Lewis Acid Platinum Complexes of Conformationally Flexible NUPHOS Diphosphines: Highly Efficient Catalysts for the Carbonyl−Ene Reaction

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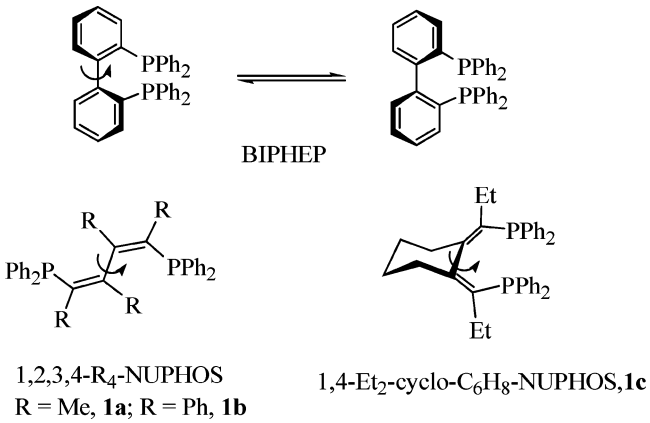
Enantiopure Lewis acid complexes of conformationally flexible acyclic and monocyclic NUPHOS diphosphines, δ- and λ-[(NUPHOS)Pt$(OTf)_2$], are efficient catalysts for the carbonyl−ene reaction between various unsymmetrical 1,1′-disubstituted alkenes and phenylglyoxal or ethyl glyoxylate. While catalyst performance was substrate dependent, ee values as high as 95% and yields up to 90% have been obtained. In a number of cases catalysts generated from δ- and λ-[(NUPHOS)Pt{(*S*)-BINOL}] showed marked enhancements in enantioselectivity in ionic liquids compared with organic media. Although an enhancement in enantioselectivity was not obtained for all substrate combinations in such cases, the enantioselectivities were comparable to those obtained in dichloromethane. Furthermore, although the ee's are initially comparable in both the ionic liquid and dichloromethane, a gradual erosion of ee with time was found in the organic solvent, whereas the ee remained constant in the ionic liquid. Preliminary kinetic investigations suggest that the decrease in ee may be due to a faster racemization of the catalyst in dichloromethane compared with the ionic liquid.

Introduction

Traditionally, ligand design for asymmetric catalysis has been guided by the principle that a rigid, conformationally restricted, enantiopure ligand is necessary to obtain high ee's.[1] However, such an approach is often an iterative, time-consuming process, since the synthesis of enantiopure ligands can involve lengthy multistep procedures. Recently, alternative strategies in asymmetric catalysis have begun to emerge which involve the use of conformationally flexible or meso ligands to either magnify the effect of another chiral ligand or act as the only source of asymmetry for an enantioselective transformation.[2] In the latter case, coordination of the ligand to a substitutionally inert metal slows interconversion of its conformations such that a metastable enantiopure metal−ligand assembly can be resolved and used as the sole source of asymmetry for catalysis.[3] One such ligand, 2,2′-bis(diphenylphosphino)biphenyl (BIPHEP),[4] belongs to the *tropos* class of diphosphine, since its axial chiral conformations cannot be resolved (Chart 1).[5] Gagné and co-workers have recently studied diastereointerconversion in chiral complexes of this diphosphine[6] and shown that δ- and λ-[Pt(BIPHEP){(*S*)-BINOL}] can be resolved, the BINOL liberated, and the resulting enantiopure Lewis acid used to catalyze the Diels−Alder and glyoxylate−ene reaction with no loss of enantiopurity of the catalyst.[7] Following this, Mikami

Chart 1



1,2,3,4-R_4-NUPHOS
R = Me, **1a**; R = Ph, **1b**

1,4-Et_2-cyclo-C_6H_8-NUPHOS,**1c**

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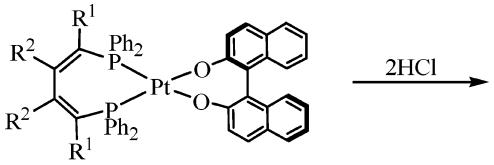
et al. adopted a similar strategy to resolve palladium complexes of BIPHEP with (*R*)-diaminobinaphthyl ((*R*)-DABN), liberated the DABN by protonation, and showed the resulting Lewis acid fragment to be an efficient catalyst for the hetero Diels−Alder reaction between ethyl glyoxylate and cyclohexadiene.[8] Interestingly, [{(*R*)-BIPHEP}Pd{(*R*)-DABN}]$^{2+}$ behaved as an activated catalyst giving markedly higher enantioselectivities than [{(*R*)-BIPHEP}Pd(MeCN)$_2$]$^{2+}$ and exhibiting a dramatic negative nonlinear effect.[9] (*R*)-DABN has also been used as a highly effective auxiliary for control of axial chirality in Ni, Pd, and Pt complexes of bis(diphenylphosphino)ferrocene, with the Ni/dppf combination proving to be significantly more efficient and enantioselective than its Pd or Pt counterparts in the glyoxylate−ene reaction.[10] The same strategy has recently been employed to resolve a Rh(I) complex of BIPHEP, which forms a highly efficient and selective catalyst for the enantioselective ene-type cyclization of 1,6-enynes.[11]

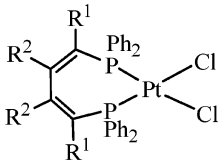
We have recently reported that acyclic and monocyclic NUPHOS diphosphines[12] **1a**−**c** (Chart 1) exhibit tropos character in much the same manner as BIPHEP, in that coordination to Pt(II) slows atropinversion[13] such that enantiopure conformations can be resolved. The resulting enantiopure Lewis acid fragments *λ*- and *δ*-[(NUPHOS)Pt(OTf)$_2$] have been used to catalyze Diels−Alder and hetero Diels−Alder reactions, often giving ee's comparable to those obtained with the corresponding BINAP-based catalysts.[14] To evaluate the potential of the NUPHOS diphosphines, we have initiated an extensive program to compare the performance of platinum group metal complexes of NUPHOS diphosphines with their BINAP counterparts in a range of asymmetric transformations.[14−16] In this paper, the enantioselective addition of olefins to glyoxylate esters has been examined, since it is an important reaction that provides access to synthetically important α-hydroxy esters[17] and has recently been catalyzed by Lewis acid platinum and palladium complexes of atropos biaryl diphosphines.[18] In one report, Hao et al. examined the influence of ligand, counterion, solvent, and temperature on the palladium-catalyzed glyoxylate−ene reaction and demonstrated that [Pd{(*S*)-Tol-BINAP}(MeCN)$_2$][SbF$_6$]$_2$ is a highly efficient catalyst at relatively high reaction temperatures.[18a] Koh et al. subsequently found that the platinum catalyzed glyoxylate−ene reaction was subject to marked anion-dependent additive effects, the addition of acidic phenols resulting in a substantial increase in rate by disrupting contact ion pairs and sequestering traces of water.[18b] Herein, we report that NUPHOS diphosphines form highly efficient catalysts for the glyoxylate−ene reaction, in most cases their performance rivaling that achieved with BINAP. In addition, the catalysts based on NUPHOS diphosphines show marked enhancements in enantioselectivity in ionic liquids compared with organic media, the latter point underpinning an increasing number of reports that ionic liquids can enhance the enantioselectivity of a catalytic asymmetric transformation.[19] For example, Meracz and Oh obtained an ee of 96% for the Diels−Alder reaction between *N*-acryloyl oxazolidinones and cyclopentadiene using copper bis(oxazoline) based Lewis acids in 1,3-dibutylimidazolium tetrafluoroborate, compared with an ee of 76% in dichloromethane.[20] Ruthenium-catalyzed hydrogenations have also been shown to give higher ee's in the ionic liquid compared with methanol.[21]

Results and Discussion

For the studies reported herein, two types of catalyst precursors were examined, the BINOL-ate complexes *λ*- and *δ*-[(NUPHOS)Pt{(*S*)-BINOL}] (*λ*-**2a**, *δ*-**2b**,**c**), since they are crystalline solids and stable with respect to racemization, and the enantiopure dichlorides *λ*- and *δ*-[(NUPHOS)PtCl$_2$] (*λ*-**3a**, *δ*-**3b**,**c**) which can be generated from the corresponding BINOL-ate complexes by reaction with hydrogen chloride in diethyl ether, according to eq 1. Addition of a slight excess of acid to a



$R^1 = R^2 =$ Me, λ(*S*)-**2a**
$R^1 = R^2 =$ Ph, δ(*S*)-**2b**
R^1 = Et, R^2 = -$(CH_2)_4$-, δ(*S*)-**2c**



(1)

$R^1 = R^2 =$ Me, λ-**3a**
$R^1 = R^2 =$ Ph, δ-**3b**
R^1 = Et, R^2 = -$(CH_2)_4$-, δ-**3c**

dichloromethane solution of *λ*- and *δ*-**2a**−**c** resulted in an immediate and dramatic color change from either deep yellow or intense orange-red to a pale yellow/colorless solution associated with rapid and quantitative formation of *λ*- and *δ*-**3a**−**c**, as evidenced by the presence of a single resonance in the ^{31}P NMR spectrum,

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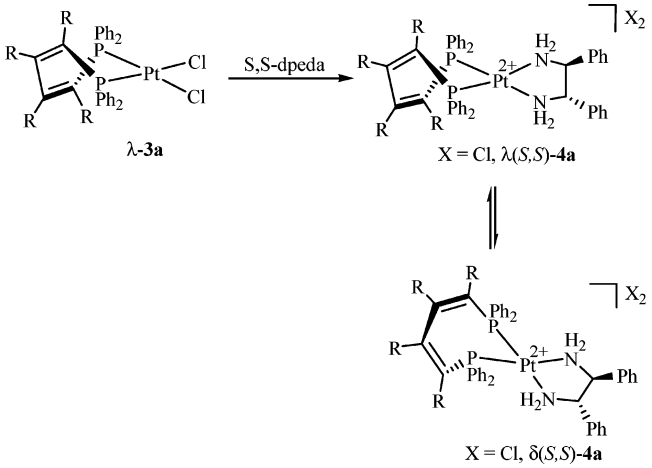
Scheme 1



shifted downfield from that of its BINOL-ate precursor. The resulting complexes were separated from the liberated BINOL with repeated precipitation from dichloromethane by addition of hexane and used without further purification to limit the extent of racemization, which occurs in solution within hours at room temperature. Prior to the conversion of these complexes into the active catalysts, their stereochemical purity and their stereochemical stability in the absence of the resolving agent was examined.

The stereochemical purity of λ-**3a** and δ-**3b**,**c** was investigated by reaction with (*S*,*S*)-1,2-diphenylethylenediamine ((*S*,*S*)-dpeda), which resulted in rapid substitution of both chlorides (<2 min) to afford diastereopure λ- and δ-[(NUPHOS)Pt{(*S*,*S*)-dpeda}]Cl_2 (**4a**−**c**). However, crystallization of λ-**4a** resulted in slow diastereointerconversion, as evidenced by the gradual appearance of an additional signal in the ^{31}P NMR spectrum (Scheme 1). Although X-ray-quality crystals of λ-**4a** could not be obtained, crystallization of its perchlorate salt, [(Me_4-NUPHOS)Pt{(*S*,*S*)-dpeda}]$[ClO_4]_2$, prepared by reaction of λ-**4a** with $NaClO_4$ in methanol, gave crystals suitable for X-ray analysis. The crystal used for the data collection contained both λ(*S*,*S*) and

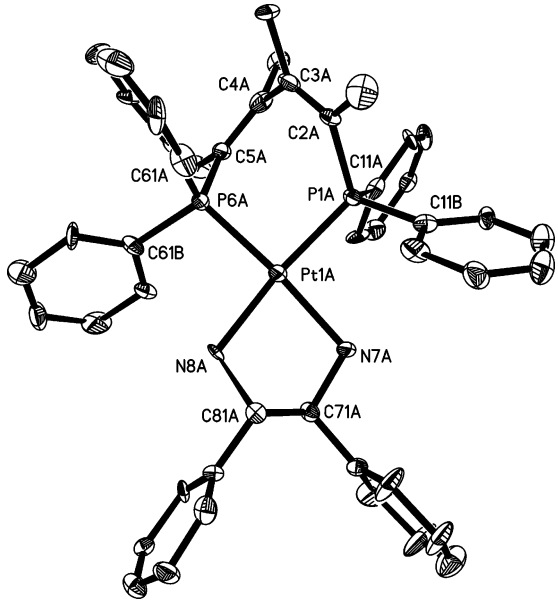


Figure 1. Molecular structure of [(Me_4-NUPHOS)Pt{(*S*,*S*)-dpeda}]$[ClO_4]_2$ (**4a**), showing the λ(*S*,*S*) diastereoisomer with a matched combination of NUPHOS and dpeda stereochemistries. Hydrogen atoms, perchlorate anions, and dichloromethane molecules of crystallization have been omitted for clarity. Ellipsoids are at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pt(1B)−P(1B), 2.255(3); Pt(1B)−P(6B), 2.252(3); Pt(1B)−N(7B), 2.091(9); Pt(1B)−N(8B), 2.110(8); C(2B)−C(3B), 1.325(14); C(3B)−C(4B), 1.491(15); C(4B)−C(5B), 1.338(13); P(1B)−Pt(1B)−P(6B), 89.62(10); N(7B)−Pt(1B)−N(8B), 79.4(3); P(6B)−Pt(1B)−N(7B), 170.6(2); P(6B)−Pt(1B)−N(8B), 94.6(2); P(1B)−Pt(1B)−N(8B), 170.0(3); P(1B)−Pt(1B)−N(7B), 97.5(2); C(2B)−C(3B)−C(4B), 123.7(10); C(3B)−C(4B)−C(5B), 123.8(10); C(2B)−C(3B)−C(31B), 121.8(10); C(21B)−C(2B)−C(3B), 122.8(10); C(31B)−C(3B)−C(4B), 114.4(9); C(41B)−C(4B)−C(5B), 122.5(10); C(3B)−C(4B)−C(41B), 113.5(9); C(4B)−C(5B)−C(51B), 123.3(9).

δ(*S*,*S*) diastereoisomers, and the molecular structure of the λ(*S*,*S*) diastereoisomer is shown in Figure 1, along with a selection of bond lengths and angles in the figure caption. As Figure 1 shows, the backbone of the coordinated NUPHOS adopts a distinctive λ-skew conformation with a dihedral angle of 64.5° between the least-squares planes containing the double bonds and their substituents, which is comparable to those reported for complexes of related four-carbon-bridged diphosphines.[22] The platinum atom is distorted from an ideal square-planar geometry with a dihedral angle of 167° (for both independent molecules) between the PtP_2 and PtN_2 planes; the latter is distorted toward the pseudoaxial P−Ph substituents. The four phenyl rings of the diphenylphosphino groups are arranged in the familiar alternating edge−face arrangement.[23] The natural bite angle of 89.62(10)° is close to the ideal value of 90° and is comparable to those reported for related complexes of BIPHEP[24] and NUPHOS diphosphines,[25] while the angle of 79.4(3)° associated with N(7B)−Pt(1B)−N(8B)

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is significantly smaller than the ideal value and manifests itself in an expansion of the remaining N−Pt−P angles, both of which are larger than 90°. The relative thermodynamic stability of the λ(*S*,*S*) and δ(*S*,*S*) diastereoisomers was investigated by monitoring a dichloromethane solution of the pure λ(*S*,*S*) diastereoisomer by ^{31}P NMR spectroscopy. After standing for several days, resonances corresponding to the δ(*S*,*S*) diastereoisomer began to appear and eventually reached equilibrium with a λ(*S*,*S*):δ(*S*,*S*) ratio of ca. 7:3. The λ(*S*,*S*) diastereoisomer is presumably thermodynamically favored, because the phenyl substituents of the (*S*,*S*)-dpeda are projected toward the less congested quadrants that are occupied by the pseudoaxial P−Ph groups.

The carbonyl−ene reaction was considered an ideal candidate for a comparative study, since the products are highly versatile chiral building blocks and because Lewis acid palladium and platinum complexes of biaryl diphosphines have already been reported to catalyze this transformation. In this study, the addition of a range of unsymmetrical 1,1′-disubstituted olefins to ethyl glyoxylate and phenylglyoxal in [emim][NTf_2] (1-ethyl-3-methylimidazolium trifluorosulfonylimide) and dichloromethane was compared, the results of which are summarized in Tables 1−4. It should be noted that, although the reactions proceeded in 1,2-dichloroethane, tetrahydrofuran, and acetonitrile as well as in dichloromethane, consistently lower ee's were found; hence, dichloromethane was used for all subsequent experiments. The catalysts examined were either generated in situ from diastereopure λ-**2a** and δ-**2b**,**c** by liberating the BINOL resolving agent with an acid of a less-coordinating counterion such as trifluoromethanesulfonic acid or produced by activation of enantiopure λ-**3a** and δ-**3b**,**c** with 2 equiv of silver triflate prior to addition of the substrates (eqs 2 and 3). Regardless of the precursor, activation should typically be carried out at low temperature to prevent racemization of the resulting Lewis acid.

Table 1 summarizes results from the benchmark Lewis acid catalyzed addition of methylenecyclohexane to ethyl glyoxylate and phenylglyoxal using catalysts generated by protonation of the BINOL-ate precursors λ-**2a** and δ-**2b**,**c**. For each of the resulting catalysts λ-**5a** and δ-**5b**,**c**, significantly higher ee's were obtained in [emim][NTf_2] compared with dichloromethane. For example, the Lewis acid λ-**5a** catalyzes the ene reaction between methylenecyclohexane and ethyl glyoxylate to afford the corresponding α-hydroxy ester with an ee of 67% in [emim][NTf_2] and only 6% in dichloromethane. Similarly, λ-**5a** also catalyzed the addition of methylenecyclohexane to phenylglyoxal to give ee's of 80 and 19% in [emim][NTf_2] and CH_2Cl_2, respectively. While [emim][NTf_2] has been chosen for the majority of our studies, catalyst λ-**5a** was shown to perform equally well in a range of ionic liquids, giving ee's of 69% in 1-butyl-3-methylimidazolium trifluorosulfonylimide ([bmim][NTf_2]), 70% in *N*-butyl-*N*-methylpyrollidinium trifluorosulfonylimide ([bmpyr][NTf_2]), and 69% in 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][OTf]), for the ene reaction between methylenecyclohexane and ethyl glyoxylate. The performance of catalysts δ-**5b**,**c** showed a trend similar to that of λ-**5a**: i.e., increased enantioselectivities in [emim][NTf_2] compared with dichloromethane for the addition of methylenecyclohexane to both ethyl glyoxylate (entries 2 and 3) and phenylglyoxal (entries 6 and 7). It should also be noted that, in general, higher isolated yields were obtained in ionic liquid for each substrate−NUPHOS-based catalyst combination compared with dichloromethane. These results show that catalyst performance depends on the NUPHOS diphosphine and that catalysts based on the monocyclic NUPHOS diphosphine **1c** consistently outperformed those formed from its acyclic counterparts **1a**,**b**.

The performance of catalysts based on (*S*)-BINAP was also investigated for the addition of methylenecyclohexane to both ethyl glyoxylate (entry 4) and phenylglyoxal (entry 8), in order to compare directly the efficiency of an atropos biaryl diphosphine with that of NUPHOS diphosphines. The Lewis acid catalyst generated by activation of [{(*S*)-BINAP}$PtCl_2$] with silver triflate gave comparable ee's in [emim][NTf_2] and dichloromethane for both dicarbonyl substrates. In addition, the ee of 75% in dichloromethane for the reaction of methylenecyclohexane with ethyl glyoxylate is similar to that of 74% reported by Koh et al., albeit with [{(*S*)-MeO-BIPHEP}-$Pt(OTf)_2$] and conducted at −50 °C.[18b] Gratifyingly,

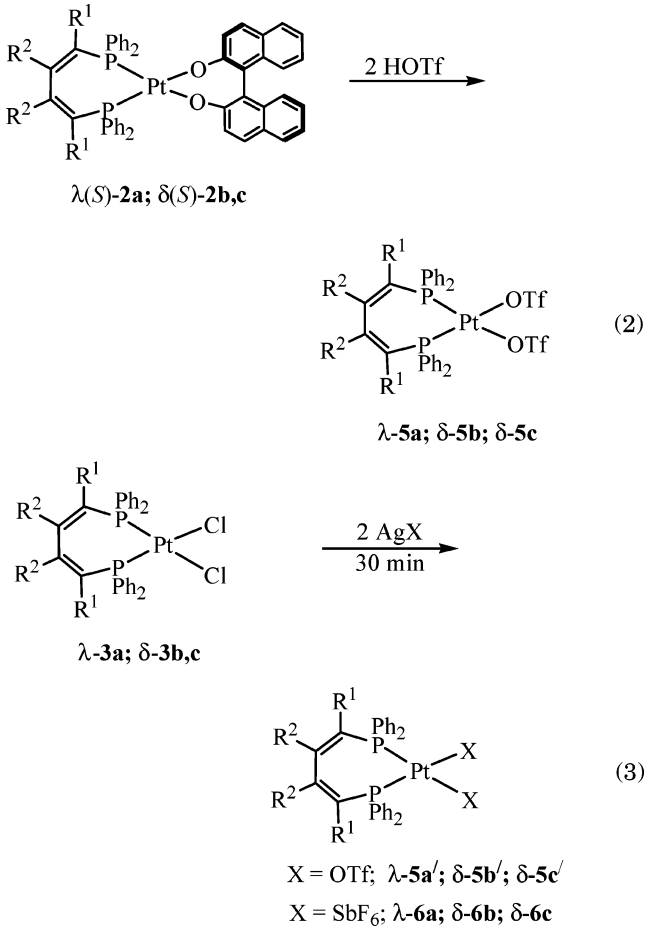

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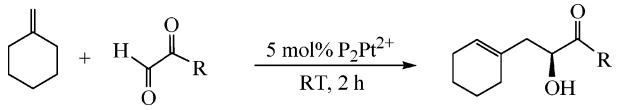
Table 1. Asymmetric Carbonyl−Ene Reaction between Methylenecyclohexane and Ethyl Glyoxylate or Phenylglyoxal Catalyzed by λ-5a and δ-5b,c in [emim][NTf_2] and CH_2Cl_2



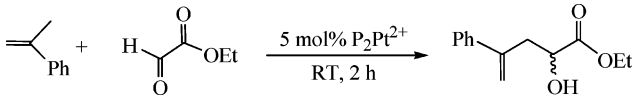
			[emim][NTf_2]		CH_2Cl_2	
entry[a]	catalyst	substrate R[1]	yield (%)[b]	% ee (confign)	yield (%)	% ee (confign)
1	λ-**5a**	OEt	73	67 (*S*)[c]	50	6 (*S*)[c]
2	δ-**5b**	OEt	82	30 (*R*)[c]	79	2 (*R*)[c]
3	δ-**5c**	OEt	74	70 (*R*)[c]	73	61 (*R*)[c]
4	Pt{(*S*)-BINAP}	OEt	56	78 (*R*)[c]	77	75 (*R*)[c]
5	λ-**5a**	Ph	30	80 (*S*)[d]	10	19 (*S*)[d]
6	δ-**5b**	Ph	22	50 (*R*)[d]	0	
7	δ-**5c**	Ph	35	87 (*R*)[d]	24	37 (*R*)[d]
8	Pt{(*S*)-BINAP}	Ph′	35	82 (*R*)[d]	78	84 (*R*)[d]

[a] Reaction conditions: 5 mol % catalyst, methylenecyclohexane (0.25 mmol), and ethyl glyoxylate or phenylglyoxal substrate (0.5 mmol) in 2.0 mL of [emim][NTf_2] or CH_2Cl_2, room temperature. [b] Isolated yields after 2 h run. [c] Enantiomeric excess determined by chiral GLC using a Chrompak Chirasil DEX CB column. [d] Enantiomeric excess determined by chiral HPLC using a Diacel Chiralcel OD-H column. Average of three runs.

these studies have demonstrated that catalysts based on NUPHOS diphosphines, particularly **1c**, can compete with their BINAP counterpart. The absolute configurations of the ene products listed in Table 1 were determined by comparing the HPLC or GC retention times with those reported in the literature. In a recent study, Yamada et al. established the absolute configuration of ene products generated with cobalt(III) complexes of β-ketoiminates derived from (*S*,*S*)-1,2-diphenylethanediamine by NMR analysis of the corresponding MPTA esters[26] and concluded that the absolute stereochemistry was that predicted by the stereochemical model developed for the corresponding hetero Diels−Alder reaction.[27] Lewis acids δ-**5b**,**c** both gave the ene product with *R* absolute configuration, and in this regard, acyclic and monocyclic NUPHOS diphosphines with a δ conformation behave in much the same manner as (*S*)-BINAP (vide infra). As expected, the λ-**5a**-catalyzed ene reaction between methylenecyclohexane and ethyl glyoxylate or phenylglyoxal gave α-hydroxy esters of opposite absolute stereochemistry to those obtained with δ-**5b**,**c**.

The efficiency of catalysts λ-**5a** and δ-**5b**,**c** was also investigated for the addition of a range of other 1,1′-disubstituted olefins to ethyl glyoxylate and phenylglyoxal in [emim][NTf_2] and dichloromethane, the results of which are listed in Tables 2−4. In the case of α-methylstyrene with ethyl glyoxylate, catalysts generated from precursors λ-**2a** and δ-**2b**,**c** each gave the α-hydroxy ester in moderate isolated yields with low to good enantioselectivities in [emim][NTf_2] (Table 2). In comparison, the same reaction in dichloromethane gave little or no yield of α-hydroxy ester and, although some starting material was recovered, significant polymeric material was also isolated. Although the catalysts are most conveniently stored as their BINOL-ate complexes and converted into the active catalyst immediately prior

Table 2. Asymmetric Carbonyl−Ene Reaction between α-Methylstyrene and Ethyl Glyoxylate Catalyzed by λ-5a, δ-5b,c, λ-5a′, and δ-5b,c′ in [emim][NTf_2] and CH_2Cl_2



		[emim][NTf_2]		CH_2Cl_2	
entry[a]	catalyst	yield (%)[b]	% ee (confign)[c]	yield (%)[b]	% ee (confign)[c]
1	λ-**5a**	47	46 (*S*)	0	
2	δ-**5b**	10	25 (*R*)	4	5 (*R*)
3	δ-**5c**	18	65 (*R*)	0	
4	λ-**5a′**	39	50 (*S*)	28	10 (*S*)
5	δ-**5b′**	12	22 (*R*)	18	5 (*R*)
6	δ-**5c′**	47	65 (*R*)	41	28 (*R*)
7	Pt{(*S*)-BINAP}	36	57 (*R*)	47	53 (*R*)

[a] Reaction conditions: 5 mol % catalyst, α-methylstyrene (0.25 mmol) and glyoxal substrate (0.5 mmol) in 2.0 mL of [emim][NTf_2] or CH_2Cl_2, room temperature. [b] Isolated yields after 2 h run. [c] Enantiomeric excess determined by chiral HPLC using a Chiralpak AS column. Average of three runs.

to the addition of substrate, the performance of catalysts generated from the corresponding enantiopure dichlorides λ-**3a** and δ-**3b**,**c** were also examined in order to determine whether the liberated BINOL was responsible for the poor performance of the BINOL-ate derived catalysts in dichloromethane. Reassuringly, Lewis acids λ-**5a′** and δ-**5b′**,**c′**, generated by activation of λ-**3a** and δ-**3b**,**c** with 2 equiv of silver triflate (eq 3), catalyzed the ene reaction between α-methyl styrene and ethyl glyoxylate in [emim][NTf_2] (entries 4−6) and gave isolated yields and enantioselectivities comparable to those obtained with the corresponding BINOL-ate derived catalysts. Interestingly, these catalysts performed markedly better in dichloromethane as compared to those generated from their BINOL-ate counterparts, although the enantioselectivities were still significantly lower than those obtained in [emim][NTf_2]. A comparative study between BINAP- and NUPHOS-based catalysts revealed that [{(*S*)-BINAP}Pt$(OTf)_2$] gave an enantioselectivity of 57% in [emim][NTf_2], slightly lower than that obtained with either δ-**5c** (65%) or δ-**5c′** (65%), while the ee of 53% in dichloromethane was significantly higher than that obtained with any of the NUPHOS-based catalysts. Regardless of the precursor and method of activation, catalysts based on the monocyclic NUPHOS diphosphine **1c** afforded markedly higher enantioselectivities in ionic liquid than either of its acyclic counterparts, as found for methylenecyclohexane (vide supra).

Lewis acids λ-**5a** and δ-**5b**,**c** also catalyze the carbonyl−ene reaction of phenylglyoxal with 2,3-dimethylbut-1-ene and 2,4,4-trimethylpent-1-ene, the results of which are summarized in Tables 3 and 4, respectively. Table 3 reveals that each of the BINOL-ate precursors forms a highly efficient catalyst for the addition of 2,3-dimethylbut-1-ene to phenylglyoxal in [emim][NTf_2] (entries 1−3), giving good to excellent enantioselectivities of (*R*)- and (*S*)-α-hydroxy ester (68−95%). As with the addition of α-methylstyrene to ethyl glyoxylate, these catalyst systems did not give any ene product in dichloromethane, although a low yield of a single byproduct was consistently isolated after aqueous workup and purification by column chromatography. While

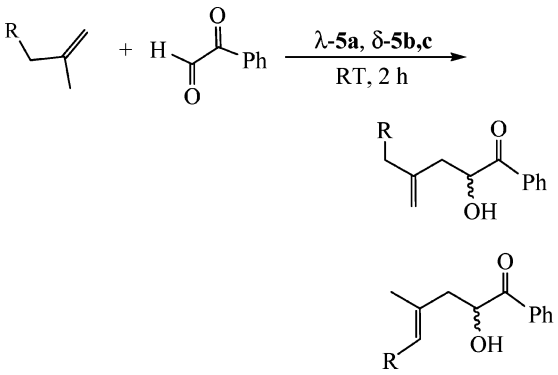
(26) (a) Kezuka, S.; Ikeno, T.; Yamada, T. *Org. Lett*. **2001**, *3*, 1937. (b) Ohtani, I.; Kusumi, T.; Kashnan, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092.

(27) Kezuka, S.; Mita, T.; Ohtsuki, N.; Ikeno, T.; Yamada, T. *Bull. Chem. Soc. Jpn* **2001**, *74*, 1333.

it has not been possible to unequivocally identify this byproduct, a molecular ion of *m/z* 375, corresponding to $[M + Na]^+$ (as well as at *m/z* 727 for $[2M + Na]^+$ and *m/z* 1079 for $[3M + Na]^+$) in the electrospray mass spectrum and its $^1H/^{13}C$ NMR spectra are consistent with a formulation based on 2 mol of phenylglyoxal combining with 1 mol of 2,3-dimethylbut-1-ene. Full details of the spectroscopic data associated with this compound are provided in the Supporting Information. In contrast, excellent enantioselectivities were obtained in both [emim][NTf_2] (83−95%) and dichloromethane (80−89%) with catalysts generated from dichlorides λ-**3a** and δ-**3b**,**c** (Table 3, entries 4−6). Thus, as found for the reaction between α-methylstyrene and ethyl glyoxylate, the precursor and/or the method of activation has a dramatic influence on catalyst performance. This was clearly demonstrated in an experiment designed to investigate whether the BINOL-ate precursor, or more specifically the liberated BINOL, was responsible for the formation of the byproduct in dichloromethane. A catalyst mixture generated by activation of δ-**3c** with 2 equiv of AgOTf, filtered and treated with 1 equiv of (*S*)-BINOL, catalyzed the carbonyl−ene reaction between 2,3-dimethylbut-1-ene and phenylglyoxal to afford the ene product in moderate isolated yield (40%) and high enantioselectivity (94%), with no evidence for the formation of byproduct (Table 3, entry 7). Similarly, a dichloromethane solution of the Lewis acid generated by activation of δ-**3c** with AgOTf and treated with (*S*)-BINOL also catalyzed the reaction between 2,4,4-trimethylpent-1-ene and phenylglyoxal to afford the ene product in 21% isolated yield with an enantioselectivity of 54% (Table 4, entry 7), whereas only starting material was isolated using catalyst generated from the BINOL-ate precursor δ-**5c** (Table 4, entry 3). Lewis acids λ-**6a** and δ-**6b**,**c**, generated by activation of δ- and λ-[(NUPHOS)$PtCl_2$] with $AgSbF_6$ (eq 3), also catalyzed the reaction between phenylglyoxal and 2,3-dimethylbut-1-ene and gave enantioselectivities, in both [emim][NTf_2] and dichloromethane, that were comparable to those obtained with their triflate counterparts (Table 3, entries 8−10). In general, the SbF_6^--based catalysts gave higher yields than the corresponding triflate-based Lewis acids, which is entirely consistent with previous reports such as the platinum(II)-catalyzed glyoxylate−ene reaction[18b] and the ruthenium-catalyzed Diels−Alder reaction between methacrolein and cyclopentadiene.[28] In both of these cases the nature of the counterion showed a marked effect on the rate but not on the enantioselectivity, the reactivity increasing in the order $OTf^- < BF_4^- < SbF_6^-$. As found for other olefins, the most selective catalyst was that based on the monocyclic NUPHOS diphosphine **1c** with both the BINOL-ate and dichloride precursors giving an ee of 95% in [emim][NTf_2], a marked improvement on that of 63% obtained with [{(*S*)-BINAP}$Pt(OTf)_2$].

Not surprisingly, the performance of catalysts λ-**5a** and δ-**5b**,**c** for the addition of 2,4,4-trimethylpent-1-ene to phenylglyoxal in both [emim][NTf_2] and dichloromethane (Table 4) parallels that obtained for 2,3-dimethylbut-1-ene in that (i) moderate to excellent enantioselectivities were obtained in [emim][NTf_2] (39−90%), with the monocyclic catalyst δ-**5c** proving to be the most efficient, giving an enantioselectivity of 90% compared with 82 and 39% obtained with their acyclic counterparts λ-**5a** and δ-**5b**, respectively, and (ii) no ene product was isolated using these catalysts in dichloromethane. It should be noted that, in contrast to 2,3-dimethylbut-1-ene, no byproduct was formed using 2,4,4-trimethylpent-1-ene. The similarity in catalyst performance between the two olefins also includes λ-**5a′**, δ-**5b′**,**c′**, λ-**6a**, and δ-**6b**,**c**, which gave moderate to excellent enantioselectivities in [emim][NTf_2] (55−87%) and dichloromethane (57−90%), with the exception of δ-**5b′**, which gave low enantioselectivities in both solvents. The ee of 88% achieved with catalyst based on (*S*)-BINAP is significantly higher than that of 63% obtained for the corresponding ene reaction with 2,3-dimethylbut-1-ene, which highlights the marked dependence of catalyst performance on substrate structure.

In the case of unsymmetrical 1,1′-disubstituted olefins such as 2,3-dimethylbut-1-ene and 2,4,4-trimethylpent-1-ene, two isomeric ene products are possible[29] (eq 4), and in order to effect a regioselective process the catalyst−glyoxylate complex must discriminate between a methyl group and isopropyl and neopentyl groups, respectively. For both substrates, ^1H NMR analysis of the



(4)

crude reaction mixture revealed complete regioselectivity for all catalysts examined, which is not surprising, given the relative sizes of the 1,1′-substituents. High levels of regioselectivity have recently been reported for these carbonyl−ene reactions catalyzed by optically active cationic cobalt(III) complexes of β-ketoimines.[26a]

This study has demonstrated that enantiopure platinum metal complexes of NUPHOS diphosphines exhibit stereoregular behavior in reactions involving carbonyl substrates capable of two-point binding. While Lewis acids δ-**5b**,**c** both gave an α-hydroxy ester with *R* absolute configuration, that based on λ-**5a** gave the ene product with the opposite absolute stereochemistry. This assignment is entirely consistent with that recently reported by Hao et al., in which Lewis acid palladium(II) complexes of (*S*)-Tol-BINAP catalyzed the asymmetric glyoxylate−ene reaction to afford the (*R*)-α-hydroxy ester.[18a] In this regard, NUPHOS diphosphines with a δ conformation behave in the same manner as atropos biaryl diphosphines in that the absolute stereochemistry of the ene product is the same as that obtained with (*S*)-BINAP and its derivatives. The sense

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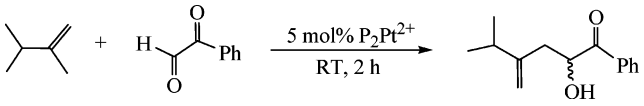
(29) (a) Evans, D. A.; Tregay, S. W.; Burgey, C. S.; Paras, N. A.; Vojkovsky, T. *J. Am. Chem. Soc.* **2000**, *122*, 7936. (b) Evans, D. A.; Wu, J. *J. Am. Chem. Soc.* **2005**, *127*, 8006.

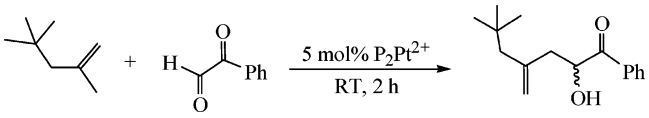
Table 3. Asymmetric Carbonyl−Ene Reaction between 2,3-Dimethylbut-1-ene and Phenylglyoxal Catalyzed by λ-5a, δ-5b,c, λ-5a′, and δ-5b,c′ in [emim][NTf_2] and CH_2Cl_2



		[emim][NTf_2]		CH_2Cl_2	
entry[a]	catalyst	yield (%)[b]	% ee (config)[c]	yield (%)[b]	% ee (config)[c]
1	λ-**5a**	25	90 (*S*)	0	
2	δ-**5b**	29	68 (*R*)	0	
3	δ-**5c**	31	95 (*R*)	0	
4	λ-**5a′**	90	90 (*S*)	54	87 (*S*)
5	δ-**5b′**	20	83 (*R*)	15	80 (*R*)
6	δ-**5c′**	34	95 (*R*)	60	89 (*R*)
7[d]	δ-**5c′**			40	94(*R*)
8	λ-**6a**[e]	95	86 (S)	66	80 (*S*)
9	δ-**6b**[e]	46	84 (*R*)	69	46 (*R*)
10	δ-**6c**[e]	57	92 (*R*)	90	94 (*R*)
11	Pt{(*S*)-BINAP}	6	63 (*R*)	0	

[a] Reaction conditions: 2 mol % catalyst, 2,3-dimethylbut-1-ene (0.25 mmol), and phenylglyoxal (0.5 mmol) in 2.0 mL of [emim][NTf_2] or CH_2Cl_2, room temperature. [b] Isolated yields after 2 h run. [c] Enantiomeric excess determined by chiral HPLC using a Diacel Chiralcel OD-H column. Average of three runs. [d] Catalyst mixture treated with 1 equiv of (*S*)-BINOL prior to addition of substrates. [e] Catalyst mixtures prepared as described for λ-**5a′** and δ-**5b′**,**c′**, by activation of λ-**3a** and δ-**3b**,**c** with 2 equiv of $AgSbF_6$ in CH_2Cl_2 for 30 min at room temperature.

Table 4. Asymmetric Carbonyl−Ene Reaction between 2,4,4-Trimethylpent-1-ene and Phenylglyoxal Catalyzed by λ-5a, δ-5b,c, λ-5a′, and δ-5b,c′ in [emim][NTf_2] and CH_2Cl_2



		[emim][NTf_2]		CH_2Cl_2	
entry[a]	catalyst	yield (%)[b]	% ee (config)[c]	yield (%)[b]	% ee (config)[c]
1	λ-**5a**	42	82 (*S*)	0	
2	δ-**5b**	53	39 (*R*)	0	
3	δ-**5c**	61	90 (*R*)	0	
4	λ-**5a′**	84	80 (*S*)	61	76 (*S*)
5	δ-**5b′**	20	26 (*R*)	47	17 (*R*)
6	δ-**5c′**	25	55 (*R*)	57	56 (*R*)
7[d]	δ-**5c′**			21	54 (*R*)
8	λ-**6a**[e]	84	80 (*S*)	90	79 (*R*)
9	δ-**6b**[e]	52	57 (*R*)	49	51 (*R*)
10	δ-**6c**[e]	94	87 (*R*)	90	85 (*R*)
11	Pt{(*S*)-BINAP}	85	88 (*R*)	82	86 (I)

[a] Reaction conditions: 2 mol % catalyst, 2,2,4-trimethylpent-1-ene (0.25 mmol) and ethyl phenylglyoxal (0.5 mmol) in 2.0 mL of either [emim][NTf_2] or CH_2Cl_2, room temperature. [b] Isolated yields after 2 h run. [c] Enantiomeric excess determined by chiral HPLC using a Diacel Chiralcel OD-H column. Average of three runs. [d] Catalyst mixture treated with 1 equiv of (*S*)-BINOL prior to addition of substrates. [e] Catalyst mixtures prepared as described for λ-**5a** and δ-**5b**,**c** by activation of λ-**3a** and δ-**3b**,**c** with 2 equiv of $AgSbF_6$ in CH_2Cl_2 for 30 min at room temperature.

of asymmetric induction for the ene reaction catalyzed by λ- or δ-[(NUPHOS)Pt]$^{2+}$ is consistent with a model in which ethyl glyoxylate coordinates through both carbonyl oxygen atoms in a bidentate manner to afford a square-planar adduct similar to that formed between [Cu{(*S*,*S*)-t-Bu-box}][SbF_6]$_2$ and glyoxylate (or pyruvate), proposed by Evans and co-workers and used to

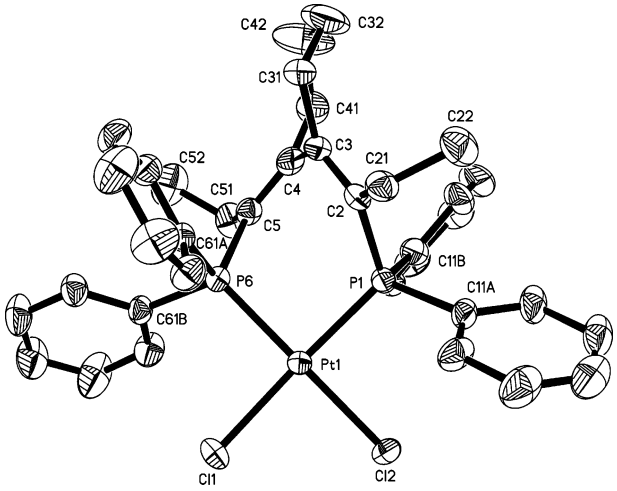


Figure 2. Molecular structure of [(1,4-Et_2-2,3-cyclo-C_6H_8-NUPHOS)$PtCl_2$] (**3c**), highlighting the alternating edge−face arrangement of the diphenylphosphino phenyl rings. Hydrogen atoms and the dichloromethane molecule of crystallization have been omitted for clarity. Ellipsoids are at the 30% probability level. Selected bond lengths (Å) and angles (deg) not discussed in the text: Pt(1)−P(1), 2.227(3); Pt(1)−P(6), 2.24(3); Pt(1)−Cl(1), 2.339(3); Pt(1)−Cl(2), 2.351(3); C(2)−C(3), 1.339(14); C(3)−C(4), 1.498(16); C(4)−C(5), 1.334(16); P(1)−Pt(1)−P(6), 90.28(9); Cl(1)−Pt(1)−Cl(2), 87.66(11); P(6)−Pt(1)−Cl(1), 92.58(11); P(1)−Pt(1)−Cl(2), 90.43(9).

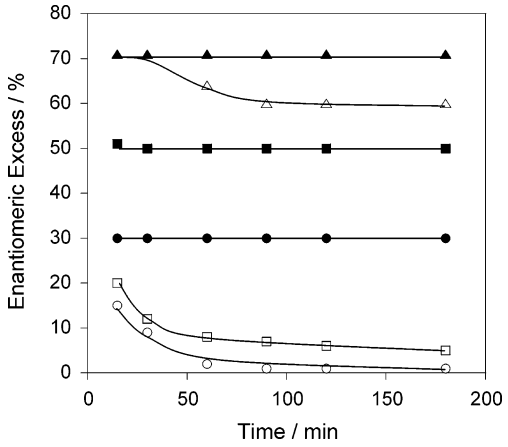


Figure 3. Variation of percent ee for the carbonyl−ene reaction between ethyl glyoxylate and methylenecyclohexane catalyzed by λ-**5a** (squares), δ-**5b** (circles), and δ-**5c** (triangles) in [emim][NTf_2] (solid symbols) and CH_2Cl_2 (open symbols) with respect to time at room temperature.

account for the stereochemical outcome of copper-catalyzed carbonyl−ene reactions.[30] Inspection of this current model (Scheme 2) reveals that the pseudoequatorial phenyl ring attached to P_B of the δ-NUPHOS diphosphine is orientated above the PtP_2 plane in such a manner that the *Si* face of the coordinated glyoxylate is sterically hindered thus favoring reaction of the olefin from the more accessible *Re* face to afford a homoallylic alcohol with an *R* configuration. The asymmetric environment created by the alternating edge−face arrangement of the P−Ph rings of δ-NUPHOS is evident in the

(30) (a) Evans, D. A.; Burgey, C. S.; Paras, N. A.; Vojkovsky, T.; Tregay, S. W. *J. Am. Chem. Soc.* **1998**, *120*, 5824. (b) Evans, D. A.; Kozlowski, M. C.; Burgey, C. S.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **1997**, *119*, 7893.

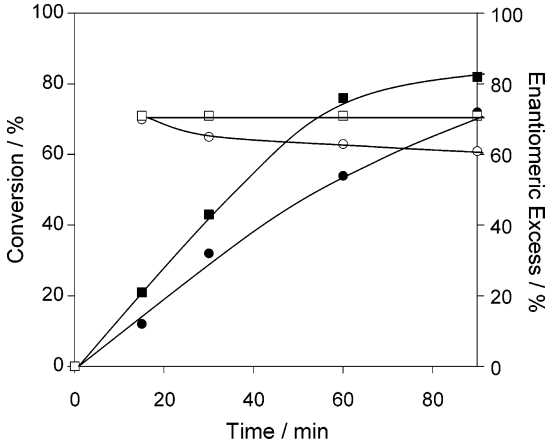
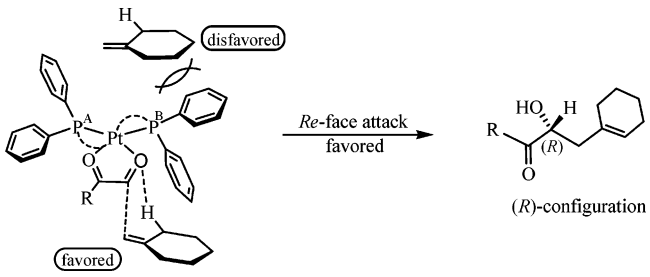


Figure 4. Variation in percent conversion (closed symbols) and percent ee (open symbols) for the ene reaction between ethyl glyoxylate and methylenecyclohexane catalyzed by δ-**5c** in [emim][NTf_2] (squares) and in dichloromethane (circles) with respect to time at room temperature.

Scheme 2



molecular structure of **4c** (Figure 2) and is similar to that adopted by palladium and platinum complexes of (*S*)-BINAP and BIPHEP. This structure shows that P−Ph(11B) and P−Ph(61B) adopt pseudoaxial positions and expose their edges toward the palladium atoms, while the spatial arrangement of the pseudoequatorial P−Ph rings P−Ph(11A) and P−Ph(61A) is between edge and face and that the quadrants occupied by the pseudoaxial P−Ph substituents are less congested than those occupied by their pseudoequatorial counterparts. This model closely resembles that recently proposed to account for the high level of enantiofacial selection obtained in palladium and platinum metal catalyzed Diels−Alder reactions between acryloyl oxazolidinones and cyclopentadiene.[31]

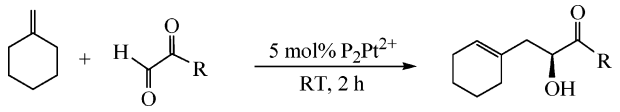
To investigate the origin of the enhancement in enantioselectivity for reactions conducted in ionic liquid compared with dichloromethane, the variation in ee with respect to time for the reaction between methylenecyclohexane and ethyl glyoxylate for each of the BINOLate catalyst precursors, λ-**2a** and δ-**2b**,**c**, in both [emim][NTf_2] and dichloromethane was studied. It is clear from Figure 3 that there is a gradual descrease in ee as the reaction proceeds in dichloromethane, whereas the enantioselectivities remained constant in [emim][NTf_2] over the same period, for each catalyst. Interestingly, while the enhancement in enantioselectivity associated with catalyst generated from δ-**2c** in [emim][NTf_2] appears to be due solely to a gradual erosion of ee in dichloromethane, since the ee's in the initial stages of reaction are similar in both solvents, the enhancement associated with precursors λ-**2a** and δ-**2b** is due to a combination of an intrinsic solvent effect and erosion in ee. The latter point is clearly evident in the markedly different ee's obtained in both solvents in the early stages of reaction; catalyst δ-**5b** gives initial ee's of 30 and 15% in [emim][NTf_2] and dichloromethane, respectively, while the corresponding ee's obtained with λ-**5a** were 51 and 20%.

It is possible that the observed erosion in ee could be associated with a faster rate of racemization of the catalyst in dichloromethane compared with ionic liquid. Indeed, preliminary kinetic studies, based on quenching solutions of catalyst with (*S*,*S*)-dpeda, revealed that the rate of racemization of the catalyst is significantly slower in ionic liquid than in dichloromethane. For example, in a comparative study the first-order rate constant for the racemization of δ-**5b** in dichloromethane, in the absence of substrate, was 1.1×10^{-5} s^{-1} at 30 °C, whereas the corresponding rate constant in [emim][NTf_2] was immeasurably low at 30 °C ($<1 \times 10^{-6}$ s^{-1}) and only 5.6×10^{-6} s^{-1} at 45 °C. While these quenching experiments occur cleanly and quantitatively to give [(NUPHOS)Pt{(*S*,*S*)-dpeda}]$^{2+}$, both in the absence of substrate and in the presence of olefin, the corresponding reactions in the presence of ethyl glyoxylate or the ene product gave rise to a multitude of products, as evidenced by the presence of several additional signals in the ^{31}P NMR spectrum, suggesting that the catalytic reaction mixture most likely comprises a complex set of equilibria. In general, the carbonyl−ene reactions are also found to be faster in [emim][NTf_2] than in dichloromethane (Figure 4). Thus, as well as the decreased racemization rate of the catalyst, this increased reaction rate could also contribute to the enhancement in ee found in the ionic liquid compared with dichloromethane, although it is likely that the more important factor is the stability of the catalyst.

This supposition is supported by the effect of temperature on the variation of enantioselectivity with time and the results from recycling the ionic liquid-catalyst mixtures. As expected, the rate of catalyst racemization may be significantly lowered by reducing the temperature. For example, the reaction between methylenecyclohexane and ethyl glyoxylate using the BINOL-ate catalyst precursor δ-**2c** showed little change in ee (71%) over a 3 h period at −20 °C in dichloromethane, indicating higher catalyst stability at low temperature and demonstrating behavior similar to that observed in [emim][NTf_2] at room temperature. Table 5 summarizes the results of a series of recycling experiments for the addition of methylenecyclohexane to ethyl glyoxylate and phenylglyoxal using catalysts λ-**5a** and δ-**5b** in [emim][NTf_2]. The extractions were performed using diethyl ether in air, and the enantioselectivity remained constant for three successive reactions, indicating little racemization of the catalyst even under reaction conditions. However, a dramatic reduction in the isolated yields over three cycles was found. ICP analysis of the ether extract showed no evidence for leaching of the platinum complexes, and the reduction in the isolated yield is likely to be due to the buildup of polymeric glyoxylate, which deactivates the catalyst, possibly by

(31) (a) Oi, S.; Terada, E.; Ohuchi, K.; Kato, T.; Tachibana, Y.; Inoue, Y. *J. Org. Chem*. **1999**, *64*, 8660. (b) Oi, S.; Kashiwaga, K.; Inoue, Y. *Tetrahedron Lett*. **1998**, *39*, 6253. (c) Ghosh, A. K.; Matsuda, H. *Org. Lett*. **1999**, *1*, 2157.

Table 5. Recycle Carbonyl−Ene Reactions between Methylenecyclohexane and Ethyl Glyoxylate or Phenylglyoxal Catalyzed by δ-5b,c in [emim][NTf$_2$]



entry[a]	catalyst	recyle[b]	substrate R^1	yield (%)[c]	% ee (confign)
1	δ-**5c**		OEt	74	71 (*R*)[d]
2		1		62	70 (*R*)[d]
3		2		43	70 (*R*)[d]
4	δ-**5b**		OEt	82	30 (*R*)[d]
5		1		54	28 (*R*)[d]
6		2		37	28 (*R*)[d]
7	δ-**5c**		Ph	38	87 (*R*)[e]
8		1		32	87 (*R*)[e]
9		2		13	86 (*R*)[e]

[a] Reaction conditions: 5 mol % catalyst, methylenecyclohexane (0.25 mmol) and ethyl glyoxylate or phenylglyoxal substrate (0.5 mmol) in 2.0 mL of [emim][NTf$_2$], room temperature. [b] Ionic liquid extracted with diethyl ether (3 × 5 mL). [c] Isolated yields after 2 h run. [d] Enantiomeric excess determined by chiral GLC using a Chrompak Chirasil DEX CB column. [e] Enantiomeric excess determined by chiral HPLC using a Diacel Chiralcel OD-H column. Average of three runs.

entrapment of the catalyst in the polymer matrix. This is supported by the observation that addition of polymer to a fresh reaction mixture resulted in a significant reduction in the isolated yield of ene product. In addition, it is not straightforward to recycle the catalyst in dichloromethane, showing a further advantage associated with the use of the ionic liquid.

In summary, enantiopure Lewis acid complexes of conformationally flexible acyclic and monocyclic NUPHOS diphosphines, δ- and λ-[(NUPHOS)Pt(OTf)$_2$], are efficient catalysts for the carbonyl−ene reaction between unsymmetrical 1,1′-disubstituted alkenes and phenylglyoxal or ethyl glyoxylate. This study has shown that the type of precursor, the method of activation, and the solvent are all critical factors in obtaining optimum catalyst performance. Without exception, the BINOL-ate precursors formed the most efficient catalysts in ionic liquid, giving marked enhancements in enantioselectivity compared with dichloromethane. In contrast, the performance of catalysts generated from the dichloride precursors depended markedly on the substrate combination, resulting in enantioselectivities at least equal, and often higher, in the ionic liquid compared with dichloromethane. Preliminary kinetic studies have shown that the enhancement in enantioselectivity obtained with catalysts generated from the BINOL-ate precursors in ionic liquids is likely to be due to a combination of decreased racemization rate in [emim][NTf$_2$] and an intrinsic solvent effect. The absolute stereochemistry can be rationalized by a stereochemical model similar to that developed by Oi et al., which was used to account for the high level of enantiofacial discrimination in palladium (*S*)-BINAP catalyzed hetero Diels−Alder reactions.[31] This study has clearly shown that the performance of catalysts based on conformationally flexible NUPHOS diphosphines can rival or even outperform that achieved with BINAP, confirming that this easy-to-prepare and relatively inexpensive class of diphosphine can be used as the sole source of chirality for efficient platinum group metal asymmetric catalysis. Further studies are currently underway to explore the applications of this class of diphosphine in a wide range of asymmetric reactions and to prepare chiral versions for a comparative study. Moreover, platinum group metal complexes based on biaryl diphosphines such as BINAP and its derivatives have recently been reported to be the catalyst of choice for numerous achiral transformations such as the chemo- and regioselective intermolecular cyclotrimerization of terminal alkynes,[32] cycloaddition and cycloisomerization of 1,6-enynes,[33] intramolecular amination of aryl bromides,[34] rhodium-catalyzed isomerization of secondary propargylic alcohols to α,β-enones,[35] and iridium-catalyzed cross coupling of terminal alkynes with internal alkynes.[36] Thus, NUPHOS-type diphosphines could provide a practical and significantly less expensive alternative to BINAP for such platinum group metal catalyzed achiral reactions.

Experimental Section

General Procedures. All manipulations involving air-sensitive materials were carried out in an inert-atmosphere glovebox or using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Diethyl ether was distilled from potassium/sodium alloy and dichloromethane from calcium hydride, and [emim][NTf$_2$] was prepared and dried by following the method of Bonhôte et al.[37] (*S*)-BINAP was purchased from Strem. Unless otherwise stated, commercially purchased materials were used without further purification. Deuteriochloroform was predried with calcium hydride, vacuum-transferred, and stored over 4 Å molecular sieves. The platinum complexes [(NUPHOS)Pt{(*S*)-BINOL}] (λ-**2a**, δ-**2b**,**c**)[13] and [Pt{(*S*)-BINAP)Cl$_2$][31a] were prepared as previously described. Ethyl glyoxylate and phenylglyoxal were purchased from Lancaster and distilled immediately prior to use. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a AMX 300 machine. Purification of reaction products was carried out by column chromatography on reagent silica gel (60−200 mesh). Analytical high-performance liquid chromatography (HPLC) was performed on an Agilent 110 Series HPLC equipped with a variable-wavelength detector using either a Daicel Chiralcel OD-H or a Chiralpak AS column. Chiral GLC was performed on a Agilent 6890N series GC using a Chrompak Chirasil DEX CB column. Enantiomeric excesses were calculated from the HPLC and GC profiles.

Synthesis of λ-[{1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene}PtCl$_2$] (λ-3a). A solution of enantiopure λ-[{1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene}platinum{(*S*)-BINOL}] (λ-**2a**; 1.1 g, 1.15 mmol) in dichloromethane (20 mL) was treated with a diethyl ether solution of HCl (2.5 mL, 2.5 mmol, 1.0 M solution in diethyl ether). Addition of HCl resulted in an immediate color change from deep yellow to near colorless. After 10 min the solution was filtered, the solvent removed under vacuum, and the resulting residue washed with diethyl ether (5 × 10 mL) and hexane (5 × 10 mL). Crystallization of the product by slow diffusion of a dichloromethane solution layered with hexane

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(33) Kezuka, S.; Okado, T.; Niou, E.; Takeuchi, *Org. Lett*. **2005**, *7*, 1711.
(34) Lebedev, A. Y.; Khartulyari, A. S.; Voskoboyonikov, A. Z. *J. Org. Chem*. **2005**, *70*, 596.
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(36) Hirabayashi, T.; Sakaguchi, S.; Ishii, Y. *Adv. Synth. Cat*. **2005**, *347*, 872.
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at −20 °C gave pale yellow λ-**3a** in 67% yield (0.61 g). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ): 6.7 (t, J_{PtP} = 3660 Hz, PPh_2). ^1H NMR (300.0 MHz, $CDCl_3$, δ): 8.36 (br, 4H, C_6H_5), 7.58 (m, 8H, C_6H_5), 7.27 (m, 8H, C_6H_5), 1.23 (d, J_{PH} = 11.2 Hz, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, δ): 149−124 (m, C_6H_5 + C=C), 19.5 (t, J_{PC} = 3.3 Hz, CH_3), 17.5 (t, J_{PC} = 5.6 Hz, CH_3). Anal. Calcd for $C_{32}H_{32}Cl_2P_2Pt$: C, 51.62; H, 4.33. Found: C, 52.06; H, 4.67. $[\alpha]_D$ = +0.216° (*c* 1.0, $CHCl_3$).

δ-[{1,4-bis(diphenylphosphino)-1,2,3,4-tetraphenyl-1,3-butadiene}PtCl$_2$] (δ-3b). Compound δ-**3b** was prepared according to the procedure described above for λ-**3a** and isolated as pale yellow crystals in 82% yield by slow diffusion of hexane into a chloroform solution at −20 °C. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ): 1.9 (t, J_{PtP} = 3607 Hz, PPh_2). ^1H NMR (500.13 MHz, $CDCl_3$, 232 K, δ): 9.57 (br m, 4H, C_6H_5), 7.9 (br m, 6H, C_6H_5), 7.2 (m, 6H, C_6H_5), 6.88, (m, 4H, C_6H_5), 6.7 (t, *J* = 7.3 Hz, 2H, C_6H_5), 6.65 (m, 6H, C_6H_5), 6.54 (t, *J* = 7.9 Hz, 4H, C_6H_5), 6.18 (br, 4H, C_6H_5), 6.11 (d, *J* = 7.3 Hz, 4H, C_6H_5). Anal. Calcd for $C_{52}H_{40}Cl_2P_2Pt$: C, 62.91; H, 4.06. Found: C, 63.23; H, 4.44. $[\alpha]_D$ = −9.07° (*c* 1.0, $CHCl_3$).

δ-[{1,2-bis((diphenylphosphino)ethylmethylene)cyclohexane}PtCl$_2$] (δ-3c). Compound δ-**3c** was prepared according to the procedure described above for λ-**3a** and isolated as yellow crystals in 71% yield by slow diffusion of a chloroform solution layered with hexane. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ): 5.2 (t, J_{PtP} = 3648 Hz, PPh_2). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.19 (br, 4H, C_6H_5), 7.56−6.98 (m, 16H, C_6H_5), 1.34 (m, 4H, Cy H_2 + CH_2CH_3), 0.92 (br m, 2H, Cy H_2), 0.85 (m, 2H, CH_2CH_3), 0.71 (br m, 4H, Cy H_2), 0.13 (t, J_{PH} = 7.2 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, δ): 156−129 (m, C_6H_5), 36.2 (s, Cy CH_2), 29.1 (s, Cy CH_2), 26.1 (t, J_{PC} = 5.2 Hz, CH_2CH_3), 14.8 (s, CH_2CH_3). Anal. Calcd for $C_{36}H_{38}Cl_2P_2Pt$: C, 54.14; H, 4.80. Found: C, 54.42; H, 5.03. $[\alpha]_D$ = −28.92° (*c* 1.0, $CHCl_3$).

Reaction of λ-[{1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene}PtCl$_2$] with (*S*,*S*)-DPEN. A dichloromethane solution of (*S*,*S*)-1,2-diphenylethylenediamine (0.071 g, 0.34 mmol in 5 mL) was added to a stirred solution of enantiopure λ-[(Me_4-NUPHOS)$PtCl_2$] (0.25 g, 0.34 mmol) in dichloromethane. After 5 min the reaction mixture was filtered, the solvent removed, and the residue crystallized from a dichloromethane solution layered with hexane to give **4a** as a 1:1 mixture of diastereoisomers in 72% yield (0.231 g). Although it was not possible to grow crystals of the chloride salt of **4a** suitable for X-ray analysis, crystals of the corresponding perchlorate salt, prepared by reaction of λ-**4a** with $NaClO_4$ in methanol, were obtained by slow diffusion of hexane into a concentrated dichloromethane solution at room temperature, again as a 1:1 mixture of diastereoisomers. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ): −1.5 (t, J_{PtP} = 3449 Hz, PPh_2), −1.6 (t, J_{PtP} = 3388 Hz, PPh_2). ^1H NMR (500.13 MHz, $CDCl_3$, δ): 7.76−7.06 (m, 30H, C_6H_5), 5.10 (d br, *J* = 6.0 Hz, 2H, CHPh), 4.91 (br, 4H, NH_aH_b + CHPh), 4.33 (br d, *J* = 9.4 Hz, 2H, NH_aH_b), 3.16 (br, 2H, NH_aH_b), 2.64 (br d, *J* = 9.6 Hz, 2H, NH_aH_b), 1.78 (d, *J* = 12.0 Hz, 3H, CH_3), 1.63 (d, *J* = 12.0 Hz, 3H, CH_3), 1.11 (s, 6H, CH_3), 1.09 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, δ): 152.8 (d, *J* = 7.8 Hz, C_6H_5), 152.6 (d, *J* = 7.9 Hz, C_6H_5), 136.0−125.4 (m, C_6H_5), 64.8 (s, CHPh), 63.4 (s, CHPh), 20.4 (d, *J* = 3.6 Hz, CH_3), 202. (d, *J* = 3.6 Hz, CH_3), 18.1 (d, *J* = 5.0 Hz, CH_3), 10.0 (d, *J* = 5.0 Hz, CH_3). Anal. Calcd for $C_{46}H_{48}Cl_2N_2O_8P_2Pt$: C, 50.93; H, 4.46; N, 2.58. Found: C, 51.22; H, 4.51; N, 2.73.

General Procedure for Platinum-Catalyzed Enantioselective Carbonyl−Ene Reactions with Catalyst Precursors λ-2a and δ-2b,c: Method A. A flame-dried Schlenk flask charged with δ-**2b** (0.0154 g, 0.0127 mmol) was cooled to 0 °C, and dichloromethane was added (2 mL). The resulting solution was treated with trifluoromethanesulfonic acid (2.1 μL, 0.024 mmol) to give an immediate color change from deep red-orange to near colorless. After the mixture was stirred for 5 min, freshly distilled carbonyl substrate (0.5 mmol) was added, followed by olefin (0.25 mmol). The resulting mixture was warmed to room temperature and stirred for a further 2 h, after which time the solution was filtered through a short plug of silica with diethyl ether, the solvent removed, and the residue purified by column chromatography over silica gel. The product was analyzed by ^1H NMR spectroscopy, and the enantiomeric excess was determined by either chiral GC or HPLC. The absolute configuration of the adduct was assigned by comparison with the retention times reported in the literature, as described below.[26a,30a,38]

General Procedure for Platinum-Catalyzed Enantioselective Carbonyl-ene Reactions with Catalyst Precursors λ-3a, δ-3b,c, and [{(*S*)-BINAP)PtCl$_2$]: Method B. A solution of [{(*S*)-BINAP)$PtCl_2$] (0.0111 g, 0.0125 mmol) in dichloromethane (2 mL) was treated with silver trifluoromethanesulfonate (0.0064 g, 0.025 mmol) or silver hexafluoroantimonate (0.0086 g, 0.025 mmol) and stirred for 30 min until a precipitate of silver chloride had formed. The resulting catalyst solution was filtered to remove AgCl and cooled to 0 °C, and freshly distilled carbonyl substrate (0.5 mmol) was added, followed by olefin (0.25 mmol). The reaction mixture was warmed to room temperature and stirred for a further 2 h, after which the solution was filtered through a short plug of silica with ethyl acetate, the solvent removed, and the resulting residue purified by column chromatography over silica gel. The product was analyzed by ^1H NMR spectroscopy, and the enantiomeric excess was determined by either chiral GC or HPLC.[26a,30a,38]

General Procedure for Platinum-Catalyzed Enantioselective Carbonyl-Ene Reactions with Catalyst Precursors λ-2a and δ-2b,c in 1-Ethyl-2-methylimidazolium Bis(trifluoromethanesulfonimide), [emim][NTf$_2$]: Method A. A flame-dried Schlenk flask charged with δ-**2b** (0.0154 g, 0.0127 mmol) was cooled to 0 °C and dichloromethane added (1 mL). The resulting solution was treated with trifluoromethanesulfonic acid (2.1 μL, 0.024 mmol) to give an immediate color change from deep red-orange to near colorless. After the mixture was stirred for 5 min, [emim][NTf_2] (2 mL) was added and the dichloromethane removed under vacuum, after which freshly distilled carbonyl substrate (0.5 mmol) was added, followed by olefin 0.25 mmol). The resulting mixture was warmed to room temperature and stirred for a further 2 h, after which time the ionic liquid was extracted with diethyl ether (5 × 3 mL) in air. The crude product was purified by column chromatography over silica gel. The product was analyzed by ^1H NMR spectroscopy, and the enantiomeric excess was determined by either chiral GC or HPLC, as described in the Supporting Information.[26a,30a,38]

General Procedure for Platinum-Catalyzed Enantioselective Carbonyl−Ene Reactions with Catalyst Precursors λ-3a and δ-3b,c in 1-Ethyl-2-methylimidazolium Bis(trifluoromethanesulfonimide), [emim][NTf$_2$]: Method B. In a typical procedure, a solution of [{(*S*)-BINAP)$PtCl_2$] (0.0111 g, 0.0125 mmol) in dichloromethane (2 mL) was treated with silver trifluoromethanesulfonate (0.0064 g, 0.025 mmol) or silver hexafluoroantimonate (0.0086 g, 0.025 mmol) and stirred for 30 min until a precipitate of silver chloride had formed. The resulting catalyst solution was filtered to remove AgCl, [emim][NTf_2] (2 mL) added, and the dichloromethane removed under vacuum. The resulting solution was cooled to 0 °C, and freshly distilled carbonyl substrate (0.5 mmol) and olefin (0.25 mmol) were added. The reaction mixture was stirred for a further 2 h, after which the solution was filtered through a short plug of silica with ethyl acetate, the solvent removed, and the resulting residue purified by column chromatography over silica gel. The product was analyzed by ^1H

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NMR spectroscopy, and the enantiomeric excess was determined by either chiral GC or HPLC, as described in the Supporting Information.

General Procedure for Platinum-Catalyzed Enantioselective Carbonyl−Ene Reactions Between Ethyl Glyoxylate and Methylenecyclohexane with Catalyst Precursors λ-3a and δ-3b,c in the Presence of Additives. In a typical procedure a solution of δ-[{1,4-bis(diphenylphosphino)-1,2,3,4-tetraphenyl-1,3-butadiene}$PtCl_2$] (δ-**3b**; 0.0123 g, 0.0125 mmol) in dichloromethane (2 mL) was treated with silver trifluoromethanesulfonate (0.0064 g, 0.025 mmol) or silver hexafluoroantimonate (0.0086 g, 0.025 mmol) and stirred for 30 min, until a precipitate of silver chloride had formed. After the mixture was filtered and stirred for 5 min at 0 °C, (*S*)-BINOL (0.0036 g, 0.0125 mmol), freshly distilled ethyl glyoxylate (0.0670 mL, 0.5 mmol), and methylenecyclohexane (0.030 mL, 0.25 mmol) were added. The resulting mixture was warmed to room temperature and stirred for a further 2 h, after which time the solution was filtered through a short plug of silica with ethyl acetate, the solvent removed, and the residue purified by column chromatography over silica gel (60−200 mesh, 20% ethyl acetate/80% hexane). The product was analyzed by ^{1}H NMR spectroscopy and either chiral GC or HPLC, as described in the Supporting Information.

Ionic Liquid Recycling Experiments. Catalyst mixtures were prepared from the BINOL-ate precursors λ-**2a** and δ-**2b**,**c**, as described above in [emim][NTf_2]. After 2 h the reaction mixture was extracted with diethyl ether (3 × 5 mL), the remaining ionic liquid solution flushed with inert gas and charged with further portions of ethyl glyoxylate (0.0670 mL, 0.5 mmol) and methylenecyclohexane (0.030 mL, 0.25 mmol), and the mixture stirred for a further 2 h. The solution was again extracted using diethyl ether, filtered through a short plug of silica, and purified by column chromatography over silica gel (60−200 mesh, 10% ethyl acetate/90% hexane). The product was analyzed by ^{1}H NMR spectroscopy and either chiral GC or HPLC as described above.

Crystal Structure Determinations of 3c and 4a. Data were collected on a Bruker-AXS SMART diffractometer at 293 K for **3c** and 153 K for **4a** using SAINT-NT software[39] with graphite-monochromated Mo Kα radiation. Selected crystal data are given in Table 6. Crystal stabilities were monitored via re-collection of the first set of frames. There were no significant variations (<1%). Lorentz and polarization corrections were applied. The structures were solved using direct methods and refined with the SHELXTL program package,[40] and the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealized positions, and a riding model was used for subsequent refinements. The function minimized was $\sum[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_o|^2 + (g_1P)^2 + (g_2P)]$, where $P = [\max |F_o|^2 + 2|F_c|^2]/3$. Additional material available from the Cambridge Crystallographic Data Center comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters.

(39) SAINT-NT, Program for Data Collection and Data Reduction; Bruker-AXS, Madison, WI, 1998.

(40) Sheldrick, G. M. SHELXTL Version 5.0, A System for Structure Solution and Refinement; Bruker-AXS, Madison, WI, 1998.

Table 6. Summary of Crystal Data and Structure Determination Details for Compounds 3c and 4a

	3c	**4a**
formula	$C_{36}H_{38}Cl_2P_2Pt\cdot 0.5CH_2Cl_2$	$C_{46}H_{50}NP_2Pt\cdot 2CH_2Cl_2\cdot 2ClO_4$
M_r	841.06	1254.65
cryst color	orange	colorless
cryst size (mm)	0.45 × 0.34 × 0.24	0.2 × 0.2 × 0.2
temp, K	293(2)	153(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$
a, Å	14.289(5)	11.647(3)
b, Å	13.482(5)	23.066(5)
c, Å	19.369(8)	19.835(4)
α, deg	90	90
β, deg	100.15(2)	102.196(4)
γ, deg	90	90
V, Å^3	3673(2)	5208.3(19)
Z	4	4
D_{calcd} (g cm^{-3})	1.5	1.6
F(000)	1668	2512
μ(Mo Kα) (mm^{-1})	10.149	3.116
θ_{max}, deg	57.50	23.30
no. of rflns measd	4973	14 838
no. of unique rflns	4235	12 403
R_{int} (on F^2)	0.0685	0.0849
no. of params	398	1215
R^a ($F^2 > 2\sigma(F^2)$)	0.0587	0.0413
$R_w{}^b$ (all data)	0.0582	0.0903
GOF^c (S)	1.127	0.976
max, min diff map (e Å^{-3})	1.828, −1.346	1.424, −0.815

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. [c] GOF = $[\sum w(F_o^2 - F_c^2)^2/((\text{no. of unique rflns}) - (\text{no. of params}))]^{1/2}$.

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Supporting Information Available: Full details of experimental procedures, characterization data, and representative GC and HPLC traces for the ene products and for **3c** and **4a** details of crystal data, structure solution, and refinement, atomic coordinates, bond distances, bond angles, and anisotropic thermal parameters in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor tables are available from the authors upon request.

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