
2	DMP	10.6[23]	3345[17a]	713
3	DBP	15.3	3470	748
4	TPP	22.6	2520	742

[a] $\Delta\delta(^{31}P) = \delta(^{31}P\ [PtCl_2(L)_2]\ complex) - \delta(^{31}P\ ligand)$

On the other hand, $[Pt(TPP)_2Cl_2]$ exhibited the two phosphole ligands in *trans* position as indicated by a $^{1}J(^{195}Pt,^{31}P)$ coupling constant of 2520 Hz (Table 1, entry 4). TPP is indeed the bulkiest ligand in our phosphole series as determined by the buried volume ($\%V_{bur}$) calculated from the X-ray crystallographic data of [Au(L)Cl] complexes.[16] Similar $^{1}J(^{195}Pt,^{31}P)$ values

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(in the range of 2030-2625 Hz) have been obtained for a number of *trans*-[Pt(L)$_2$Cl$_2$] complexes prepared from sterically hindered phospholes.[17b, 17e-h].

The molecular structures of *cis*-[Pt(TMP)$_2$Cl$_2$] and *cis*-[Pt(DBP)$_2$Cl$_2$] have been established by X-ray diffraction studies (Figure 1) on suitable single crystals suitable grown from diffusion of pentane into a dichloromethane solution of the complexes. Unfortunately, similar procedure failed in the case of *trans*-[Pt(TPP)$_2$Cl$_2$] complex.

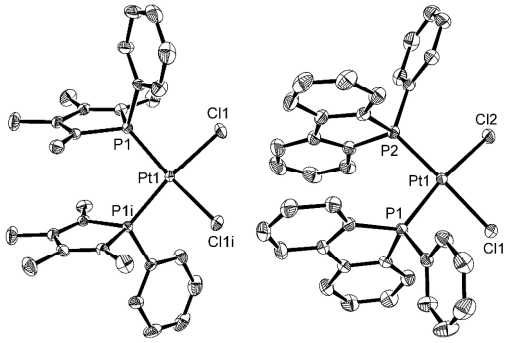

Figure 1. Ortep plots of *cis*-[Pt(TMP)$_2$Cl$_2$] and *cis*-[Pt(DBP)$_2$Cl$_2$]. Thermal ellipsoids are drawn at the 50% probability level, the hydrogen atoms and the solvent molecule in *cis*-[Pt(TMP)$_2$Cl$_2$] have been omitted for clarity. [Symmetry code : (i) 1-x, y, 0.5-z].

Table 2: Selected bond lengths and angles in *cis*-[Pt(L)$_2$Cl$_2$] complexes.

complex	**Pt-Cl (Å)**	**Pt-P(Å)**	**P-Pt-P (°)**	**P-Pt-Cl (°)**	**Cl-Pt-Cl (°)**
cis [Pt(TMP)$_2$Cl$_2$]	2.3611(5)	2.2325(5)	98.24(3)	87.62(2)	90.06(3)
cis [Pt(DBP)$_2$Cl$_2$]	2.3570(4) 2.3469(4)	2.2293(4) 2.2400 (4)	95.59(2)	92.45(2) 84.14(2)	87.65 (2)
cis [Pt(DMP)$_2$Cl$_2$][23]	2.336 (2) 2.360 (2)	2.239 (2) 2.227 (1)	94.1(1)	90.2 (1) 85.8 (1)	89.9 (1)

Geometrical parameters within the P-Pt-P backbone in three *cis*-[Pt(L)$_2$Cl$_2$] phosphole complexes are summarized in Table 2. X-ray data show that in spite of an expected mirror plane, the two halves of *cis*-[Pt(DBP)$_2$Cl$_2$] molecules have significantly different dimensions, as already reported for *cis*-[Pt(DMP)$_2$Cl$_2$][23]. In these complexes, the platinum centre is coordinated by two *cis* phosphole phosphorus atoms and two *cis* chloride ions in a distorted

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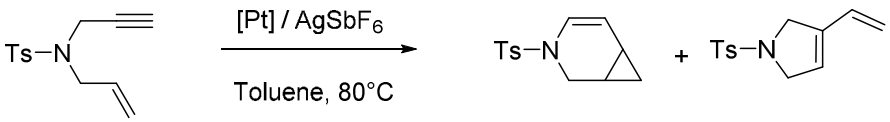
square-planar geometry with P-Pt-P angles in the range of 94-98°, Pt-Cl bond lengths in the range of 2.33-2.36 Å and Pt-P bond lengths in the range of 2.22-2.24 Å, as typically observed in *cis*-[Pt(L)$_2$Cl$_2$] phosphole complexes.[23] Notably, larger Pt-P bond lengths in the range of 2.29-2.33 Å have been reported in *trans*-[Pt(L)$_2$Cl$_2$] complexes prepared from phospholes ligands.[17b, 17f-h]

Catalytic tests

To evaluate the catalytic performance of the phosphole Pt(II)-complexes, the N-tethered 1,6-enyne **1a** has been selected as a model substrate[3] for the cycloisomerisation reaction (Table 3). For comparison purposes, the reaction was also conducted with $PtCl_2$ and *cis*-[Pt(PPh$_3$)$_2$Cl$_2$].

Table 3: Cycloisomerisation of 1,6-enyne **1a**.



1a **2a** **3a**

Entry	[Pt] (5mol%)	$AgSbF_6$ (mol%)	t (h)	Conversion[a] (%)	**2a/3a** ratio [a]
1	$PtCl_2$	-	3	49	93/7
2	*cis*-[Pt(PPh$_3$)$_2$Cl$_2$]	-	3	-	-
3	*cis*-[Pt(PPh$_3$)$_2$Cl$_2$]	10	3	17	33/67
4	*cis*-[Pt(TMP)$_2$Cl$_2$]	10	1	96	48/52
5	*cis*-[Pt(DBP)$_2$Cl$_2$]	10	3	55	83/17
6	*trans*-[Pt(TPP)$_2$Cl$_2$]	10	3	37	47/53

[a]determined by ^{1}H-NMR.

$PtCl_2$-catalysed cycloisomerisation of enyne **1a**, in toluene at 80°C, mainly afforded cyclopropane **2a** in moderate yield (Table 3, entry 1), while no reaction was observed in the same conditions by using [Pt(PPh$_3$)$_2$Cl$_2$] alone (Table 3, entry 2). In the presence of $AgSbF_6$ as the halide scavenger, a partial conversion was observed leading to a mixture of **2a** (type **IV**

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compound) and **3a** (type **V** compound) in a ratio 33/67 (Table 3, entry 3). These products results from a competition between the 5-*exo-dig* and the 6-*endo-dig* processes (Scheme 1). This selectivity contrasts with the selectivity obtained in the absence of ligands[3, 24] and thus highlights the key role of the ligands in the 5-*exo-dig* versus 6-*endo-dig* competition.

Based on these results, cationic Pt(II) complexes, generated *in situ* from 5 mol.% of TMP-, DBP- and TPP- Pt(II) complexes and 10 mol.% of $AgSbF_6$,were evaluated. Results presented in Table 3 (entries 4-6) show the influence of the phosphole ligand on both activity and selectivity of the Pt-catalysed reaction. With TMP as ligand,, the Pt-catalysed rearrangement of enyne **1a** proceeds more readily than with $[Pt(PPh_3)_2Cl_2]/AgSbF_6$ catalytic system as higher conversion was observed after 1 h in toluene at 80°C affording a mixture of cyclopropane **2a** and diene **3a** in a 48/52 ratio (Table 3, entry 4). With DBP-based complex, the cycloisomerisation of **1a** is slower but more selective in cyclopropane **2a** (Table 3, entry 5), which can be attributed to the higher steric hindrance of DBP versus TMP. *Trans* TPP-based complex was the least active catalyst (Table 3, entry 6), with a low selectivity because of the *trans* configuration of the complex, despite of the bulkiness of TPP ligand. TMP appeared thus as the best ligand of the series in terms of activity in the cycloisomerisation of **1a**, as already observed in Au-catalysed cycloisomerisation.[16]

Following this preliminary screening, *cis*-$[Pt(TMP)_2Cl_2]$ was selected as the preferred catalytic precursor and a second series of experiments was performed in order to determine the optimal experimental conditions. Recent studies disclosed a profound influence of counterion and/or solvent on the efficiency and selectivity of gold-catalysed reactions involving alkyne activation.[25] A marked effect of the counterion has also been recently reported on the cyclopropane *versus* diene selectivity in a manganese-catalysed cycloisomerisation of 1,6-enynes.[26] In this context, the effects of the counterion and the solvent were evaluated in the platinum-catalysed cycloisomerisation of enyne **1a** (Table 4). It

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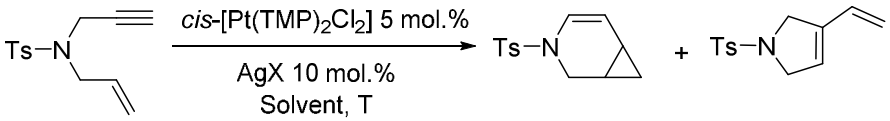
was found that in toluene the nature of the counterion affects the *exo*/*endo* selectivity in the cycloisomerisation of **1a** (Table 4, entries 1-3). Using $AgBF_4$, the 6-*endo-dig* cyclisation was favored promoting the cyclopropane formation (Table 4, entry 3) whereas the *exo*- and *endo*-cyclisations occur in the same time with $AgSbF_6$ and $AgNTf_2$, as compound **2a** and **3a** were obtained in a 48/52 ratio (Table 4, entries 1-2). These results support the proposal that the *exo*- and *endo*-cyclisation modes of 1,6-enyne differ little in energy[27] and also suggest that the nature of the counterion could influence the cyclisation pathways in a slightly dissociating solvent.

Interestingly, switching from toluene to 1,2-dichloroethane reverses the selectivity in favor to the diene **3a** (Table 4, entry 3 *versus* entry 4). This result shows that the cyclisation pathways, *exo*- versus *endo*-cyclisation modes, can also be influenced by the polarity of the solvent.

Moreover, the reaction could be performed at room temperature using $AgSbF_6$ although the reaction is slower (Table 4, entry 6, 79% conversion in 15h). The low conversion obtained at room temperature with $AgBF_4$ (Table 4, entry 5) is probably due to a low solubility of the cationic Pt-complex, generated *in situ* from $[Pt(TMP)_2Cl_2]$ and $AgBF_4$. Notably, in such a dissociative solvent as 1,2-dichloroethane which could be able to break-up the contact ion-pairs between cationic Pt(II) complex and SbF_6^- or BF_4^-, the anion has no influence on the selectivity of the reaction: the 5-*exo*-process is favored whatever the anion.

Table 4 : Survey of reaction conditions for the *cis*-$[Pt(TMP)_2Cl_2]$-catalysed cycloisomerisation of enyne **1a.**



1a **2a** **3a**

Entry	AgX	t (h)	T(°C)	Solvent	Conversion[a] (%)	**2a**[a] (%)	**3a**[a] (%)
1	$AgSbF_6$	1	80	toluene	96	48	52

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2	$AgNTf_2$	1	80	toluene	97	48	52
3	$AgBF_4$	1	80	toluene	88	87	13
4	$AgBF_4$	3	80	DCE	91	1	99
5	$AgBF_4$	15	23	DCE	6	0	100
6	$AgSbF_6$	15	23	DCE	79	1	99

[a]determined by ^{1}H-NMR.

Finally, TMP-based cationic Pt(II) complexes displayed a high degree of selectivity which could be controlled by the nature of the counterion and the solvent. The diene formation via 5-*exo dig* process is favored in DCE at 80°C with $AgBF_4$ or at room temperature with $AgSbF_6$ whereas the cycloisomerisation is orientated towards the cyclopropane formation via 6-*endo-dig* process in toluene at 80°C with $AgBF_4$.

Following this observation, a second series of experiments was then performed to examine the scope of the 1,6-enyne partner. Using optimised conditions, $[Pt(TMP)_2Cl_2]$ /$AgSbF_6$ system catalysed the cycloisomerisation of N-tethered 1,6-enynes **1b-c** and C-tethered 1,6-enyne **1d** in DCE at room temperature (Table 5). Enyne **1b** (Table 5, entry 2) underwent cycloisomerisation into a 20/80 mixture of 1,3-dienes **3b** (type **V** compound) and **4b** (type VI compound) both resulting from a *5-exo-dig* process. [6]. The selectivity observed in this cyclisation is in contrast to that obtained with $PtCl_2$ in acetone which led to cyclopropane **2b** and an 1,4-diene in a 55/45 ratio,[28] which again underlies the key-influence of the ligands. On the other hand, the cycloisomerisation of enyne **1c** lead to cyclopropane **2c** as the major product (Table 5, entry 3): the 6-*endo*-process was favored as expected for N-tethered enynes bearing a phenyl-substituant on the alkyne[24] and as already reported with our phosphole-based gold catalysts.[16] Finally, enyne **1d** was efficiently converted in 3 h at room temperature into the *exo*-diene **3d** from a 5-*exo-dig* process as expected for a C-tethered 1,6-enyne (Table 5, entry 4). This result shows again the efficiency of $[Pt(TMP)_2Cl_2]$ /$AgSbF_6$ system compare to $PtCl_2$ that requires higher temperature (80°C) to reach good conversions in 3h.[3-4] In addition, $[Pt(TMP)_2Cl_2]$/$AgSbF_6$ system appears more efficient on C-tethered 1,6-enynes than cationic

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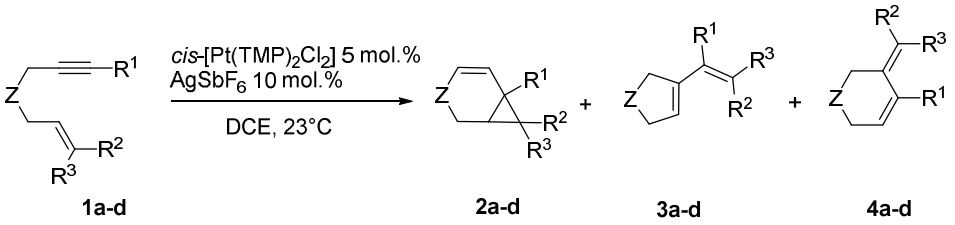
platinum complexes such as $[Pt(dppp)(PhCN)_2](BF_4)_2$ which requires longer reaction time (20h) at room temperature.[5]

Table 5: *cis*-$[Pt(TMP)_2Cl_2]$-catalysed cycloisomerisation of 1,6-enynes.



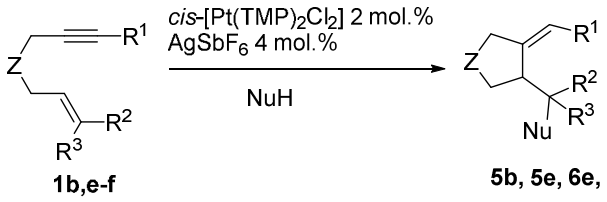
1a: Z= NTs, $R^1=R^2=R^3=H$;
1b: Z= NTs, $R^1=H$, $R^2=R^3=Me$;
1c: Z= NTs, $R^1=Ph$, $R^2=R^3=H$;
1d: Z= $C(CO_2Et)_2$, $R^1=R^2=R^3=H$

Entry	Enyne	t (h)	Conversion[a] (%)	**2**[a] (%)	**3**[a] (%)	**4**[a] (%)
1	**1a**	15	79	1	99	-
2	**1b**	15	99	-	20	80
3	**1c**	15	47	85	15	-
4	**1d**	3	99	-	100	-

[a]determined by ^{1}H-NMR.

To extend the scope of reactions catalysed by $[Pt(TMP)_2Cl_2]/AgSbF_6$ system, we finally investigated the tandem nucleophilic addition/cycloisomerisation of 1,6-enynes (Table 6). The reactions were carried out at 60°C in the presence of the Pt(II)-catalyst generated *in situ* from 2% mol. of *cis*-$[Pt(TMP)_2Cl_2]$ and 4% mol. of $AgSbF_6$.

Table 6: *cis*-$[Pt(TMP)_2Cl_2]$-catalysed nucleophilic addition to 1,6-enynes.



1b: Z= NTs, $R^1=H$, $R^2=R^3=Me$;
1e: Z= NTs, $R^1=R^2=H$, $R^3=Ph$;
1f: Z= $C(CO_2Et)_2$, $R^1=R^2=H$, $R^3=Ph$

5b: Z= NTs, $R^1=H$, $R^2=R^3=Me$, NuH=MeOH
5e: Z= NTs, $R^1=R^2=H$, $R^3=Ph$, NuH=MeOH
6e: Z= NTs, $R^1=R^2=H$, $R^3=Ph$, NuH=1-H-indole
6f: Z= $C(CO_2Et)_2$, $R^1=R^2=H$, $R^3=Ph$, NuH=1-H-indole

Entry	Enyne	NuH	Conditions	Product	Isolated yield (%)

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1	**1b**	MeOH	60°C, MeOH, 20h	**5b**	66
2	**1e**	MeOH	60°C, MeOH, 20h	**5e**	78
3	**1e**	1-H-indole	60°C, DCE, 15h	**6e**	74
4	**1f**	1-H-indole	60°C, DCE, 15h	**6f**	77

With N-tethered 1,6-enynes **1b** and **1e,** methoxycyclisation was exclusively observed to give five-membered ring alkoxy-compounds **5b** and **5e** (type **VIIIa** compounds) in high yields (Table 6, entries 1-2). The $[Pt(TMP)_2Cl_2]$ /$AgSbF_6$ catalytic system proved to be at least as efficient as $[Pt(CH_3CN)_2Cl_2]$ catalyst.[8d] Using 1H-indole as nucleophile, a similar intermolecular addition was observed on enynes **1e** and **1f** leading to the corresponding five-membered ring compounds **6e-f** (Table 6, entries 3-4). These results show again the efficiency of $[Pt(TMP)_2Cl_2]/AgSbF_6$ system compare to other cationic platinum complexes that require higher catalyst loading for analogous reactions.[9d] In addition, $[Pt(TMP)_2Cl_2]/AgSbF_6$ system appears more selective than gold(I) catalysts that promote also the formation of type **IX** compounds from C-tethered 1,6-enynes.[9a, 9b, 9d] Finally, *cis*-$[Pt(TMP)_2Cl_2]$-catalysed methoxycyclisation/cyclisation and hydroarylation/cyclisation tandem reactions occur with a regioselective addition of nucleophiles on the 5-*exo*-cyclopropyl carbene leading to type **VIIIa** coumpounds exclusively whatever the enyne's substitution pattern and its tether Z.

Conclusions

In summary, a series of platinum(II) complexes featuring two phosphole ligands has been prepared, fully characterised and evaluated in various reactions implying electrophilic activations of 1,6-enynes.

TMP appears as the best ligand, leading to a very active catalytic system able to achieve selective cycloisomerisation, alkoxycyclisation or tandem hydroarylation/cyclisation reactions in soft conditions. Moreover, the present work has highlighted that the regiochemical outcome of the reactions could be influenced by both the ligand and the counter-anion of the cationic

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catalyst and even that the reaction pathways could be somehow controlled by changing the solvent. Further studies are being launched to get insights into the mechanisms underlying these influences with the final objective of determining the optimal conditions to selectively convert an enyne into a valuable polycyclic compound in a single atom-economical step.

Experimental section

General methods

All commercially available reagents were used as received. Silver salts were stored under argon in Schlenk tubes. Unless otherwise stated, all reactions were run under Argon using Schlenk techniques. Dichloromethane and pentane were dried under N_2 using a solvent purification system (SPS). DCE was degassed with Argon for 10 minutes prior to use. NMR spectra were recorded at 25 °C on a Bruker Avance 500, 400 Ultrashield, a DPX300 or Fourier 300 Ultrashield apparatus. ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR chemical shifts are referenced to the solvent signal. $^{31}P\{^{1}H\}$ NMR chemical shifts are referenced to an external standard (85% aqueous H_3PO_4). Multiplicity as follows: s = singlet, d = doublet, t = triplet. ESI analysis were performed on a API-365 spectrometer.

Complex synthesis

For the synthesis of $[PtCl_2(L)_2]$ complexes, phosphole ligand L (0.373 mmol, 2.2 eq) was added to a solution of $[PtCl_2(PhCN)_2]$ (80 mg, 0.169 mmol, 1 eq) in 10 mL of DCM. The reaction mixture was stirred 3 h at room temperature. Then it was concentrated to approximately 0.5 mL, precipitated and washed with 3x15 mL of pentane. $[PtCl_2(TMP)_2]$ $[PtCl_2(DBP)_2]$ and $[PtCl_2(TPP)_2]$ complexes were obtained as air- and moisture-stable powders.

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***cis*-[$PtCl_2(TMP)_2$]**

White powder, yield: 76%. Crystals were grown from air diffusion of a solution of pentane to a DCM solution of the complex. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.51-7.35 (m, 5H, Ph), 1.95 (s, 6H, CH_3), 1.90 (d, 6H, *J* = 12Hz, CH_3). $^{13}C\{^1H\}\{^{31}P\}$ NMR (125 MHz, CD_2Cl_2) δ 147.8, 131.4, 130.3, 129.7, 128.2, 127.9, 13.8, 12.1. ^{31}P NMR (202 MHz, $CDCl_3$) δ 24.6 (s+sat., $^1J(^{195}Pt/^{31}P) = 3330$ Hz). ESI m/z calc. for $C_{28}H_{34}Cl_2P_2Pt$:698.5, found 663 $[M\text{-}Cl]^+$.

***cis*-[$PtCl_2(DBP)_2$]**

White powder, yield: 72%. Crystals were grown from air diffusion of a solution of pentane to a DCM solution of the complex. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.58 (t, 1H, *J* = 6Hz, Ph), 7.45 (m, 4H, Ph), 7.39-7.20 (m, 8H, arom). $^{13}C\{^1H\}\{^{31}P\}$ NMR (125 MHz, CD_2Cl_2) δ 142.5, 131.9, 131.3, 131.1, 130.5, 130.3, 129.0, 128.0, 121.9. $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$) δ 5.2 (s+sat., $^1J(^{195}Pt/^{31}P) = 3492$ Hz). ESI m/z calc. for $C_{36}H_{26}Cl_2P_2Pt$: 786.5, found 786.1 $[M]^+$.

***trans*-[$PtCl_2(TPP)_2$]**

Yellow powder, yield: 84%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.09 (d, 2H, *J* = 4Hz, $C_\beta H$), 7.62 (m, 5H, Ph), 7.38-7.20 (m, 10H, Ph). $^{13}C\{^1H\}\{^{31}P\}$ NMR (100 MHz, CD_2Cl_2) δ 135.7, 133.5, 133.2, 131.0, 128.8, 128.7, 128.5, 128.2, 127.5, 126.8. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.34 (s+sat., $^1J(^{195}Pt/^{31}P) = 2520$ Hz). ESI m/z calc. for $C_{44}H_{34}Cl_2P_2Pt$: 890.7, found: 855.1 $[M\text{-}Cl]^+$.

Crystal structure determination

Diffraction data were collected at low temperature (180 K) on a Bruker Kappa Apex II using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The diffractometer is equipped with an Oxford Cryosystems Cryostream cooler device. The structures were solved by direct

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methods SHELXS-97. All non-hydrogen atoms were refined anisotropically by means of least-squares procedures on F^2 with the aid of the program SHELXL-97.[29] Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with deposition numbers CCDC 974005 and 974006.

Catalytic tests

General procedure for enyne cycloisomerisation:

In a dried schlenk was added the enyne (0.16 mmol, 1 eq) and the platinum complex (0.008 mmol, 5 mol.%) in 1.6 mL of DCE or toluene (0.1 M). The silver salt (10 mol.%) was then added and the reaction mixture was stirred for the appropriate time. Then it was filtered through a pad of silica, eluting with DCM to remove precipitates. Finally, it was concentrated for analysis. Structural data of the cycloisomerised products **2a**,[3] **3a**,[3] **3b**,[30] **4b**,[31] **2c**,[24] **3c**[24] and **3d**[3] were in agreement with the literature.

General procedure for methoxycyclisation reation:

In a dried schlenk was added the enyne (0.5 mmol, 1 eq) and the platinum complex (0.025 mmol, 5 mol.%) in DCE/MeOH (2/1, 0.2 M). The solution was warmed up to 60 °C and $AgSbF_6$ (0.05 mmol, 10 mol.%) was then added. After stirring for the appropriate time at 60°C, the crude was submitted to silica gel chromatography using Hexanes/AcOEt as eluent. The structural data of **5b** and **5e** were perfectly in agreement with the literature.[8d]

General procedure for hydroarylation/cyclisation:

In a dried schlenk was added the enyne (0.5 mmol, 1 eq), 1-H-indole (0.15 mmol, 3 eq) and the platinum complex (0.025 mmol, 5 mol.%) in DCE (0.3 M). The solution was warmed up to 60°C, and $AgSbF_6$ (0.05 mmol, 10 mol.%) was then added. After stirring for the appropriate time at 60°C, the crude was submitted to silica gel chromatography using

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Hexanes/AcOEt as eluent. The structural data of **6e** and **6f** were perfectly in agreement with the literature. [9a]

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Notes and References

1 For recent reviews see: (a) A. Fürstner and P. W. Davies, *Angew. Chem., Int. Ed.*, 2007, **46**, 3410-3449; (b) V. Michelet, P. Y. Toullec and J.-P. Genêt, *Angew. Chem., Int. Ed.*, 2008, **47**, 4268-4315; (c) A. Furstner, *Chem. Soc. Rev.*, 2009, **38**, 3208-3221; (d) E. Jimenez-Nunez and A. M. Echavarren, *Chem. Commun.*, 2007, 333-346; (e) E. Jimenez-Nunez and A. M. Echavarren, *Chem. Rev.*, 2008, **108**, 3326-3350; (f) E. Herrero-Gomez and A. M. Echavarren, in *Handbook of Cyclization Reactions*, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, vol. 2, pp. 625-686.

2 E. Soriano and J. Marco-Contelles, *Acc. Chem. Res.*, 2009, **42**, 1026-1036 and references therein.

3 A. Fürstner, F. Stelzer and H. Szillat, *J. Am. Chem. Soc.*, 2001, **123**, 11863-11869.

4 N. Chatani, N. Furukawa, H. Sakurai and S. Murai, *Organometallics*, 1996, **15**, 901-903.

5 S. Oi, I. Tsukamoto, S. Miyano and Y. Inoue, *Organometallics*, 2001, **20**, 3704-3709.

6 N. Cabello, E. Jiménez-Núñez, E. Buñuel, D. J. Cárdenas and A. M. Echavarren, *Eur. J. Org. Chem.*, 2007, 4217-4223.

7 C. Obradors and A. M. Echavarren, *Acc. Chem. Res.*, ASAP, DOI**:**10.1021/ar400174p.

8 Selected references: (a) M. Méndez, M. P. Muñoz and A. M. Echavarren, *J. Am. Chem. Soc.*, 2000, **122**, 11549-11550; (b) M. P. Munoz, M. Mendez, C. Nevado, D. J. Cardenas and A. M. Echavarren, *Synthesis*, 2003, 2898-2902; (c) M. P. Muñoz, J. Adrio, J. C. Carretero and A. M. Echavarren, *Organometallics*, 2005, **24**, 1293-1300; (d) C. Nevado, L. Charruault, V. Michelet, C. Nieto-Oberhuber, M. P. Munoz, M. Mendez, M.-N. Rager, J.-P. Genet and A. M. Echavarren, *Eur. J. Org. Chem.*, 2003, 706-713; (e) L. Charruault, V. Michelet, R. Taras, S. Gladiali and J.-P. Genet, *Chem. Comm.*, 2004, 850-851; (f) V. Michelet, L. Charruault, S. Gladiali and J.-P. Genet, *Pure Appl. Chem.*, 2006, **78**, 397-407; (g) C.-M. Chao, M. R. Vitale, P. Y. Toullec, J.-P. Genêt and V. Michelet, *Chem. Eur. J.*, 2009, **15**, 1319-1323; (h) N. Mezailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **7**, 4133-4136.

9 (a) C. H. M. Amijs, C. Ferrer and A. M. Echavarren, *Chem. Commun.*, 2007, 698-700; (b) C. H. M. Amijs, V. n. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer and A. M. Echavarren, *J. Org. Chem.*, 2008, **73**, 7721-7730; (c) P. Y. Toullec, E. Genin, L. Leseurre, J.-P. Genet and V. Michelet, *Angew. Chem., Int. Ed.*, 2006, **45**, 7427-7430; (d) P. Y. Toullec, C.-M. Chao, Q. Chen, S. Gladiali, J.-P. Genet and V. Michelet, *Adv. Synth. Catal.*, 2008, **350**, 2401-2408; (e) L. Leseurre, C.-M. Chao, T. Seki, E. Genin,

Dalton Transactions Accepted Manuscript

P. Y. Toullec, J.-P. Genet and V. Michelet, *Tetrahedron*, 2009, **65**, 1911-1918; (f) A. Pradal, C.-M. Chao, M. R. Vitale, P. Y. Toullec and V. Michelet, *Tetrahedron*, 2011, **67**, 4371-4377.

10 (a) A. Fürstner and P. W. Davies, *J. Am. Chem. Soc.*, 2005, **127**, 15024-15025; (b) A. Fuente-Hernàndez, P. Costes, P. Kalck, U. Jáuregui-Haza, O. Dechy-Cabaret and M. Urrutigoïty, *Appl. Organomet. Chem.*, 2011, **25**, 815-819.

11 S. Baumgarten, D. Lesage, V. Gandon, J.-P. Goddard, M. Malacria, J.-C. Tabet, Y. Gimbert and L. Fensterbank, *ChemCatChem*, 2009, **1**, 138-143.

12 Y. Gimbert, L. Fensterbank, V. Gandon, J.-P. Goddard and D. Lesage, *Organometallics*, 2013, **32**, 374-376.

13 C. Ferrer, M. Raducan, C. Nevado, C. K. Claverie and A. M. Echavarren, *Tetrahedron*, 2007, **63**, 6306-6316.

14 (a) D. Brissy, M. Skander, P. Retailleau and A. Marinetti, *Organometallics*, 2007, **26**, 5782-5785; (b) D. Brissy, M. Skander, H. Jullien, P. Retailleau and A. Marinetti, *Org. Lett.*, 2009, **11**, 2137-2139; (c) D. Brissy, M. Skander, P. Retailleau, G. Frison and A. Marinetti, *Organometallics*, 2009, **28**, 140-151; (d) H. Jullien, D. Brissy, R. Sylvain, P. Retailleau, J.-V. Naubron, S. Gladiali and A. Marinetti, *Adv. Synth. Catal.*, 2011, **353**, 1109-1124.

15 D. Carmichael, in *Phosphorus(III) Ligands in Homogeneous Catalysis*, John Wiley & Sons Ltd., 2012, pp. 267-285.

16 K. Fourmy, S. Mallet-Ladeira, O. Dechy-Cabaret and M. Gouygou, *Organometallics*, 2013, **32**, 1571-1574.

17 (a) J. J. MacDougall, J. H. Nelson and F. Mathey, *Inorg. Chem.*, 1982, **21**, 2145-2153; (b) Y. Matano, M. Fujita, A. Saito and H. Imahori, *Comptes Rendus Chimie*, 2010, **13**, 1035-1047; (c) Y. Matano, M. Nakashima, A. Saito and H. Imahori, *Org. Lett.*, 2009, **11**, 3338-3341; (d) Y. Dienes, M. Eggenstein, T. Neumann, U. Englert and T. Baumgartner, *Dalton Trans.*, 2006, 1424-1433; (e) Z. Csók, G. Keglevich, G. Petőcz and L. Kollár, *Inorg. Chem.*, 1999, **38**, 831-833; (f) J. Hydrio, M. Gouygou, F. Dallemer, G. G. A. Balavoine and J.-C. Daran, *J. Organomet. Chem.*, 2002, **643-644**, 19-26; (g) M. Ogasawara, K. Yoshida and T. Hayashi, *Organometallics*, 2001, **20**, 1014-1019; (h) T. Nakabuchi, Y. Matano and H. Imahori, *Organometallics*, 2008, **27**, 3142-3152.

18 Z. Csók, G. Keglevich, G. Petöcz and L. Kollár, *J. Organomet. Chem.*, 1999, **586**, 79-84.

19 (a) P. J. Fagan and W. A. Nugent, *Org. Synth.*, 1992, **70**, 272-275; (b) P. J. Fagan, W. A. Nugent and J. C. Calabrese, *J. Am. Chem. Soc.*, 1994, **116**, 1880-1889.

20 S. Affandi, R. L. Green, B. T. Hsieh, M. S. Holt, J. H. Nelson and E. C. Alyea, *Synth. React. Inorg. Met.-Org. Chem.* , 1987 **17**, 307-318.

21 I. G. M. Campbell, R. C. Cookson, M. B. Hocking and A. N. Hugues, *J. Chem. Soc.*, 1965, 2184-2193.

22 J. Forniés-Cámer, A. M. Masdeu-Bultó and C. Claver, *Inorg. Chem. Comm.*, 2002, **5**, 351-354.

23 M. S. Holt, J. H. Nelson and N. W. Alcock, *Inorg. Chem.*, 1986, **25**, 2288-2295.

24 A. Fürstner, H. Szillat and F. Stelzer, *J. Am. Chem. Soc.*, 2000, **122**, 6785-6786.

25 (a) T. Zhou, L. Xu and Y. Xia, *Org. Lett.*, 2013; (b) Y. Yu, W. Yang, F. Rominger and A. S. K. Hashmi, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 7586-7589; (c) A. S. Dudnik, Y. Xia, Y. Li and V. Gevorgyan, *J. Am. Chem. Soc.*, 2010, **132**, 7645-7655; (d) W. Li, Y. Li and J. Zhang, *Chem. Eur. J.*, 2010, **16**, 6447-6450; (e) P. W. Davies and N. Martin, *Org. Lett.*, 2009, **11**, 2293-2296.

26 T. Ozawa, T. Kurahashi and S. Matsubara, *Org. Lett.*, 2012, **14**, 3008-3011.

Dalton Transactions Accepted Manuscript

27 C. Nevado, D. J. Cardenas and A. M. Echavarren, *Chem. Eur. J.*, 2003, **9**, 2627-2635.
28 M. Mendez, M. P. Munoz, C. Nevado, D. J. Cardenas and A. M. Echavarren, *J. Am. Chem. Soc.*, 2001, **123**, 10511-10520.
29 G. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.
30 C. Nieto-Oberhuber, M. P. Munoz, S. Lopez, E. Jimenez-Nunez, C. Nevado, E. Herrero-Gomez, M. Raducan and A. M. Echavarren, *Chem. Eur. J.*, 2006, **12**, 1677-1693.
31 W. Cao and B. Yu, *Adv. Synth. Catal.*, 2011, **353**, 1903-1907.

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Platinum(II) – phosphole complexes : synthesis and evaluation as enyne cycloisomerisation catalysts.

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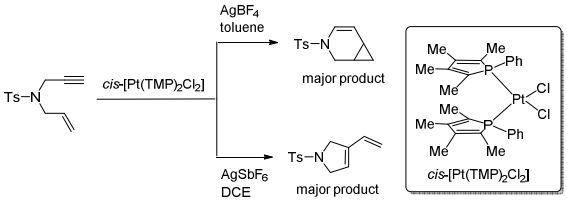
Graphic for Table of Contents



Text for Table of Contents

Cis-[$Pt(TMP)_2Cl_2$] is the most efficient of a series of Platinum(II)-monophosphole complexes synthesized and used in various enyne cycloisomerisations.

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