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(dppe)Pt(OTf)$_2$ and (*R*-BINAP)Pt(OTf)$_2$ Lewis Acids Catalyze the Diels−Alder Reaction by Different Mechanisms

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In situ observation, by ^{31}P and ^{1}H NMR at 195−240 K, of acryloyl-*N*-oxazolidinone (**4**)/cyclopentadiene (HCp) Diels−Alder reactions catalyzed by the Pt(II) Lewis acids $P_2Pt(OTf)_2$ (**2**; P_2 = dppe (**a**), *R*-BINAP (**b**)) revealed that the ditriflate catalysts are consumed by HCp at different rates to produce the catalytically inactive 18-electron complexes $[P_2Pt(\eta^5\text{-Cp})]^+[OTf]^-$ (**9**). Mechanistic studies point to formal loss of HOTf from the proposed intermediate diene complex $[P_2Pt(HCp)]^{2+}[OTf]^-_2$, facilitated by a necessary second equivalent of HCp; ill-defined HCp/HOTf byproducts, whose ^{1}H NMR resonances include a broad singlet at 12.7 ppm, are also formed. Both catalyst decomposition and Diels−Alder catalysis proceeded faster in reactions involving dppe Lewis acid **2a** than in those involving *R*-BINAP Lewis acid **2b**. In the **2b** reaction at 195 K, Pt-bound dienophile **4** was immediately converted to the Pt-bound Diels−Alder adduct 2*S*-**5** on addition of HCp; however, no turnover occurred and no η^5-Cp complex was detected until the temperature was raised to 225 K. At this temperature, no low-field resonances were observed by ^{1}H NMR, a highly enantiopure Diels−Alder adduct was obtained, and TOFs less than the rates of ligand exchange were observed. These data are consistent with catalysis by a chiral $[P_2Pt]^{2+}$ Lewis acid, in which ligand substitution is the turnover-limiting step of the catalytic cycle. In contrast, **9a** and Diels−Alder adduct *rac*-**5** formed rapidly at 195 K in the **2a** reaction. The observation of low-field HCp/HOTf resonances (^{1}H NMR) and TOFs greater than the rates of ligand exchange together suggest that, in this case, the Diels−Alder reaction is catalyzed primarily by a Brønsted acid mechanism involving the HCp/HOTf byproduct of **2a** decomposition, rather than by $[(dppe)Pt]^{2+}$.

Introduction

Group 10 transition-metal complexes of the type $[P_2M]^{2+}[A]^-_2$ (P_2 = diphosphine; M = Pd, Pt; A^- = OTf^-, BF_4^-, PF_6^-, SbF_6^-, ClO_4^-) have recently been shown to act as excellent Lewis acid catalysts and, when equipped with chiral diphosphines, have demonstrated the ability to perform highly enantioselective transformations.[1] Because of their unique stereoelectronic properties, which differ substantially from those of p-block, octahedral early-metal, or even first-row late-metal Cu(II) or Zn(II) Lewis acids, these square-planar, 16-electron catalysts could impart unprecedented reactivity and selectivity to Lewis acid catalyzed reactions. For example, the metal centers in this new class of catalysts are considerably “softer” than those of any other type of Lewis acid, making them more carbophilic and less oxophilic than their predecessors.[2] This trait has already been shown to alter the mechanisms of $[P_2Pd]^{2+}$-catalyzed imine or aldehyde alkylations by Mukaiyama-type nucleophiles.[3] Additionally, the fact that ligand exchange is much less facile for group 10 P_2M^{II} complexes than for their early-metal or first-row counterparts (and always proceeds via associative mechanisms)[4] could change the way that catalytic turnover is achieved in these Lewis acid catalyzed reactions. However, little information concerning the effects of these unusual properties on the mechanisms of $[P_2M]^{2+}$-catalyzed reactions has so far been reported. Thus, we elected to study in detail the mechanisms of Diels−Alder reactions (eq 1) catalyzed by the $P_2Pt(OTf)_2$ Lewis acids **2** (P_2 = dppe (**a**), *R*-BINAP (**b**)), with the ultimate aim

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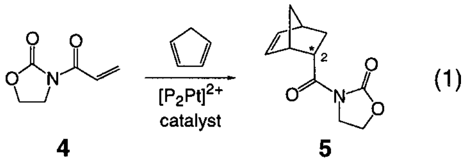
[1] (a) Ghosh, A. K.; Matsuda, H. *Org. Lett.* **1999**, *1*, 2157−2159. (b) Pignat, K.; Vallotto, J.; Pinna, F.; Strukul, G. *Organometallics* **2000**, *19*, 5160−5167. (c) Hao, J.; Hatano, M.; Mikami, K. *Org. Lett.* **2000**, *2*, 4059−4062. (d) Oi, S.; Terada, E.; Ohuchi, K.; Kato, T.; Tachibana, Y.; Inoue, Y. *J. Org. Chem.* **1999**, *64*, 8660−8667 and ref 12 and 13 therein. (e) Hattori, T.; Suzuki, Y.; Uesugi, O.; Oi, S.; Miyana, S. *Chem. Commun.* **2000**, 73−74. (f) Ferraris, D.; Young, B.; Dudding, T.; Lectka, T. *J. Am. Chem. Soc.* **1998**, *120*, 4548−4549. (g) Hori, K.; Kodama, H.; Ohta, T.; Furukawa, I. *J. Org. Chem.* **1999**, *64*, 5017−5023. (h) Hori, K.; Ito, J.; Ohta, T.; Furukawa, I. *Tetrahedron* **1998**, *54*, 12737−12744. (i) Fürstner, A.; Voigtländer, D.; Schrader, W.; Giebel, D.; Reetz, M. T. *Org. Lett.* **2001**, *3*, 417−420.

[2] (a) Brunkan, N. M.; White, P. S.; Gagné, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 11002−11003. (b) Bergens, S. H.; Leung, P.-H.; Bosnich, B. *Organometallics* **1990**, *9*, 2406−2408. (c) See also: Kocovsky, P.; Vyskocil, S.; Cisarova, I.; Sejbal, J.; Tislerova, I.; Smrcina, M.; Lloyd-Jones, G. C.; Stephen, S. C.; Butts, C. P.; Murray, M.; Langer, V. *J. Am. Chem. Soc.* **1999**, *121*, 7714−7715.

[3] (a) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450−5458. (b) Fujii, A.; Sodeoka, M. *Tetrahedron Lett.* **1999**, *40*, 8011−8014. (c) Fujimura, O. *J. Am. Chem. Soc.* **1998**, *120*, 10032−10039.

[4] (a) Cross, R. J. *Adv. Inorg. Chem.* **1989**, *34*, 219−292. (b) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739−740.

10.1021/om010987t CCC: $22.00

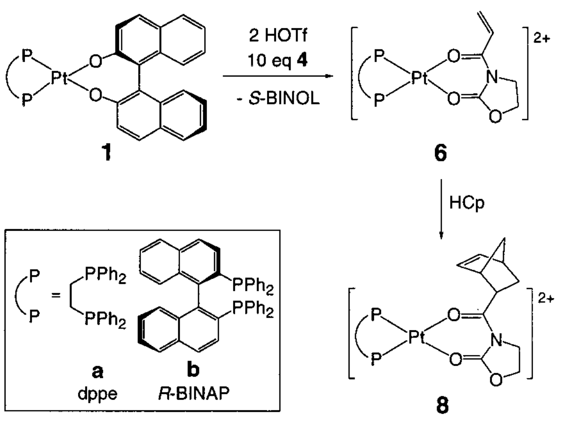


of understanding these reactions at a sufficiently detailed level to reveal their unique properties.

This paper is the second in a set of two that describe our investigation of Lewis acids **2** and their roles as Diels−Alder catalysts. In the first paper,[5] we reported that the active catalysts can be generated in situ by addition of 2 equiv of triflic acid (HOTf) to the precursors P_2Pt(*S*-BINOL) (**1**). Lewis acids **2**, as well as complexes **6** and **8**, which were obtained by reaction of **2** with the catalytically relevant Lewis bases **4** (dienophile; eq 1) and 2*S*-**5** (Diels−Alder adduct; eq 1), respectively, proved amenable to characterization by ^{31}P and ^{1}H NMR at 195 K; spectroscopic data were consistent with bidentate coordination of **4** and 2*S*-**5** to Pt (see Scheme 1). Investigation of the thermodynamic and kinetic relationships between catalysts **2**, catalyst−substrate complexes **6**, and catalyst−product complexes **8** revealed that ground-state energy differences between the species are small (<2.4 kcal mol^{-1} at 195 K) compared to the barriers for their interconversion by associative ligand substitution (11−15 kcal mol^{-1} at 270 K). These barriers are also diphosphine dependent, as significantly faster ligand exchange rates were measured (through line shape analysis of dynamic ^{31}P NMR spectra) for dppe than for *R*-BINAP complexes. Finally, monitoring the reaction of cyclopentadiene (HCp) with catalyst−substrate complexes **6** by ^{31}P and ^{1}H NMR at 195 K demonstrated that diene attack on the Pt-coordinated dienophile **4** occurs more rapidly than ligand substitution (vide infra), making ligand exchange the turnover-limiting step of the catalytic cycle.

Collectively, the data presented in the preceding paper point to ligand substitution rates, *not* electrophilicity of the metal center, as the key factor controlling the activity of $[P_2Pt]^{2+}$ Diels−Alder catalysts. Consistent with this scenario, the data further suggest that faster turnover should be observed in Diels−Alder reactions catalyzed by the dppe Lewis acid **2a** rather than *R*-BINAP Lewis acid **2b** (despite the weaker electrophilicity of **2a** relative to **2b**), simply because ligand exchange should be turnover-limiting and it occurs more rapidly in dppe than *R*-BINAP complexes. To test this hypothesis, we investigated the effects of the diphosphine P_2 on catalytic activity by directly comparing **2a**- and **2b**-catalyzed Diels−Alder reactions (eq 1) in situ by ^{31}P and ^{1}H NMR at 195 K. These experiments, alluded to in the first paper because they demonstrated that cycloaddition proceeds faster than ligand substitution, provided additional mechanistic information that is presented here in detail. Essentially, the experiments revealed that the ditriflate Lewis acids **2** react with HCp under catalysis conditions to produce catalytically inactive 18-electron Pt(II) complexes $[P_2Pt(\eta^5\text{-Cp})]^+[OTf]^-$ (**9**) and a poorly characterized HOTf/HCp byproduct. Diphosphine-dependent rates of catalyst decomposition in conjunction with a temperature-dependent quenching of the reactive byproduct then cause Diels−Alder reactions catalyzed by **2a** and **2b** to proceed by different mechanisms.

Scheme 1



Results and Discussion

(1) In Situ Observation of 2b-Catalyzed Diels−Alder Reactions by ^{31}P and ^{1}H NMR. The Lewis acid catalyst (*R*-BINAP)Pt(OTf)$_2$ (**2b**) was generated at room temperature by addition of 2 equiv of triflic acid (HOTf) to binaphtholate **1b** in the presence of 10 equiv of dienophile **4**, immediately producing the catalyst−substrate complex **6b** (Scheme 1). Since HOTf itself is an efficient catalyst for the Diels−Alder reaction, care was taken to avoid adding excess acid during catalyst activation.[6] ^{31}P and ^{1}H NMR spectra of the reaction mixture, acquired at 195 K, revealed that 91% of the Lewis acid **2b** was converted to the Pt−dienophile complex **6b** under these conditions (Figure 1A,G).[7] Resonances for free and coordinated **4** were easily distinguished in the ^{1}H NMR spectrum (Figure 1G).

Fifty equivalents of freshly cracked HCp was then added to the reaction mixture at 195 K, and low-temperature ^{31}P and ^{1}H NMR spectra were recorded periodically (Scheme 1 and Figure 1). The first spectra[8] acquired after HCp addition showed only the Pt−cycloadduct complex *R*,2*S*-**8b** and no Pt−dienophile complex **6** (Figure 1B), indicating that the Pt-coordinated dienophile (**4***, Figure 1G) was immediately converted to a Pt-coordinated Diels−Alder adduct (**5***, Figure 1H) by HCp. Despite the rapid cycloaddition step, however, essentially no free product **5** appeared in the ^{1}H NMR spectrum while it remained at 195 K, even after 50 min. Clearly, the **2b**-catalyzed Diels−Alder reaction *does not appreciably turn over* at this temperature. As discussed in the preceding paper, these results indicate that the stereochemistry-determining cycloaddition of HCp and **6** occurs faster than ligand exchange, making ligand substitution the turnover-limiting step of the catalytic cycle.[5]

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[5] Brunkan, N. M.; White, P. S.; Gagné, M. R. *Organometallics* **2002**, *21*, 1565−1575.

[6] In the *R*-BINAP system, addition of 1.9 equiv of HOTf to yellow-orange **1b** produces catalyst solutions that remain slightly yellow instead of losing all color, indicating that protonation of **1b** is not complete. Also, the fact that highly enantiopure product 2*S*-**5** is obtained from the **2b**-catalyzed Diels−Alder reaction (96−98% ee) indicates that catalysis by excess HOTf does not occur.

[7] Residual **2b** (4%) and a small amount of $[P_2Pt(OH_2)_2]^{2+}[OTf]^-{}_2$ (**3b**) were also present.

[8] Acquired after 4 min reaction time; not shown in Figure 1.

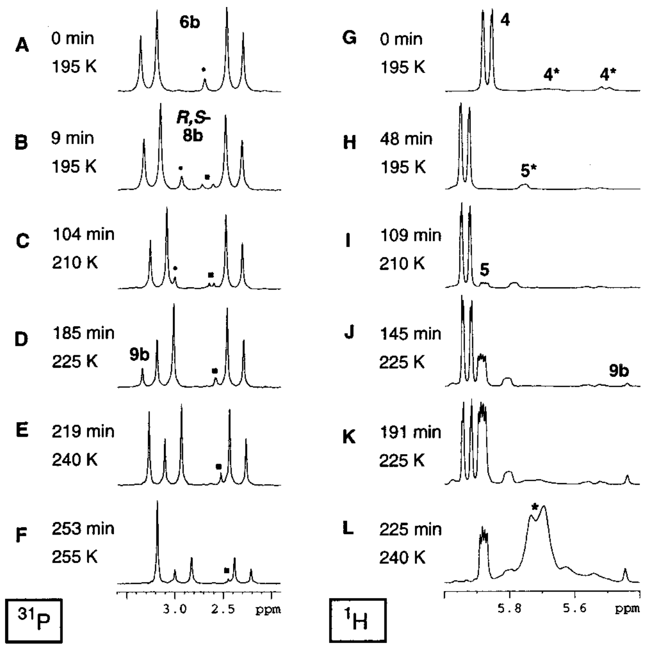

Figure 1. ^{31}P (A–F) and ^{1}H (G–L) NMR spectra acquired during the **2b**-catalyzed Diels–Alder reaction (eq 1). On the ^{31}P side, • denotes **3b** and ■ denotes *R*,2*R*-**8b**. On the ^{1}H side, **4*** denotes Pt-coordinated **4**, **5*** indicates Pt-coordinated **5**, and * denotes HCp polymer.

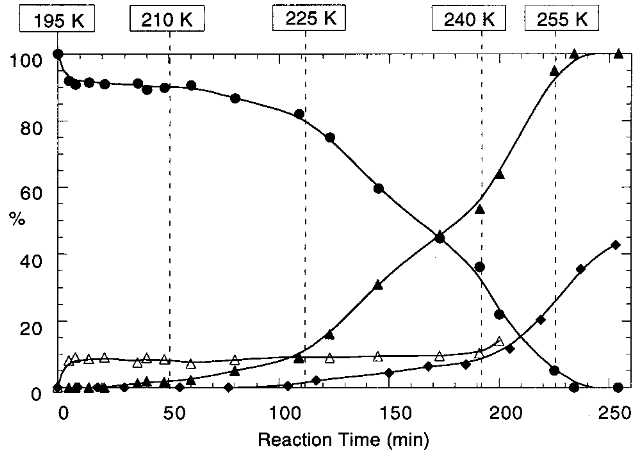

Figure 2. Conversion vs time for the **2b**-catalyzed Diels–Alder reaction (eq 1): (●) % **4**; (▲) % **5**; (△) % Pt-coordinated **5**; (♦) % **9b**. The reaction temperature was increased at the times indicated by the vertical lines.

When the NMR probe temperature was raised to 210 K, the **2b**-catalyzed Diels–Alder reaction began to turn over sluggishly (Figure 1C,I). Although ^{1}H NMR spectra of the reaction mixture were complex, all resonances could be assigned to **8b**, **4**, **5**, free *S*-BINOL, or HCp,[9] and the reaction progress could be assessed by integrating the ^{1}H NMR resonances for free **4**, free **5**, and Pt-coordinated **5** at 5.95, 5.85, and 5.75 ppm, respectively (Figure 1). The evolution of the **2b**-catalyzed reaction in eq 1, determined from spectral integration data, is plotted in Figure 2.

After one turnover was completed (50 min at 210 K), the NMR temperature was elevated to 225 K (Figure 2), at which point the reaction accelerated and completed five turnovers in 70 min (Figure 1J,K). Concurrently, however, a singlet at 3.1 ppm with an unusually large P–Pt coupling of 4587 Hz ($^{1}J_{\text{P-Pt}}$ = 4210 Hz for **2b**) grew slowly in the ^{31}P NMR spectrum of the reaction mixture (Figure 1D). The growth of this new complex (**9b**) coincided with both the loss of *R*,2*S*-**8b** (Figure 1D) and the appearance of a singlet at 5.4 ppm in the ^{1}H NMR spectrum (Figure 1J,K). When the NMR temperature was raised to 240 K, rapid Diels–Alder catalysis occurred until all the dienophile present was converted to 2*S*-**5** (another four turnovers in 35 min; Figure 2). Formation of **9b** was also accelerated (Figure 1E), and large, broad resonances characteristic of poly(HCp) grew in the ^{1}H NMR spectrum at 5.6–5.8 and 1.0–3.0 ppm (Figure 1L).[10] Finally, raising the reaction temperature to 255 K increased the rates of both **9b** production (43% conversion at the end of the experiment; Figure 1F) and HCp polymerization. Upon removal from the probe, the NMR tube contained a bright orange solution that turned black when warmed to room temperature. Viscous, white polymeric material also appeared in the reaction vessel at room temperature.

Table 1. Turnover Frequencies for Catalysis of Eq 1 by 2a and 2b Compared with Dienophile/OTf^{-} Ligand Exchange Rates (k_2)[a]

Lewis acid	temp (K)	10^4(TOF) (s^{-1})	$10^4 k_2$ (s^{-1})
2b	195	0.6	1.5
2b	210	3.3	18
2b	225	12	150
2a	195	26	16

[a] Dienophile/OTf^{-} ligand exchange rates (k_2) were measured by line-shape analysis of dynamic ^{31}P NMR spectra at higher temperatures and extrapolated to the indicated temperatures (see the Supporting Information).

Chiral HPLC analysis of the cycloadduct obtained from this reaction confirmed that it was 97% ee 2*S*-**5**, consistent with the enantioselectivities reported by Ghosh.[1a] Preparative-scale **2b**-catalyzed reactions, monitored over time by GC analysis, proceeded at rates similar to that of the NMR-scale reaction described above and likewise yielded 96–98% ee 2*S*-**5**.[11] Reactions conducted at 195 K reached 30–50% completion and then died, indicating that turnover, although slow at this temperature, is not completely absent.

Disregarding (for the moment) the unanticipated appearance of **9b**, the **2b**-catalyzed Diels–Alder reaction proceeded in a manner consistent with the data presented in the preceding paper, which indicated that cycloaddition should be rapid and ligand substitution should be turnover-limiting in the catalytic cycle.[5] In situ monitoring of 2*S*-**5** formation at different temperatures allowed calculation of crude turnover frequencies (TOFs) at these temperatures (Table 1). These TOFs were expected to roughly correlate with the dienophile/OTf^{-} ligand exchange rates k_2 measured in the previous paper, if ligand substitution actually is the slowest step of the catalytic cycle.[5] Indeed, comparison of TOFs and k_2 values (Table 1) showed that, at each temperature, catalysis rates were similar to but slightly slower than the **4**/OTf^{-} exchange rates obtained from ^{31}P NMR line-

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[9] See the Supporting Information for the complete ^{1}H NMR spectrum.

[10] (a) Ma, J.; Corcoran, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 8973–8975 and ref 23 therein. (b) Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 3176–3181.

[11] Preparative-scale reaction conditions were exactly the same as those for NMR reactions, except 3 times less concentrated.

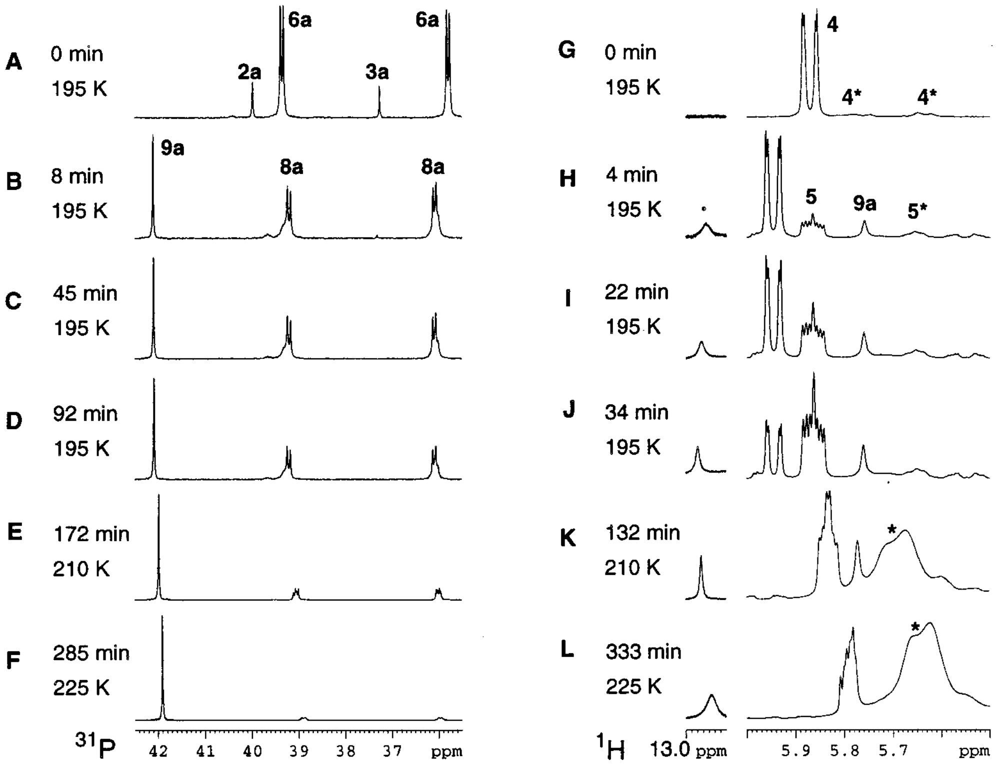

Figure 3. ^{31}P (A–F) and ^{1}H (G–L) NMR spectra acquired during the **2a**-catalyzed Diels–Alder reaction (eq 1). On the ^{1}H side, • denotes the HOTf/HCp byproduct, **4*** indicates Pt-coordinated **4**, **5*** denotes Pt-coordinated **5**, and * denotes HCp polymer.

shape analysis. These data further support a mechanistic scenario in which ligand substitution rates control the activity of the Pt Lewis acid catalyst.

(2) In Situ Observation of 2a-Catalyzed Diels–Alder Reactions by ^{31}P and ^{1}H NMR. Since **4**/OTf$^-$ ligand exchange occurs more quickly in dppe than in *R*-BINAP complexes, **2a**-catalyzed Diels–Alder reactions were predicted to proceed faster than their **2b**-catalyzed counterparts.[5] To test this prediction experimentally, a reaction promoted by dppe Lewis acid **2a** was similarly monitored by ^{1}H and ^{31}P NMR (Figure 3). Unexpectedly, significant differences between the dppe and *R*-BINAP reactions were observed.

Initially, generating Pt Lewis acid catalyst **2a** from precursor **1a** and HOTf in the presence of 10 equiv of dienophile **4** afforded the expected equilibrium mixture of **2a** and Pt–dienophile complex **6a** (Figure 3A,G). Addition of 50 equiv of HCp to the reaction mixture at 195 K immediately and quantitatively converted **6a** to **8a**, as in the *R*-BINAP reaction (Figure 3B,H). However, unlike in the **2b** case, conversion of the active $[P_2Pt]^{2+}$ catalyst to a symmetric Pt complex with a large P–Pt coupling constant (42.1 ppm, $^{1}J_{P-Pt}$ = 4512 Hz; **9a**) occurred rapidly at 195 K, yielding 20% **9a** after only 8 min reaction time (Figure 3B)! In the ^{1}H NMR spectrum, unidentified resonances appeared at 5.75 ppm (analogous to the resonance at 5.4 ppm in the *R*-BINAP reaction) and 12.7 ppm; the 12.7 ppm resonance remained approximately constant in size (0.2 H compared to *S*-BINOL) throughout the reaction (Figure 3H-L). Because of its chemical shift, this downfield signal was initially assigned to HOTf (vide infra). Note that this resonance was *not* present before HCp was added to the reaction mixture (Figure 3G), and it was certain that no excess HOTf had been added during catalyst activation.[12] Therefore, unlike in the *R*-BINAP case, it appeared that HOTf was generated by reaction of $P_2Pt(OTf)_2$ with HCp.

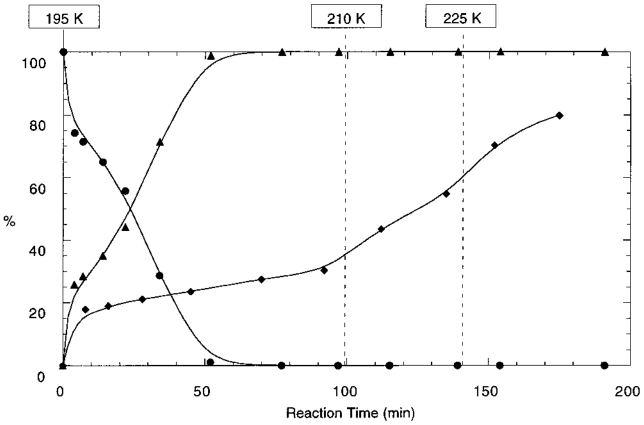

Figure 4. Conversion vs time for the **2a**-catalyzed Diels–Alder reaction (eq 1): (●) % **4**; (▲) % **5**; (♦) % **9a**. The reaction temperature was increased at the times indicated by the vertical lines.

The Diels–Alder reaction proceeded rapidly at 195 K (Figure 3I,J), reaching complete conversion in 65 min, while **9a** grew in the ^{31}P NMR spectrum (Figure 3C,D; see also Figure 4). When the Diels–Alder reaction was complete, the NMR probe temperature was raised to 210 K, which accelerated formation of **9a** (Figure 3E).

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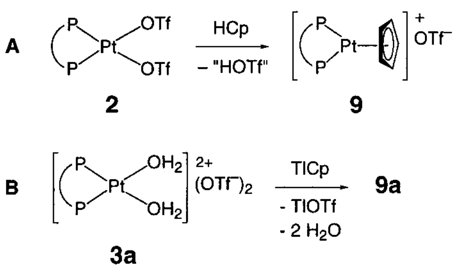
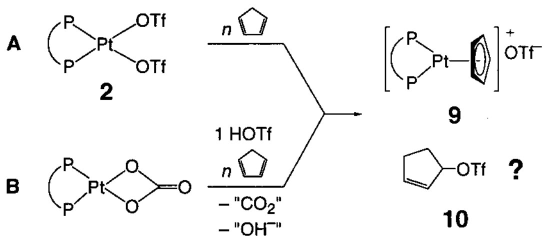
[12] A small amount (3%) of a complex that we propose to be a $Pt_2(\mu\text{-BINOL})$ dimer was present in the reaction mixture after addition of HOTf. This species only forms when *less than 2* equiv of acid is added to **1a** (manuscript in preparation).

Scheme 2



Scheme 3



n	% yield
1	50
2	100

Additionally, HCp oligomers and polymers appeared by ^{1}H NMR (Figure 3K). Increasing the probe temperature to 225 K eventually produced **9a** in 78% yield (Figure 3F,L), and removal of the NMR tube from the probe revealed a bright yellow reaction solution. As in the *R*-BINAP case, this solution turned black on warming to room temperature, and viscous, polymeric material was deposited in the NMR tube. A ^{31}P NMR spectrum of this sample at 300 K consisted exclusively of **9a**, while ^{1}H NMR showed that all free HCp had polymerized.[10,13] Preparative-scale reactions proceeded at rates similar to those of the NMR-scale reaction.[11]

(3) Identification of 9 as $[P_2Pt(\eta^5\text{-}Cp)]^+[OTf]^-$. Because adding HCp to $[P_2Pt]^{2+}$ precipitated the formation of complex **9** (at least in the dppe case), we attempted to prepare **9a** independently by adding 2 equiv of HCp to **2a** at 195 K (Scheme 2A). Indeed, quantitative conversion of colorless **2a** to yellow **9a** was observed by ^{31}P NMR under these conditions. A ^{1}H NMR spectrum of the reaction mixture contained a sharp triplet ($^3J_{P-H} = 1.5$ Hz) with Pt satellites ($^2J_{Pt-H} = 11.8$ Hz) at 5.8 ppm (5 H), consistent with coordination of an η^5-Cp ligand to the P_2Pt^{II} fragment (Scheme 2A). On the basis of these NMR data, **9a** was identified as the 18-electron complex $[(dppe)Pt(\eta^5\text{-}Cp)]^+[OTf]^-$, previously prepared by Anderson from $[(dppe)Pt(OH_2)_2]^{2+}[OTf]^-{}_2$ (**3a**) and TlCp (Scheme 2B).[14] Small broad resonances at 12.2 and 17.5 ppm (0.2 H each) and in the aliphatic region of the spectrum were also observed and were assigned to ill-defined HOTf/HCp byproducts. When it was warmed to room temperature, the reaction mixture turned brown, and the downfield resonances disappeared from the ^{1}H NMR spectrum.

The analogous *R*-BINAP η^5-Cp complex **9b** was prepared independently as a crystalline, red-orange solid by addition of 1 equiv of TlCp to the μ-chloro dimer $[(R\text{-BINAP})Pt(\mu\text{-}Cl)]_2{}^{2+}[OTf]^-{}_2$, in a modification of Anderson's protocol for **9a**. The ^{31}P and ^{1}H (5.4 ppm, $^3J_{P-H} =$ 1.6 Hz; $^2J_{Pt-H} \approx 7.2$ Hz) NMR spectra of **9b** identified it as the unknown decomposition product from the *R*-BINAP Diels–Alder reaction (Figure 1).[15] Control experiments showed that **9a** and **9b** (10 mol %) are not catalysts for the Diels–Alder reaction, consistent with their 18-electron formulations.

(4) Mechanism of 9a Formation from 2a and HCp. While Anderson's metathetical synthesis of **9a** is intuitively reasonable, the production of **9a** from **2a** and HCp, as shown in Scheme 2A, is not. Several experiments were carried out to probe the mechanism by which **9a** forms from **2a** and HCp. First, to assess the feasibility of an intermediate η^2- or η^4-coordinated diene on the reaction surface, we investigated the Pt(II) coordination chemistry of cyclohexadiene (CHD), a less reactive diene than HCp. Preliminary experiments showed that a combination of **2a** and CHD does not produce a complex akin to **9a**, although it does generate a black, polymer-containing solution and small amounts of benzene on warming to room temperature. When 50 equiv of CHD was added to **2a** at 195 K, a ^{31}P NMR spectrum of the reaction mixture consisted of two singlets 24 Hz apart (53.1 ppm), with a single set of broad Pt satellites ($^1J_{Pt-P} = 3580$ Hz), as well as residual **2a** (41%). Though the ^{31}P spectrum is not readily interpretable, the magnitude of the P–Pt coupling constant is in the range reported for phosphorus ligands trans to η^2-coordinated olefins in Pt(II) complexes,[16] suggesting that coordination of a 1,3-diene to the electrophilic $[P_2Pt]^{2+}$ center is feasible, and could reasonably represent a first step in the conversion of **2** to **9** by HCp.

Counterintuitively, addition of 1 equiv rather than 2 equiv of HCp to **2a** at 195 K produced **9a** in only 50% yield (Scheme 3A). This observation led to the hypothesis that the second equivalent of HCp might function as the base that deprotonates the $[P_2Pt(\eta^4\text{-}HCp)]^{2+}$ complex to give the η^5-Cp ligand. However, the logical byproduct of such a reaction, cyclopentallyl triflate (**10**), was never observed by ^{1}H NMR, even though the related species allyl triflate is stable at low temperature and gives sharp, well-defined ^{1}H NMR resonances between 4.9 and 6.0 ppm.[17] The spectrum of the present reaction contained only broad resonances downfield of 12 and upfield of 3 ppm, casting doubt on the role of **10**. Equally puzzling was the fact that *2* equiv of HCp was required to produce 1 equiv of **9a** from $(dppe)PtCO_3$ and 1 equiv of HOTf in the presence of HCp (Scheme 3B). We predicted that an intermediate "$[P_2PtOH]^+[OTf]^-$"[18] or "$[(dppe)Pt(CO_3H)]^+[OTf]^-$" species would be sufficiently

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[13] The cycloadduct obtained from **2a**-catalyzed Diels–Alder reactions was racemic, as expected for the achiral dppe-based catalyst.

[14] Fallis, S.; Rodriguez, L.; Anderson, G. K.; Rath, N. P. *Organometallics* **1993**, *12*, 3851–3855.

[15] The spectroscopic data are similar to those of a recently isolated $[(biphep)Pt(\eta^5\text{-}Cp)]^+[OTf]^-$ complex: Becker, J. J.; White, P. S.; Gagné, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 9478–9479.

[16] (a) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1987**, 139–143. (b) Kurosawa, H.; Asada, N.; Urabe, A.; Emoto, M. *J. Organomet. Chem.* **1984**, *272*, 321–329.

[17] (a) Vedejs, E.; Engler, D. A.; Mullins, M. J. *J. Org. Chem.* **1977**, *42*, 3109–3113. (b) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673–3677.

[18] $[P_2Pt(\mu\text{-}OH)]_2{}^{2+}[A]^-{}_2$ complexes are well-known in the literature. See for example: (a) Bandini, A. L.; Banditelli, G.; Demartin, F.; Manassero, M.; Minghetti, G. *Gazz. Chim. Ital.* **1993**, *123*, 417–423. (b) Li, J. J.; Li, W.; Sharp, P. R. *Inorg. Chem.* **1996**, *35*, 604–613.

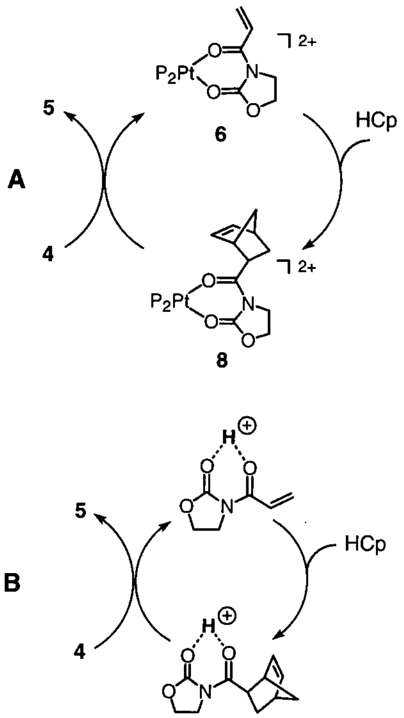
basic to deprotonate the acidic Pt(HCp) intermediate to afford **9a** and 1 equiv of carbonic acid or water/CO_2 (Scheme 3B). However, 1 equiv of HCp converted only 50% of the putative monotriflate intermediate to **9a**.[19]

The identity of the 12.7 ppm resonance in ^1H NMR spectra of the **2a**-catalyzed Diels−Alder reaction was probed by combining **4**, **5**, *S*-BINOL, and HCp with 1 equiv of HOTf in separate NMR tubes. These species were all present in the **2a**-catalyzed reaction mixture, and each could conceivably deprotonate Pt-coordinated HCp and produce an acid−base adduct with a resonance at 12.7 ppm. However, combining HOTf with the Lewis bases **4**, **5**, and *S*-BINOL at 195 K generated protonated products with the acidic proton appearing at 9 ppm (*S*-BINOL, 3 H),[20] 17 ppm (cycloadduct **5**, 1 H),[21] or 18 ppm (dienophile **4**, 1 H) rather than 12.7 ppm in the ^1H NMR spectrum (CD_2Cl_2; free HOTf at 9.25 ppm). In the case of HCp, a ^1H NMR spectrum acquired immediately after addition of HOTf at 195 K already consisted primarily of unidentified broad resonances upfield of 6 ppm, but a resonance at 12.3 ppm, similar to the one observed in the catalytic reaction mixture, was also observed, suggesting that the downfield peak observed during **2a** catalysis is derived from a combination of HCp and HOTf. If this is indeed the case, then the proposed intermediate $[(dppe)Pt(HCp)]^{2+}[OTf]^-{}_2$ must be acidic enough to protonate free cyclopentadiene, pointing to a remarkably electrophilic $[P_2Pt]^{2+}$ fragment.

(5) dppe vs *R*-BINAP: Mechanisms of 2a- and 2b-Catalyzed Diels−Alder Reactions. Figures 2 (*R*-BINAP) and 4 (dppe) show the time courses of **2b-** and **2a**-catalyzed Diels−Alder reactions (eq 1), respectively, as well as decomposition of $[P_2Pt]^{2+}$ to the η^5-Cp complexes **9**. Comparison of these plots reveals that both Diels−Alder catalysis and production of **9** occur more rapidly for $[(dppe)Pt]^{2+}$ than for $[(R\text{-BINAP})Pt]^{2+}$. Although the fact that **2a**-catalyzed Diels−Alder reactions proceed faster than their **2b**-catalyzed counterparts is consistent with our initial, simple hypothesis that faster ligand exchange rates for dppe complexes should enhance turnover rates for **2a**-catalyzed reactions,[5] the mechanistic data described here suggest a situation more complex than previously appreciated.

The key difference between the dppe and *R*-BINAP Pt-catalyzed Diels−Alder reactions is the difference in rates of $[P_2Pt]^{2+}$ decomposition to the η^5-Cp complexes **9**, which mirrors the difference in ligand exchange rates observed previously. In **2a**-catalyzed reactions (dppe), addition of HCp to the reaction mixture at 195 K rapidly produces **9a** and an unknown form of HOTf/HCp, observed by ^1H NMR as a broad resonance at 12.7 ppm, which is evidently acidic enough to catalyze the Diels−Alder reaction by a Brønsted acid mechanism that is rapid at 195 K (Scheme 4A).[22] The HOTf/HCp product formed at 195 K apparently does *not* initiate HCp oligomerization, since evidence of HCp polymerization does not appear in the ^1H NMR spectrum until the reaction temperature is raised to 225 K. In contrast, decomposition of $[P_2Pt]^{2+}$ to **9b** does *not* occur at 195 K in the *R*-BINAP case but begins slowly when the reaction temperature is raised to 225 K. At this temperature, however, no resonances for acidic protons are observed in the downfield region of the ^1H NMR spectrum; instead, HCp oligomers appear immediately. Thus, the HOTf/HCp product formed at 225 K must initiate HCp polymerization, rather than getting involved in Brønsted catalysis of the Diels−Alder reaction. The high enantioselectivity of **2b**-catalyzed reactions (96−98% ee, as reported by Ghosh)[1a] also indicates that a conventional Lewis acid pathway mediated by a chiral metal complex (Scheme 4A), rather than an achiral proton-catalyzed process (Scheme 4B), is the operative mechanism in **2b**-catalyzed reactions.

Scheme 4



The rapid rates observed for Diels−Alder reactions involving dppe Lewis acid **2a** provide additional evidence that these reactions probably proceed primarily through the Brønsted acid catalyzed route shown in Scheme 4B, which is expected to turn over more quickly than the $[P_2Pt]^{2+}$-mediated cycle. (Diels−Alder reactions catalyzed by 10 mol % of HOTf are complete in <5 min at 195 K.) Comparison of the catalyst TOF at 195 K with the dienophile/OTf^- ligand exchange rate k_2 measured in the preceding paper (Table 1)[5] reveals that in contrast to the situation observed for the *R*-BINAP Lewis acid-catalyzed reaction (catalysis rates *slower* than dienophile/OTf^- exchange were measured), turnover actually occurs *faster* than dienophile/OTf^- ligand exchange in the dppe system. This discrepancy between the dppe and *R*-BINAP cases strongly suggests that the rate of the **2a**-promoted Diels−Alder reactions is augmented by a

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(19) Besides **9a** (50% yield), the reaction of $(dppe)PtCO_3$ with 1 equiv of HOTf and 1 equiv of HCp (Scheme 3B) afforded the μ-OH dimer $[(dppe)Pt(\mu\text{-}OH)]_2{}^{2+}[OTf]^-{}_2$, the same product formed in the absence of HCp.[18]

(20) The 9 ppm resonance in the 195 K ^1H NMR spectrum of protonated *S*-BINOL integrated for 3 H, indicating that exchange of the acidic proton with the OH protons of *S*-BINOL is rapid on the NMR time scale.

(21) Warming to room temperature caused reaction of **5** with HOTf (complete in 10−15 min), producing new, unidentified species and a very small resonance at 12.5 ppm in the ^1H NMR spectrum. No reaction was observed in the case of dienophile **4**.

(22) A carbonium ion catalyst (in analogy to trityl cation) cannot be ruled out, though an H^+ mechanism seems more plausible.

non-Pt, Brønsted acid catalysis pathway, making different mechanisms operative in Diels−Alder reactions involving Pt catalysts **2a** and **2b**.

Summary and Conclusions

Diels−Alder reactions catalyzed by the $P_2Pt(OTf)_2$ Lewis acids **2a** (dppe) and **2b** (*R*-BINAP) were monitored in situ at 195 K by ^{31}P and ^{1}H NMR. These experiments confirmed that ligand substitution is the turnover-limiting step of the **2b**-catalyzed reaction and that the reaction turns over at a rate similar to previously measured **4**/OTf^- ligand exchange rates. Unexpectedly, decomposition of the $[P_2Pt]^{2+}$ catalysts by reaction with HCp to give the noncatalysts $[P_2Pt(\eta^5\text{-}Cp)]^+[OTf]^-$ occurred in both the dppe and *R*-BINAP systems. Mechanistic studies of the dppe case revealed that a second equivalent of HCp was required to convert **2a** to **9a**, presumably to deprotonate a (highly acidic) $[(dppe)Pt(HCp)]^{2+}[OTf]^-{}_2$ intermediate and form an acidic HOTf/HCp species with a resonance at 12.7 ppm.

Comparison of the NMR data for **2a-** and **2b**-promoted Diels−Alder reactions suggest that the two reactions proceed by different mechanisms because **2a** and **2b** decompose to **9** at different temperatures. In the dppe case, **9a** forms rapidly at 195 K; at this temperature, the acidic HOTf/HCp byproducts that are formed do not initiate HCp polymerization but, instead, promote the Diels−Alder reaction by a Brønsted acid catalyzed route (Scheme 4B). In the *R*-BINAP reaction, decomposition of $[P_2Pt]^{2+}$ to **9b** does not occur until 225 K. At this temperature the acidic species visible in the ^{1}H NMR spectrum of the **2a** reaction (12.7 ppm) is not observed, apparently because it more quickly initiates HCp polymerization. Therefore, the **2b**-promoted Diels−Alder reaction proceeds via a true Pt-catalyzed mechanism (Scheme 4A).

From the experiments described above, several broad conclusions regarding the reactivity of $[P_2Pt]^{2+}$ Lewis acid catalysts can be drawn. (1) Despite the change in mechanism documented herein, the data still show that ligand exchange rates dominate the activity of $[P_2Pt]^{2+}$ catalysts, though not in the direct way that was envisioned at the onset of the work. (2) Rapid (−78 °C) conversion of Pt-coordinated dienophile to Pt-coordinated Diels−Alder product demonstrates the significant Lewis acidity and activating potential of the $[P_2Pt]^{2+}$ fragment. Moreover, the high enantioselectivities observed with the bulky *R*-BINAP catalyst show that even when the stereochemistry-determining step of a reaction is fast, the chiral P_2 ligand is extremely efficient at directing reaction selectivity. (3) Although ultimately detrimental to the catalyst's integrity in this case, the carbophilicity of $[P_2Pt]^{2+}$ enhances the rate of a unique reactivity pathway (**9** formation) that is atypical for conventional Lewis acids. During other transformations, this type of reactivity may prove beneficial, especially in combination with the highly electrophilic character of these Pt catalysts.

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Supporting Information Available: Text giving additional experimental details and figures giving ^{1}H NMR spectra of **2a**- and **2b**-catalyzed Diels−Alder reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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