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Cationic Complexes of Palladium(II) and Platinum(II) as Lewis Acid Catalysts for the Diels−Alder Reaction

Kristian Pignat, Jacopo Vallotto, Francesco Pinna, and Giorgio Strukul*

Department of Chemistry, University of Venice, 30123 Venezia, Italy

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The synthesis of a series of Pd(II) and Pt(II) cationic complexes of the types [(P−P)M(solv)](Y)$_2$, [(P−P)M(η^2-Y)](Y), and [(P−P)M(μ-Cl)]$_2$(Y)$_2$ (where P−P = various diphosphines including chiral diphosphines (M = Pd, Pt; Y = TfO$^-$, ClO$_4^-$, BF$_4^-$) is reported. All complexes are excellent catalysts for the Diels−Alder reaction between cyclopentadiene or cyclohexadiene and a number of simple dienophiles such as acrolein, methacrolein, and methylvinyl ketone. Some of the complexes modified with chiral diphosphines can act as enantioselective catalysts in the Diels−Alder reaction under mild condition with moderate ee's. A critical point in this respect is the presence of only one vacant coordination site in the catalyst.

Introduction

Square-planar complexes of Pd(II) and, to a minor extent, Pt(II) have long been recognized to play a central role in homogeneous catalysis in processes such as the classical Wacker process[1] or, more recently, the copolymerization of carbon monoxide and olefins.[2] In the past two decades we have extensively studied the properties of cationic Pd(II) and Pt(II) complexes in a variety of oxidation reactions using hydrogen peroxide as oxidant.[3−5] A typical feature displayed by the metal in the latter reactions is the ability to increase the reactivity of the substrate by coordination, thereby making it more prone to attack by the peroxidic oxidant. An essential requirement to promote this kind of reactivity is the presence of a positive charge on the metal, which, therefore, possesses a significant Lewis acidity.

The Lewis acidity of these complexes has been recently exploited in the acetalyzation of a variety of aldehydes and ketones,[6] where some unusual selectivities with respect to ordinary Brønsted acids were observed, especially in the case of α,β-unsaturated substrates.[7]

The Diels−Alder reaction is a typical Lewis acid catalyzed process, which consists of a 4+2 cycloaddition between a diene and a dienophile. Being concerted and stereoselective, it is widely used in synthetic organic chemistry.[8] In the past two decades several attempts have been made to accomplish the reaction enantioselectively, initially, by complexing ordinary Lewis acids (AlX$_3$, BX$_3$, SnX$_4$, etc.) with suitable chiral ligands[9] and, subsequently, by using transition metal complexes, among which those of Co,[9c] Fe,[9c,10] Mo,[11] Ni,[12] Cu,[13] Ru,[14] V,[15] W,[11] Yb,[16] and Ti[9c,17] have proved to be particularly interesting, often showing ee's in the >95% range.

The behavior of noble metal complexes in the Diels−Alder reaction has not been satisfactorily exploited,

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* Corresponding author at: Department of Chemistry, University of Venice, Dorsoduro 2137, 30123 Venezia, Italy. Tel: +39 041 257 8551. Fax: +39 041 257 8517. E-mail: strukul@unive.it.

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[2] See for example: (a) Drent, E.; van Broekhoven, J. A. M.; Budzelaar, P. H. M. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1997; Vol. 1, Chapter 2.3.4, p 333. (b) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (c) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (d) Drent, E. Eur. Patent Appl. 251373, 1987, and references therein.

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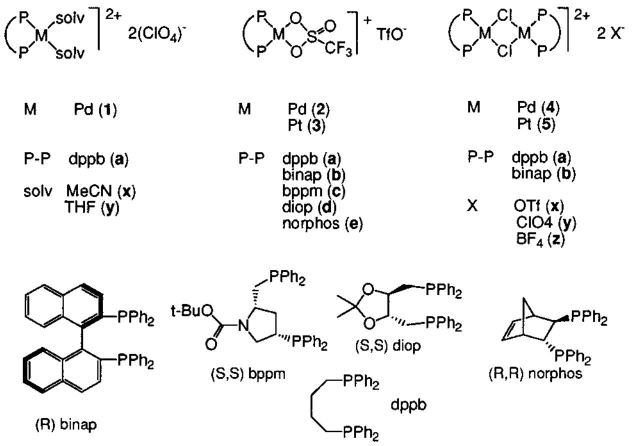
10.1021/om0003943 CCC: $19.00

Table 1. Spectroscopic Features of the Complexes Shown in Chart 1[a]

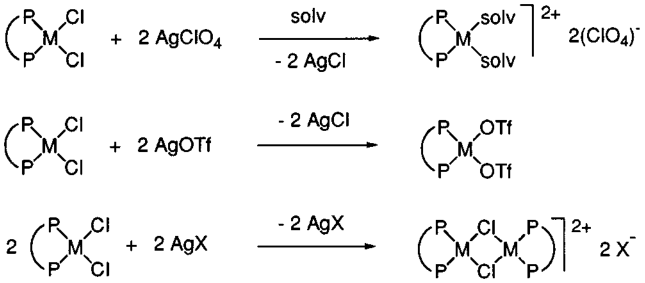
complex	IR (cm^{-1})	^{31}P{^{1}H} NMR (ppm, J in Hz)	Λ_M (Ω^{-1} mol^{-1} cm^2)
1ax	2294, 2322 1096	33.0 (s); 37.2 (s)[b]	259[c]
1ay	1097	37.6 (s)[b]	265[c]
2a	1286, 1258, 1224, 1153, 1100, 1034	36.87 (s); 33.86 (s)	124
2b	1282, 1256, 1227, 1167, 1098, 1032	34.47 (s); 32.2 (s)	123
2c	1290, 1261, 1227, 1163, 1099, 1032	24.27 (d), $^2J_{P-P}$ 16, 48.0 (d) $^2J_{P-P}$ 46; 28.9 (d), $^2J_{P-P}$ 16, 48.8 (d), $^2J_{P-P}$ 16	100
2d	1289, 1261, 1225, 1167, 1100, 1027	21.86 (s); 24.85 (s)	140
2e	1288, 1250, 1227, 1167, 1101, 1030	42.03 (d), $^2J_{P-P}$ 21, 42.96 (d), $^2J_{P-P}$ 21	118
3a	1291, 1259, 1225, 1153, 1104, 1030	13.58 (s), $^1J_{P-Pt}$ 3656	151
3b	1284, 1254, 1227, 1167, 1101, 1030	2.31 (s), $^1J_{P-Pt}$ 4039	141
4ax	298, 278	36.93 (s)	143[d]
4bx	303, 279	34.55 (s); 29.82 (s)[b]	
4by	303, 280	34.32 (s); 29.76 (s)[b]	177
4bz	303, 280	34.29 (s); 32.8 (d), $^2J_{P-P}$ 7.9, 31.0 (d), $^2J_{P-P}$ 7.9; 29.76 (s)[b]	203
5az	295, 282	13.49 (s), $^1J_{P-Pt}$ 3668	272
5bx	303, 280	8.78 (s), $^1J_{P-Pt}$ 3816	216
5by	303, 280	8.53 (s), $^1J_{P-Pt}$ 3820	227
5bz	303, 280	8.60 (s), $^1J_{P-Pt}$ 3819	218

[a] Experimental conditions: IR in KBr pellet, NMR in CD_2Cl_2 at room temperature unless otherwise posted, conductivity 10^{-3}M solutions in acetone. [b] At −70 °C. [c] 10^{-3} M solutions in MeCN. [d] 10^{-3} M solutions in MeOH.

Chart 1



Scheme 1



probably because being electron-rich their choice is less obvious, as they are generally considered more as bases rather than acids. Some interesting examples in which Pd(II) and Pt(II) species have been used to catalyze the asymmetric aldol reaction or asymmetric 1,3-dipolar cycloadditions have recently appeared in the literature.[18,19] In this paper we wish to report our attempts to apply the Lewis acidity of a wide class of homologous, cationic complexes of Pd(II) and Pt(II) in the Diels–Alder reaction, with the ultimate aim of performing this transformation enantioselectively.

Results and Discussion

The Catalysts. A summary of the complexes used in the present study is shown in Chart 1, and their synthetic route is reported in Scheme 1. The basic idea behind the choice of these complexes is to have at least one positive charge located on the potential catalytically active fragment, to have a sufficient Lewis acid character. As will be clear in the foregoing, the different types of complexes shown in Chart 1 reflect an evolution of the catalyst that was found necessary depending on the results observed in the catalytic reactions. Although the synthetic procedures outlined in Scheme 1 are quite well known, the formulation of the complexes as in Chart 1 is in many cases merely conventional, as is shown by their characterization data based on IR and ^{31}P{^{1}H} NMR spetroscopies and on molar conductivity measurements (Table 1).

Complex **1ax** shows the typical asymmetric and symmetric IR bands of coordinated acetonitrile along with a strong, broad band centered at 1096 cm^{-1} typical of ClO_4^-. The homologous **1ay** does not give evidence for the coordination of THF; however an IR spectrum in DCE where a stoichiometric amount of MeCN was added showed again the presence of bands at 2291 and 2325 cm^{-1}, indicating the presence in the original complex of labile solvento ligands. Conductivity data in MeOH for both **1ax** and **1ay** are consistent with the presence of 2:1 electrolytes.[20] The NMR spectra of these complexes in CD_2Cl_2 are more complex than expected. In the case of **1ax**, two singlets are present at room temperature (Figure 1 middle), which can be associated with species having magnetically equivalent phosphorus nuclei. Addition of an excess of MeCN increased significantly the intensity of the signal at 32.8 ppm (Figure

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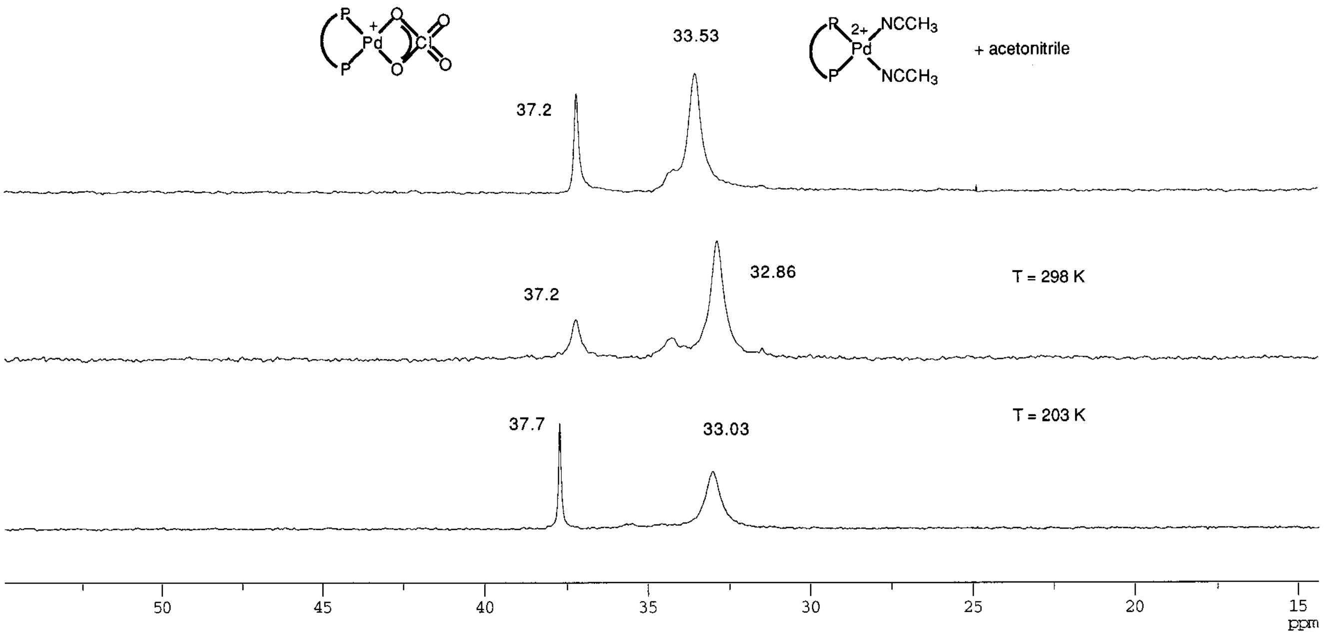
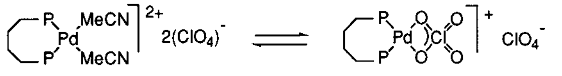


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of complex **1ax** in CD_2Cl_2: middle, the spectrum at room temperature; top, the same + excess MeCN added; bottom, at −70 °C.

1, top), indicating that this was most likely the expected bis-solvento complex. We suggest that the species at 37.2 ppm is probably a η^2 perchlorate derivative in equilibrium with the expected complex (eq 1), probably



(1)

via the Pd(NCMe)($OClO_3$) mixed ligand complex, which would account for the broad minor signals present in the spectrum. The formation of η^2 perchlorate complexes has already been suggested in the literature during the synthesis of bis-solvento complexes of the type here reported.[21] The η^2 perchlorate derivative appears to be more favored at −70 °C as shown by the corresponding NMR spectrum (Figure 1, bottom). The $^{31}P\{^1H\}$ NMR spectrum of complex **1ay** is quite similar. At room temperature singlets at 33.9 and 37.0 ppm are observed together with new singlets at 31.3 and 36.4 ppm. At −70 °C the singlet at about 37 ppm is the only detectable signal, indicating that the η^2 perchlorate derivative most likely becomes the dominant species, in agreement with the lower coordination properties of THF with respect to MeCN.

The apparent discrepancy between the NMR data and the molar conductivity data can be explained by simply considering the different solvents (CD_2Cl_2 and MeOH, respectively).

Complexes **2** and **3** show in all cases a series of bands in the 1000−1300 cm^{-1} region (Table 1) that can be attributed to the different stretching modes of the coordinated $CF_3SO_3^-$ anion, in agreement with that reported in the literature[22] for Pt(II) complexes, together with other minor bands due to the stretching of uncoordinated triflate. In agreement with this assignment is the observation that the molar conductivity data of all complexes in MeOH fall in the range of 1/1 electrolytes. These observations are a strong argument in favor of a formulation like the one reported in Chart 1. However, the $^{31}P\{^1H\}$ NMR spectrum of **2a** at room temperature shows two moderately broad singlets, one at 36.87 ppm and a much weaker (~10% in intensity) one at higher fields (33.86 ppm). At −60 °C the former signal becomes the only one present in the spectrum, indicating that this is the most stable species at low temperature. Consistently with the IR and the molar conductivity data, we suggest that the major species observed in the NMR spectrum is a cationic complex containing one OTf moiety coordinated η^2 to the metal and one TfO^- moiety as external anion (eq 2), as was

(2)

already suggested in the literature for other triflate complexes,[23] while the minor component is most likely the bis-triflate neutral complex. The situation is similar for complexes **2b** and **2d**, where a formulation like the one reported in Chart 1 applies to the major component (~90%) of the mixture observed by NMR. This is associated with the signals at 34.37 ppm (**2b**) and 21.86 ppm (**2d**). In the case of **2e** only two doublets are observed with evidence for P−P coupling, in agreement with the magnetic inequivalence of the P donors in norphos. No evidence for other signals to be associated with the neutral species is seen in the $^{31}P\{^1H\}$ NMR spectrum. The case of **2c** is apparently more complex. Two sets of signals of similar intensity are evident in the $^{31}P\{^1H\}$ NMR spectrum, each corresponding to a species having two inequivalent phosphorus nuclei mutually coupled. As has been previously observed in the case of some Pt complexes[5] and in the case of the

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[21] Davis, J. A.; Hartley, F. R.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2246.

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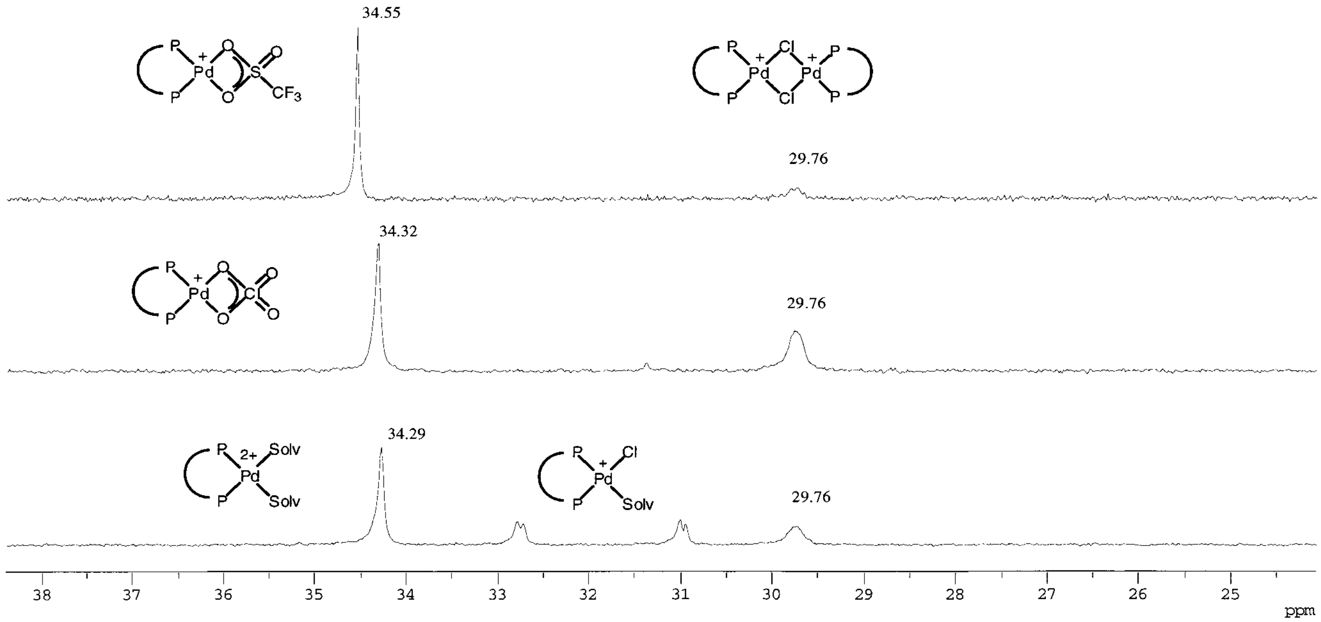
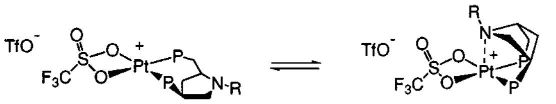


Figure 2. $^{31}P\{^1H\}$ NMR spectra of different complexes in CD_2Cl_2 at −70 °C: top, complex **4bx**; middle, complex **4by**; bottom, complex **4bz**.

corresponding Pd dichlorides,[5] these signals are attributed to an equilibrium of the type shown in eq 3,



(3)

where the N donor in the diphosphine is able to bind the metal from the axial position giving rise to a square pyramidal isomeric species. Other minor signals (<10%) present in the NMR spectrum are attributed to neutral species as in the previous cases, on the basis of the extent of the molar conductivity of complex **2c**.

The corresponding complexes of platinum (**3a**, **3b**) show simpler $^{31}P\{^1H\}$ NMR spectra, where only one singlet is present at room temperature flanked by ^{195}Pt satellites. Molar conductivity data correspond to 1/1 electrolytes,[20] supporting the formulation of complexes as in Chart 1.

All complexes of type **4** and **5** show M−Cl stretching frequencies in the range 270−310 cm^{-1} as well as molar conductivities that fall in the range of 2/1 electrolytes. The corresponding $^{31}P\{^1H\}$ NMR spectra at room temperature are regular and correspond to the formulation of Chart 1 in the cases of complex **4ax** and complexes of type **5**. In all cases a sharp singlet (with P−Pt coupling in the case of platinum species) is observed, and lowering the aquisition temperature causes no appreciable changes. Conversely, binap-containing palladium complexes **4bx**, **4by**, and **4bz** all give a very broad signal centered at 31−33 ppm at room temperature. At −70 °C the spectra shown in Figure 2 are observed. As can be seen, they all show a singlet at 29.8 ppm and another stronger singlet in the 34.3−34.6 range. In the case of the complex containing BF_4^- also a third species appears, showing inequivalent phosphorus nuclei with evidence of P−P coupling. The singlet at 29.8 that is present in all spectra can be most likely attributed to the expected cationic bridging chloro complex with different counterions. The species at ∼34.5 ppm for complex **4bx** is the same observed in complex **2b** and is attributed to $[(binap)Pd(\eta^2\text{-}OTf)]^+$, where the Cl ligand has been replaced by TfO^- and is present only as the external counterion. By analogy, the signal at 34.32 ppm in the spectrum of the perchlorate derivative (**4by**) is attributed to a monomeric species having the same features (Figure 2), similarly to what was already observed for **1ax** and **1ay**. The case of **4bz** may be different. Indeed, examples of η^2 coordination in the case of BF_4^- have never been reported in the literature. A formulation like in **4bx** and **4by** implies the presence of two F atoms coordinated to the metal mutually *cis*, and this would require in the $^{31}P\{^1H\}$ NMR spectrum a coupling of each P atom with both the F atom in *cis* and the F atom in *trans*. The spectrum in Figure 2 gives no evidence for that, and the species at 34.32 ppm is probably better described as a bis-solvento species. Additionally, the third species present in **4bz** is consistent with a complex having both Cl and a solvent molecule coordinated to Pd.

In summary, complexes **4b** display significant differences from what was initially expected. The proposal for the existence of η^2-coordinated ClO_4 ligands although not common is not unprecedented,[21,24] while the case of the BF_4^- derivative is to some extent surprising, as it seems to evidence that Cl^- when coordinated to Pd is so labile that it can be replaced by a weak donor such as CH_2Cl_2. For the understanding of the catalytic results that will be presented below, it has to be pointed out that although at −70 °C the spectra of **4bx** and **2b** are practically identical, at the temperature at which catalytic runs have been carried out the composition of the catalyst mixture is most likely different.

Catalytic Experiments. Complexes **1a**, **2a**, and **3a** were tested to check their suitability as catalysts for the Diels−Alder reaction. A selection of the results

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Scheme 2

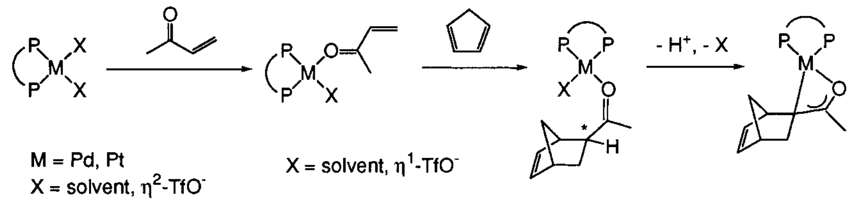
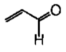
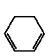
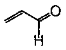
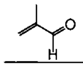
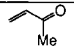
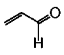
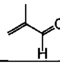
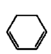
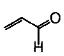


Table 2. Catalytic Activity in the Diels–Alder Reaction of Achiral Complexes 1–3

Complex	Diene	Dienophile	Conversion (%)	Time (min)	endo/exo
1ay			99	5	6.1
1ax			98[a]	55	7.3
1ay			99[a]	55	7.3
3a			90	2	6.5
1ay			90	93	19
3a			84	230	25
2a			80	240	32
1ay			82	1560	0.25
1ax			93	240	49

[a] Reaction conditions: catalyst 10 μmol, diene 1 mmol, dienophile 1 mmol, DCE 3 mL, T 25 °C, N_2 1 atm. a. Catalyst 1 μmol, T 0 °C.

Table 3. Enantioselective Diels–Alder Transformations Using Complexes 2 and 3 as Catalysts[a]

Cmplx	Diene	Dienophile	T (°C)	Conv (%)	Time (min)	endo/exo	e.e. (%) exo	e.e. (%) endo
2b			0	99	21	7.3	9	2
2b			-20	98	97	8.1	10	2
2c			-20	84	1200	8.1	10	3
2d			-20	83	1200	8.1	12	3
2e			-20	88	92	7.3	8	2
3b			0	90	20	7.8	9	10
3b			-20	92	1500	6.0	7	15
2b			-5	72	25	0.18	5	0
2b			25	80	1200	49	0	0
3b			25	90	1400	31	18	8

[a] Reaction conditions: catalyst 10 μmol, diene 1 mmol, dienophile 1 mmol, DCE 3 mL, N_2 1 atm.

obtained is presented in Table 2. As can be seen, in the reaction between cyclopentadiene and acrolein the solvento complexes of type **1** show excellent activity (even at low temperature) and a moderate selectivity toward endo compounds. In the case of less reactive substrates such as cyclohexadiene again a good catalytic activity is observed even with dienophiles such as methacrolein and methylvinyl ketone that are known to be moderately reactive. Some interesting features are also observed, namely, the generally higher selectivity toward endo compounds and the preferential formation of the exo isomer in the reaction with methacrolein with **1ay** as catalyst. In these experiments, no particular differences were observed between Pd and Pt complexes.

On the basis of the good results reported above, complexes **2** and **3** were tested in the enantioselective version of some of the reactions reported in Table 3. Cyclopentadiene and cyclohexadiene were chosen as the dienes, while acrolein was chosen as the dienophile, at least for the initial screening. The results are summarized in Table 3. As can be seen, the reactivity in the conversion of cyclopentadiene is good for most complexes even at low temperature. The Pt complex **3b** shows a conversion similar to the Pd homologue **2b** at 0 °C, while at −20 °C its reactivity is lower. With cyclohexadiene, reactions were carried out at 25 °C because at lower temperatures the reaction times become exceedingly long. In the case of Pd complexes the ee's observed are virtually negligible, whereas in the case of the Pt complex **3b** the results are only slightly better. It has to be pointed out that, in the case of exo isomers, ee apparent values around 10% may fall within the experimental error associated with analysis (GC).

It is conceivable that the Diels–Alder transformation proceeds through the displacement of the labile ligands (solvent molecules in the case of **1** and TfO^- in the case of **2** and **3**), leading to intermediates in which the dienophile binds the catalyst through the oxygen donor. Under these circumstances the use of complex **1** and that of complexes **2** and **3** as catalysts should lead to the formation of closely related intermediates probably still containing a very labile ligand (a solvent molecule or η^1-TfO^-). The possibility that after the 4+2 cycloaddition the presence of a vacant coordination site on the metal may easily lead to the formation of an enolate (Scheme 2, charges omitted for simplicity), washing out possible ee's, was checked using methacrolein that does not contain enolizable hydrogens. As can be seen in Table 2, negligible ee's are observed even in this case.

The idea that two adjacent vacant coordination sites on the catalyst may lead to a negative effect on the asymmetric induction seems to be confirmed by the work of Inoue and co-workers.[25] While the present work was in progress, these authors reported that using Pd complexes very similar to **1** and **2**, good ee values could be observed only using *N*-acryloyloxazolidinone as the dienophile. This dienophile is rather common in asymmetric transition metal catalyzed Diels–Alder reactions as, being able to chelate the transition metal as in Figure 3A, it creates a rigid template and forces the system to present preferentially one side of the C=C double bond to the incoming diene. With ordinary dienophiles (see in Figure 3B,C the case of acrolein) the availability of two adjacent coordination sites will lead to two alternative situations, *pro-R* and *pro-S*, with

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[25] Oi, S.; Kashiwagi, K.; Inoue, Y. *Tetrahedron Lett.* **1998**, *39*, 6253.

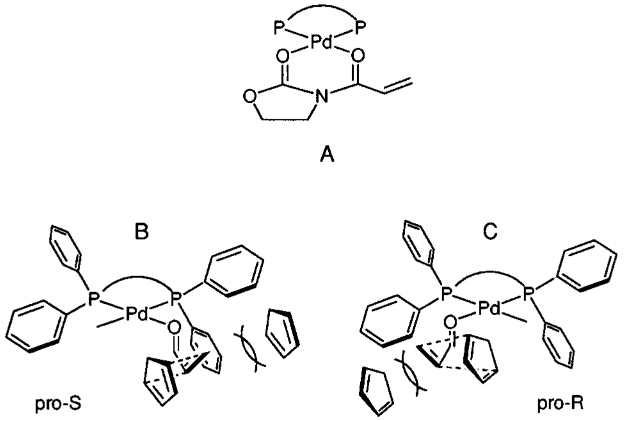


Figure 3. Intermediates involved in the interaction between (P−P)Pd fragments and the dienophile: A, with *N*-acryloyloxazolidinone according to ref 25; B and C, diastereoisomers formed with acrolein.

Scheme 3

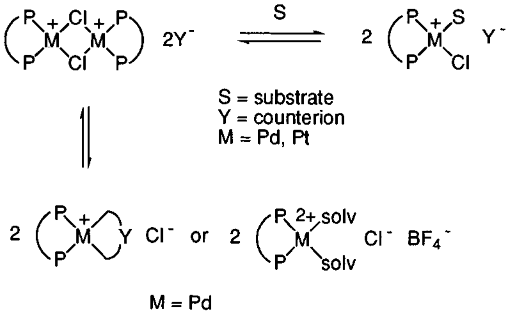
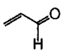
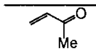
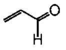
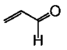
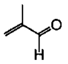
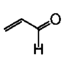


Table 4. Catalytic Activity in the Diels−Alder Reaction of Achiral Complexes 4 and 5[b]

Complex	Diene	Dienophile	Conversion (%)	Time (min)	endo/exo
4ax			85	20	7
5az			97	300	4.5
4ax			97	50	19.5
4ax			64	5900	33
5az			66	7000	65
4ax			82[a]	2700	6

[a] *T* 73 °C. [b] Reaction conditions: catalyst 10 μmol, diene 1 mmol, dienophile 1 mmol, DCE 3 mL, *T* 25 °C, N_2 1 atm.

Table 5. Enantioselective Diels−Alder Transformations Using Chiral Complexes 4 and 5 as Catalysts[a]

Cmplx	Diene	Dienophile	T	Conv	Time	endo/	e.e. (%)	
			(°C)	(%)	(min)	exo	exo	endo
4bx			0	86	2800	6.0	17	33
4by			0	90	2800	6.0	22	29
4bz			0	93	1400	8.5	19	18
5bx			0	89	180	7.0	28	42
5by			0	86	270	7.0	35	45
5bz			0	100	270	7.5	24	40
4bx			-20	65	3800	7.5	18	49
4by			-20	47	2600	7	21	42
4bz			-20	60	2900	7.5	17	46
5bx			-20	72	280	9	25	47
5by			-20	78	290	8	19	49
5bz			-20	67	315	9	27	45
4bx			0	95	1200	17	2	3
4bx			25	13	5700	>99		5
5bz			25	33	10000	>90	-	16

[a] Reaction conditions: catalyst 10 μmol, diene 1 mmol, dienophile 1 mmol, DCE 3 mL, N_2 1 atm.

virtually equivalent probability. It seems therefore that the use of transition metal systems having only one available coordination site may probably be beneficial in maximizing the energy difference between the transition states corresponding to the attack of the diene from either side of the C=C double bond.

Evolution of the Catalyst. In view of the above considerations, our attention shifted toward complexes **4** and **5**, which in principle, generating fragments that possess only one coordination site upon bridge splitting (Scheme 3), represent an evolution of catalysts **1**−**3** considered so far. Indeed, the characterization data reported above indicate that, at least for complexes **4b**, the formulation as in Chart 1 is not exhaustive, as species generated as indicated in Scheme 3 are also present. The latter, except for the external counterion, bear close similarities (or are identical) to complex **2b** (the case of **4bz** may be different).

As can be seen in Table 4, the catalytic performance of the achiral complexes **4** and **5** is in general rather good, with a moderate selectivity toward endo compounds. Asymmetric transformations are reported in Table 5 using the chiral complexes **4** and **5**, all modified with binap, and confirm the idea of the single vacant site. The first reaction studied was the one between cyclopentadiene and acrolein at 0 and −20 °C. Palladium complexes display a moderate activity and fair enantioselectivities that increase upon lowering the temperature. The homologous Pt complexes appear to be more effective catalysts at both 0 and −20 °C, as the reaction times are about 1 order of magnitude shorter. Ee's are higher for Pt at 0 °C and practically equivalent to Pd at −20 °C. The other reactions reported in Table 5 yield poor ee's.

The data of Table 5 for the Pd complexes at 0 °C in the reaction between cyclopentadiene and acrolein indicate the existence of an effect of the counterion (TfO^-, ClO_4^-, BF_4^-) on the enantioselectivity and on the activity (see also Figure 4). As can be seen, the effect of the couterion on the activity follows the order $BF_4^- > ClO_4^- \sim TfO^-$. A significant contribution by the noncatalyzed reaction may also be present (Figure 4). The opposite effect is observed on the enatioselectivity. While the effect on the activity could be easily related to the coordinating ability of the counterion (TfO^- and ClO_4^- bind more strongly, BF_4^- is probably noncoordinated), the effect on the enantioselectivity is less obvious.

A comparison of the catalytic behavior between Pd−Cl complexes and the homologous Pt complexes indicates that the latter have a number of advantages, probably related to their more uniform composition and

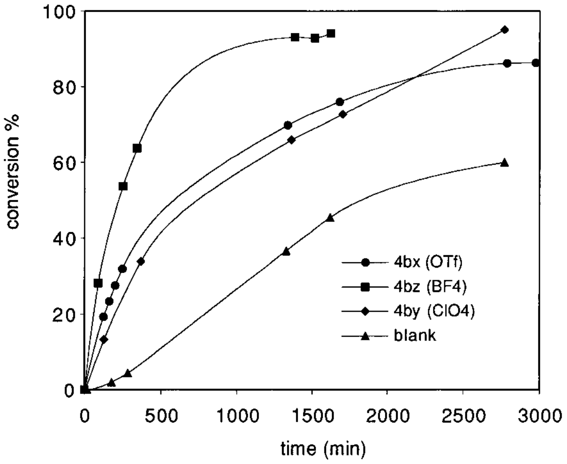
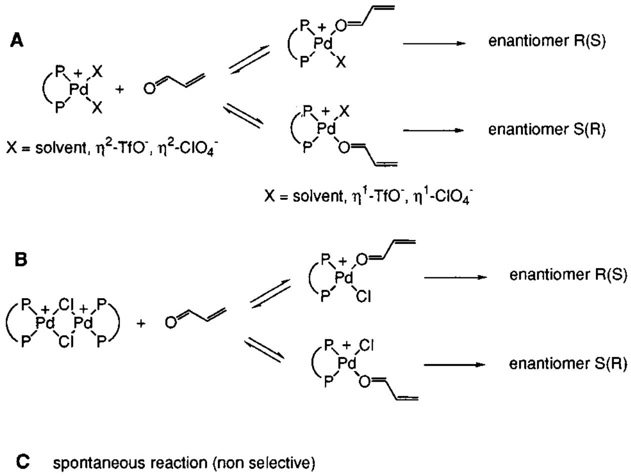


Figure 4. Reaction profiles for the reaction between cyclopentadiene and acrolein with different Pd complexes as catalysts: circles, complex **4bx**; diamonds, complex **4by**; squares, complex **4bz**; triangles, no catalyst.

Scheme 4



the absence of equilibria, i.e., a higher activity in the temperature range explored, a higher enantioselectivity, and no dependence on the specific counterion used.

Possible Origin of the Enantioselectivity. It should be reminded that at the temperature of catalytic operations complexes **4b** are indeed a mixture of two different species, both catalytically active, i.e., [(binap)Pd(η^2-Y)](Cl) (Y = ClO_4, TfO) or [(binap)Pd(solv)$_2$](BF_4)(Cl) and [(binap)Pd(μ-Cl)]$_2$(Y)$_2$ (Y = BF_4, ClO_4, TfO). Therefore, the enantioselective transformation, as well as the catalytic transformation more generally, will be the result of three different pathways (Scheme 4): the spontaneous reaction (at least in the case of acrolein and cyclopentadiene), i.e., pathway C, and the two metal-mediated pathways A and B. In both cases the interaction of the metal complex with the dienophile leads to the formation of two diastereoisomers from which the enantiomers are produced. Pathway A is practically nonselective, as is demonstrated by the results of Table 3, but on the other hand, it is sensitive to the effect of the couterion on the activity. Therefore it must be concluded that the enantiodifferentiating ability of the overall system is due almost completely to pathway B, which on the other hand is insensitive to the counterion effect on the activity, as the species involved is always [(binap)Pd(μ-Cl)]$^+$. This view is supported by the observation that Pt complexes **5b** where the catalytically active species is only [(binap)Pt(μ-Cl)]$^+$ show no effect of the counterion on both the activity and the enantioselectivity. Under these circumstances, the overall effect of the counterion on the enantioselectivity can be rationalized as follows: for all complexes **4b** there will be a constant positive contribution due to pathway B; in addition where pathway A is more favorable in terms of reaction rate (i.e., with **4bz**) its contribution to the overall process will be relatively more significant and hence the overall ee lower. Summarizing, it can be said that a lower association of the counterion will result in a higher weight of pathway A and hence lower ee's. Platinum complexes for which only pathway B is viable yield higher ee's and no effect of the counterion.

This conclusion could be better supported by the knowledge of the catalyst mixture composition at 0 and −20 °C. Unfortunately, the $^{31}P\{^1H\}$ NMR spectra at these temperatures are not helpful, as the composition can be determined only at −70 °C. Given the existence of two nonselective contributions to the overall ee, i.e., pathway A and the likely involvement of the noncatalyzed reaction (Figure 4), it can be concluded that the intrinsic enantiodifferentiating ability of [(binap)Pd(μ-Cl)]$_2^{2+}$ is probably much better than it appears from Table 5.

Conclusions

This work has led to the synthesis of a variety of cationic complexes of Pd(II) and Pt(II) that proved active as catalysts in the Diels−Alder reaction. Spectroscopic studies of these complexes have evidenced in some cases the unexpected existence of an equilibrium in which the external counterion (TfO^-, ClO_4^-, BF_4^-) is able to displace Cl^- from the coordination sphere of the metal and act as an η^2 donor. All complexes have a high catalytic activity (some are among the most active catalysts reported in the literature), in many cases even at low temperature, and some of them have an interesting (albeit moderate) enantioselective discrimination capacity. We have also demonstrated that in order to observe enantiodiscrimination with simple reagents such as acrolein only one coordination site must preferably be available in the catalytically active intermediate. This is probably due to the formation of a more rigid template interacting with the incoming diene in the subsequent 4+2 cycloaddition.

Experimental Section

Synthesis of New Complexes. Full details on the spectroscopic methods, the starting materials, the complete experimental synthetic procedures, and the elemental analyses of the new complexes are given separately in the Supporting Information.

Catalytic Reactions. These were carried out in a 25 mL round-bottomed flask equipped with a stopcock for vacuum/N_2 operations and a sidearm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (±0.1 °C) was maintained by water circulation through an external jacket connected with a thermostat. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer.

The following general procedure was followed. The required amount of catalyst was placed solid in the reactor, which was evacuated and filled with N_2. Purified, N_2-saturated solvent was added in the required amount. After thermostating at the required temperature for a few minutes, the dienophile and the diene in the appropriate amount were sequentially injected through the septum, and time was started.

All reactions were monitored with GC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Separation of the products was performed on a 25 m HP-5 capillary column using a thermal conductivity detector. Conversion percent was determined through the use of calibration curves between the individual substrates and toluene as internal standard.

The extent of the asymmetric induction (ee %) was determined with GC with the use of a Lipodex E chiral column. The analytical conditions for the separation of the different enantiomers are reported in the Supporting Information.

Acknowledgment. This work was supported by the Ministry of University and Scientific Research. G.S. wishes to thank Professor C. Bolm (RWTH, Aachen, Germany) for first suggesting the possible use of Pd and Pt complexes in the reaction here reported.

Supporting Information Available: Complete experimental procedures, elemental analyses of the new compounds, and analytical conditions for the separation of the enantiomers (Table 6). This material is available free of charge via the Internet at http://pubs.acs.org.

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