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Metal-Dependent Reactivity of Electrophilic Platinum Group Metal Lewis Acid Catalysts: Competitive Alkene Dimerization, Intramolecular Friedel−Crafts Alkylation, and Carbonyl-Ene Reactivity

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Lewis acid complexes of the type [M{(*R*)-BINAP}][SbF_6]$_2$ (M = Pt, Pd, Ni) catalyze the reaction between α-methylstyrenes and ethyl trifluoropyruvate to afford products resulting from the expected carbonyl-ene reactivity as well as tandem alkene dimerization−carbonyl-ene addition and alkene dimerization−Friedel−Crafts alkylation pathways, the distribution of which depends on the metal and the substituent attached to the aromatic ring of the styrene substrate. Kinetic studies reveal that the Lewis acid platinum complex catalyzes the dimerization of 4-chloro-α-methylstyrene much faster than its palladium counterpart and that the corresponding nickel system has platinum-like reactivity and selectivity.

Introduction

Platinum group metal Lewis acid complexes of the type [M(diphosphine)]$^{2+}$ (M = Pt, Pd, Ni) have recently emerged as a highly versatile class of catalyst for a number of important asymmetric transformations including Diels−Alder[1] and hetero-Diels−Alder reactions,[2] the carbonyl-ene reaction,[3] conjugate addition of amines to activated alkenes,[4] asymmetric Prins cyclizations,[5] 1,3-dipolar cycloadditions,[6] and the Conia-ene reaction[7] as well as a host of reactions based on palladium enolate intermediates.[8] In contrast to conventional Lewis acid catalysts,[9] those based on group 10 are characterized by well-defined coordination geometries, slow rates of ligand exchange, high carbophilicity, tunable electrophilicity/steric environment through ligand modification, and good functional group tolerance.[10] Consequently, new reaction pathways are beginning to emerge using Lewis acids of group 10, for example, the palladium-catalyzed Mukaiyama reaction, which proceeds through a C-bound enolate rather than by conventional Lewis acid activation of the electrophilic substrate.[11] Platinum(II) has also been shown to have exceptional properties as a Lewis acid in that it promotes the catalytic outersphere addition of nucleophiles to alkenes followed by an intermediate rearrangement/addition prior to M−C cleavage.[12] While platinum(II) and palladium-

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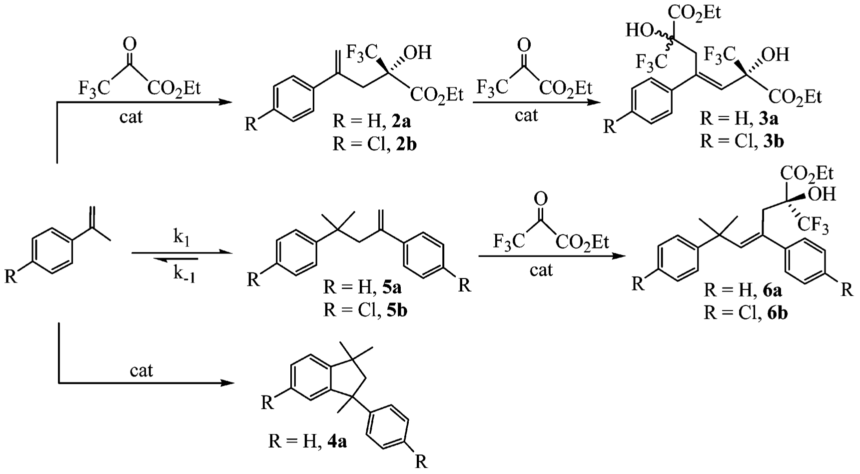
Scheme 1



(II) both efficiently activate alkenes toward nucleophilic addition, they differ quite markedly in the subsequent M−C bond cleavage, which often leads to complementary reactivity patterns. The unique reactivity of platinum(II) appears to be associated with strong metal−ligand bonding, slow ligand substitution, and slow rates of metal-based reactions compared with palladium. In such cases catalyst turnover occurs via M−C protonolysis, cation rearrangement, and cyclopropanation chemistry rather than conventional pathways such as β-elimination−dissociation. Although a relatively recent discovery, platinum(II) is showing enormous potential for applications in synthetic chemistry, and several useful transformations have already been identified/developed including hydroarylation,[13] hydrovinylation,[14] diene cycloisomerization,[15] ring expansion,[16] and alkene dimerization.[17]

Not surprisingly, the use of platinum-based Lewis acid catalysts in synthesis could therefore result in competitive reaction pathways, depending on the combination of reactants. In this regard, we have been investigating the platinum group metal-catalyzed carbonyl-ene reaction between styrene substrates and ethyl trifluoropyruvate and discovered that alkene dimerization, tandem alkene dimerization−carbonyl-ene reactivity, and intramolecular Friedel−Crafts alkylation all compete with the desired reaction, to give a range of products, the distribution of which depends on the metal center. In this paper, we emphasize a subtle but potentially important difference between the reactivity of Lewis acid complexes of platinum(II) and palladium(II) as well as platinum-like behavior of the corresponding nickel(II) catalyst.

Results and Discussion

The Lewis acid catalysts **1a**−**c** used in this study were all generated by treatment of a dichloromethane solution of the corresponding platinum dichloride complex [M{(*R*)-BINAP}Cl_2] (M = Pt, Pd, Ni) with 2 equiv of silver hexafluoroantimonate for 30 min immediately prior to addition of substrate (eq 1).

$$\begin{array}{c}[M\{(R)\text{-BINAP})Cl_2]\\ +\\ 2\ AgSbF_6\end{array} \xrightarrow[\text{2 AgCl}]{CH_2Cl_2\text{,30 min}} \begin{array}{c}[M\{(R)\text{-BINAP}\}](SbF_6)_2\\ M = Pt,\ \mathbf{1a}\\ M = Pd,\ \mathbf{1b}\\ M = Ni,\ \mathbf{1c}\end{array} \quad (\mathbf{1})$$

This study began with a comparison of the performance of Lewis acids **1a**−**c** as catalysts for the carbonyl-ene reaction between α-methylstyrene and ethyl trifluoropyruvate, which, rather unexpectedly, gave a mixture of products that result from metal-dependent competing reaction pathways, full details of which are summarized in Scheme 1 and Table 1. In the case of Lewis acid **1a** the expected α-hydroxy ester **2a** formed only a minor component of the reaction mixture, and the major product was identified as **3a** together with a significant amount of **4a**, after purification by column chromatography and analysis by NMR spectroscopy and mass spectrometry (entry 1). The identity of **3a** was also unequivocally established by single-crystal X-ray analysis. α-Hydroxy ester **3a** is the product of a double ene reaction and results from addition of **2a** to ethyl trifluoropyruvate, while **4a** is postulated to arise via platinum-catalyzed dimerization of α-methylstyrene followed by intramolecular Friedel−Crafts alkylation of the intermediate platinum alkyl cation **I** (Scheme 2). In stark contrast, catalyst **1b** is entirely selective for ene reactivity and gave α-hydroxy ester **2a** as the major product together with a minor amounts of **3a** (entry 3). Qualitatively the product distribution obtained with Lewis acid **1c** most closely resembles that obtained with its platinum counterpart in that α-hydroxy ester **3a** is the major product, while **4a** is formed as a minor component with only a small amount of **2a** (entry 5). While reactions were typically run for 60 min and reached 100% conversion, reactions stopped after 1 min showed a similar distribution of products in that the (**2a**+**3a**):**4a** ratios are similar to those obtained after 60 min and differ only in the relative amounts of **2a** and **3a**, i.e., the extent of double ene reaction. A brief survey of the solvent revealed that there was no evidence for reaction in THF, dioxane, or acetonitrile, and hence dichloromethane was used for all subsequent experiments.

Each of the catalysts **1a**−**c** gave excellent conversions, complete *E*-selectivity for **3a**, moderate to good enantioselectivity for **2a**, and low to moderate diastereoselectivity for **3a**. In addition catalysts **1a**−**c** were all completely selective for the

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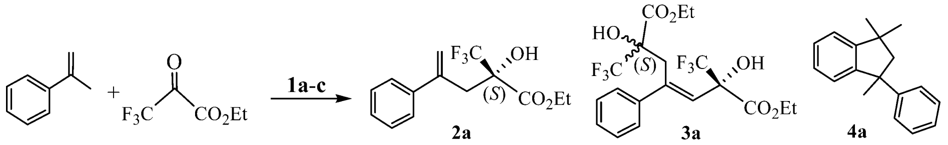
Table 1. Asymmetric Carbonyl-Ene Reaction between α-Methylstyrene and Ethyl Trifluoropyruvate Catalyzed by (*R*)-1a−c in CH_2Cl_2[a]

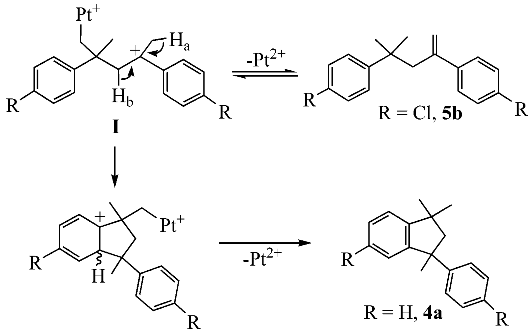


2a **3a** **4a**

entry	catalyst	time (min)	conv[b] (%)	product ratio[c] 2a:3a:4a	dr[d] 3a	% ee[e] 2a	% ee[e] 3a
1	(*R*)-**1a**	60	100	4:69:27	37:32	36	48, 92
2	(*R*)-**1a**	1	>99	55:20:25	14:6	35	47, 91
3	(*R*)-**1b**	60	100	89:11:0	8:1	79	nd, nd
4	(*R*)-**1b**	1	>99	100:0:0		78	
5	(*R*)-**1c**	60	100	23:64:13	36:28	79	49, 97
6	(*R*)-**1c**	1	>99	80:7:13	6:1	79	nd, 97

[a] Reaction conditions: 5 mol % catalyst, α-methylstyrene (0.4 mmol), and ethyl trifluoropyruvate (0.6 mmol) in 2.0 mL of CH_2Cl_2, room temperature. [b] Conversions determined by GC using a Supelco Beta DEX column. [c] Product ratios determined by ^1H NMR spectroscopy and GC. [d] Diastereoisomeric ratio of **3a** determined by ^1H NMR spectroscopy and chiral GC and listed as *R**,*S**:*S**,*S**. Relative configuration determined by single-crystal X-ray analysis of **3a**. [e] Enantiomeric excess determined by chiral GC using a Supelco Beta DEX column and for **3a** listed as (*R*,*S*),(*S*,*S*). Absolute configuration assigned by analogy. Average of three runs. nd = not determined.

Scheme 2



Friedel−Crafts dimer, with no evidence for the formation of acyclic dimer **5a**, which would result from elimination of the hydrocarbon from **I** by loss of H_a (Scheme 2), which is in marked contrast to the corresponding transformation with 4-chloro-α-methylstyrene (*vide infra*). Peppe has recently reported that indium(III) bromide catalyzes the dimerization of α-methylstyrene to afford **5a** as the kinetic product, which ultimately isomerizes into **4a** after 4 h, presumably via an intermediate similar to **I**.[18] In this regard, we found no evidence for the formation of **5a**, and even after performing the reaction at 0 °C for 1 min **2a**, **3a** and **4a** were the only identifiable products, although this does not conclusively rule out rapid and reversible formation of **5a** under these conditions. A separate experiment involving **4a**, 1 equiv of ethyl trifluoropyruvate, and Lewis acids **1a−c** showed no evidence for the formation of α-hydroxy esters **2a** or **3a**, confirming that Friedel−Crafts alkylation is irreversible. Even though **4a** was obtained as a racemic mixture, we suggest that it forms via the *σ*-bonded platinum cation **I** (R = H) since the rate of dimerization of 4-chloro-α-methylstyrene to afford **5b**, which presumably involves the corresponding intermediate where R = Cl, is markedly dependent on the metal (*vide infra*).

The distribution of products obtained with these catalysts most likely reflects the relative rates of styrene dimerization/Friedel−Crafts alkylation versus ene reactivity, which is qualitatively consistent with the observed **2a**:**3a**:**4a** ratios since fast dimerization would consume α-methylstyrene, increase the concentration of pyruvate relative to α-hydroxy ester **2a**, and thus favor formation of the double ene product, as is observed with catalysts **1a** and **1c**. The absolute stereochemistry of **2a** was assigned by analogy with the corresponding product obtained from the reaction between methylenecyclohexane and ethyl trifluoropyruvate;[3f] the relative stereochemistry of the major diastereoisomer of **3a** was unequivocally determined to be (2*R**,6*S**) by single-crystal X-ray structure analysis (Figure 1),[19] and the absolute stereochemistry has been assigned by analogy with that established for **3b** (*vide infra*).

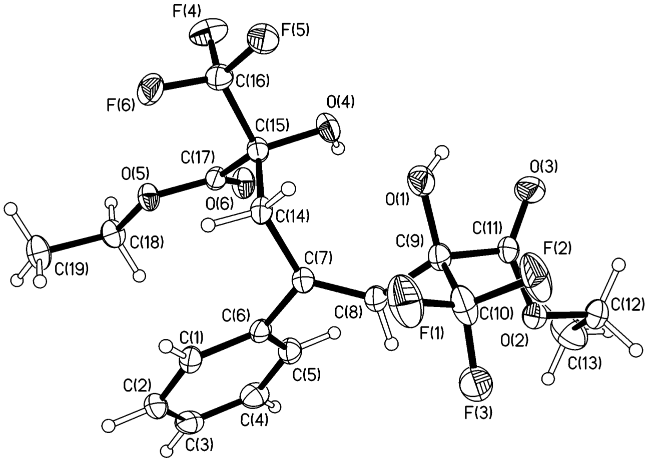


Figure 1. Molecular structure of diethyl 2,6-dihydroxy-4-phenyl-2,6-bis(trifluoromethyl)hept-3-enedioate (**3a**) with 40% probability displacement ellipsoids showing the relative stereochemistry of C(9) and C(15).

The differing reactivity of Lewis acids **1a−c** also extends to the corresponding addition of 4-chloro-α-methylstyrene to ethyl trifluoropyruvate, albeit with a much less marked variation in product distribution (Table 2). For this substrate combination, catalysts **1a−c** each gave α-hydroxy ester **2b** as the major

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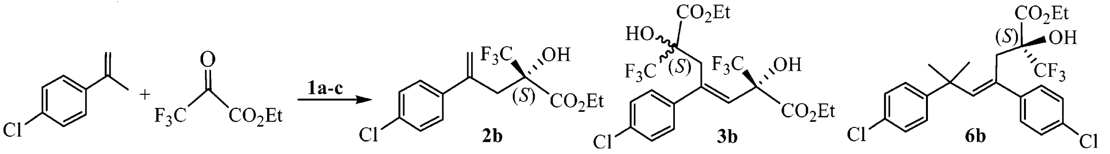
(19) (a) Crystal data for **3a**: $C_{19}H_{20}F_6O_6$, $M_r = 458.4$, triclinic, $P\bar{1}$, $a = 9.6109(12)$ Å, $b = 11.0995(14)$ Å, $c = 11.2859(14)$ Å, $\alpha = 99.188(2)°$, $\beta = 113.528(2)°$, $\gamma = 105.054(2)°$, $V = 1017.7(2)$ Å^3, $Z = 2$, $T = 150$ K, $R(F, F^2 > 2\sigma) = 0.0480$, $R_w(F^2$, all data$) = 0.1571$, using data from a twinned crystal. (b) Crystal data for **3b**: $C_{19}H_{19}ClF_6O_6$, $M_r = 492.8$, monoclinic, $P2_1/n$, $a = 11.715(3)$ Å, $b = 11.8054(15)$ Å, $c = 16.619(4)$ Å, $\beta = 108.851(18)°$, $V = 2175.0(8)$ Å^3, $Z = 4$, $T = 150$ K, $R(F, F^2 > 2\sigma) = 0.0498$, $R_w(F^2$, all data$) = 0.1462$.

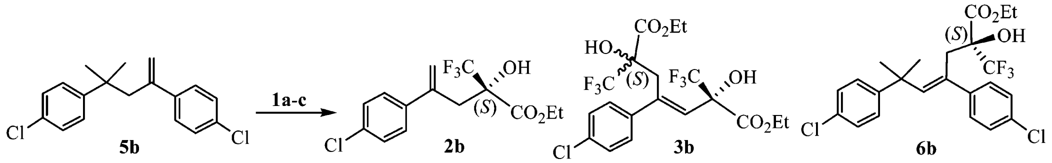
Table 2. Asymmetric Carbonyl-Ene Reaction between 4-Chloro-α-methylstyrene and Ethyl Trifluoropyruvate Catalyzed by (*R*)-1a−c in CH_2Cl_2[a]



				product ratio[c]	dr[d]	% ee[e]	% ee[e,f]	% ee[g]
entry	catalyst	time (min)	conv[b] (%)	**2b**:**3b**:**6b**	**3b**	**2b**	**3b**	**6b**
1	(*R*)-**1a**	60	100	85:12:3	5:7	58	53, 98	82
2	(*R*)-**1a**	1	>99	94:2:4	1:1	58	nd	81
3	(*R*)-**1b**	60	100	98:1.7:0.3	7:10	88	nd	nd
4	(*R*)-**1b**	1	97	100:0:0		88		
5	(*R*)-**1c**	60	100	86:13:1	6:7	68	47, 99	nd
6	(*R*)-**1c**	1	99	98:1.3:0.7	5:8	68	nd	nd

[a] Reaction conditions: 5 mol % catalyst, 4-chloro-α-methylstyrene (0.4 mmol), and ethyl trifluoropyruvate (0.6 mmol) in 2.0 mL of CH_2Cl_2, room temperature. [b]Conversions determined by GC using a Supelco Beta DEX column. [c]Product ratios determined by ^{1}H NMR spectroscopy. [d]Diastereoisomeric ratio of **3b** determined by ^{1}H NMR spectroscopy and chiral GC and listed as *R**,*S**:*S**,*S**. Relative configuration determined by single-crystal X-ray analysis of **3b**. [e]Enantiomeric excess determined by chiral GC using a Supelco Beta DEX column and for **3b** listed as (*R*,*S*),(*S*,*S*). [f]Absolute configuration assigned by analogy and by analysis of the ee's of **3b** obtained from two parallel carbonyl-ene reactions using samples of (2*S*)-**2b** with different enantiopurity. [g] Enantiomeric excess determined by HPLC using a Diacel Chiralpak AD-H column. Absolute configuration assigned by analogy and by analysis. Average of three runs. nd = not determined.

Table 3. Asymmetric Carbonyl-Ene Reaction between 5b and Ethyl Trifluoropyruvate Catalyzed by (*R*)-1a−c in CH_2Cl_2[a]



				product ratio[c]	dr[d]	% ee[e]	% ee[e,f]	% ee[g]
entry	catalyst	time (min)	conv[b] (%)	**2b**:**3b**:**6b**	**3b**	**2b**	**3b**	**6b**
1	(*R*)-**1a**	60	100	81:11:8	5:6	58	53, 99	82
2	(*R*)-**1b**	60	100	20:9:71	2:7	88	nd	98
3	(*R*)-**1c**	60	100	87:10:3	1:2	68	45, 99	84

[a] Reaction conditions: 5 mol % catalyst, 2,4-di(4′-chlorophenyl)-4-methylpent-1-ene (0.4 mmol), and ethyl trifluoropyruvate (0.6 mmol) in 2.0 mL of CH_2Cl_2, room temperature. [b] Conversions determined by GC using a Supelco Beta DEX column. [c] Product ratios determined by ^{1}H NMR spectroscopy. [d] Diastereoisomeric ratio of **3b** determined by ^{1}H NMR spectroscopy and chiral GC and listed as *R**,*S**:*S**,*S**. Relative configuration determined by single-crystal X-ray analysis of **3b**. [e] Enantiomeric excess determined by chiral GC using a Supelco Beta DEX column. [f] Absolute configuration assigned by analogy and by analysis of the ee's of **3b** obtained from two parallel carbonyl-ene reactions using (2*S*)-**2b** of differing enantiopurity. [g] Enantiomeric excess determined by HPLC using a Diacel Chiralpak AD-H column. Absolute configuration assigned by analogy. Average of three runs. nd = not determined.

product, in high yield and moderate to good enantioselectivity, a minor amount of **3b**, in poor diastereoselectivity, and a new α-hydroxy ester, **6b**, the identity of which was unequivocally established on the basis of spectroscopic and analytical data. As for α-methylstyrene, the performance of catalyst **1a** most closely resembles that of **1c** in that the **2b**:**3b**:**6b** ratios are similar, whereas Lewis acid **1b** is markedly more selective for α-hydroxy ester **2b**. Formation of **6b** can be accounted for by dimerization of 4-chloro-α-methylstyrene to afford **5b** followed by addition to ethyl trifluoropyruvate, which was confirmed by reaction of **5b**, prepared independently by the Lewis acid-catalyzed dimerization of 4-chloro-α-methylstyrene, with ethyl trifluoropyruvate in the presence of Lewis acids **1a**−**c**. Fortuitously, the dimerization of 4-chloro-α-methylstyrene was highly regioselective with no evidence for the internal alkene that would result from loss of H_b from the intermediate platinum alkyl cation **I** (Scheme 2). In this regard, Shirakawa has recently reported that a palladium−indium−triflate system catalyzes the dimerization of vinylarenes to afford a mixture of terminal and internal isomers, although the ratios were not reproducible.[20] In addition to demonstrating that **6b** results from an ene reaction between **5b** and ethyl trifluoropyruvate, this experiment also revealed that dimerization of 4-chloro-α-methylstyrene is reversible since α-hydroxy esters **2b** and **3b** were also formed in this reaction. Interestingly, the distribution of α-hydroxy esters **2b**, **3b**, and **6b** obtained from the reaction between **5b** and ethyl trifluoropyruvate also showed a marked dependence on the Lewis acid catalyst, which is clearly evident in the product ratios listed in Table 3. In particular, while catalyst **1b** gave α-hydroxy ester **6b** as the dominant product, in good enantioselectivity (entry 2), Lewis acids **1a** and **1c** both gave **2b** as the major product, also in good enantioselectivity, together with a minor amount of **3b** (entries 1 and 3). Even though **4b** and **5b** both form via platinum alkyl cation **I**, there was no evidence for the Friedel−Crafts product derived from 4-chloro-α-methylstyrene, which is entirely consistent with the deactivating influence of the electron-withdrawing substituent, rendering elimination of H_a to afford **5b** more favorable than Friedel−Crafts alkylation. Preferential elimination of a proton rather than a Friedel−Crafts

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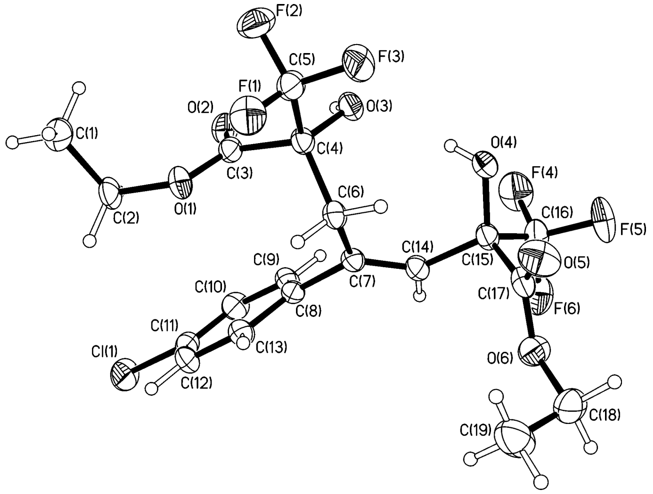

Figure 2. Molecular structure of diethyl 4-(4-chlorophenyl)-2,6-dihydroxy-2,6-bis(trifluoromethyl)hept-3-enedioate (**3b**) with 40% probability displacement ellipsoids showing the relative stereochemistry of C(4) and C(15).

alkylation pathway has recently been reported for less activated arenes in the platinum(II) chloride-catalyzed rearrangement of methylenecyclopropanes; the same study also demonstrated that Friedel−Crafts alkylation is favored for electron-rich arenes.[16] As for the reaction involving α-methylstyrene, the absolute stereochemistry of **2b** was assigned by analogy and the relative configuration of the major diastereoisomer of **3b** was established to be (2*S**,6*S**) by single-crystal X-ray structure analysis (Figure 2); on the basis that the major enantiomer is derived from (*S*)-**2b** we are confident that the absolute configuration is (2*S*,6*S*). In the case of the minor diastereoisomer, the absolute configuration has been determined by analysis of the products generated from two parallel ene reactions between ethyl trifluoropyruvate and **2b**, of 87 and 53% ee, both catalyzed by Lewis acid **1a**.[21] This analysis is entirely consistent with the major enantiomer of (2*S**,6*R**)-**3b** having (2*R*,6*S*) absolute configuration; the stereochemistry of (2*S**,6*R**)-**3a** was assigned by analogy (*vide infra*). Finally, this conclusion is supported by a similar analysis of the product distribution obtained from the ene reaction between *rac*-**2b** and ethyl trifluoropyruvate, also catalyzed by **1a**.[21] Although these experiments do not allow the relative rates of formation of (2*R*,6*S*)-**3b** and (2*S*,6*R*)-**3b** to be determined, we have established relative rates for the formation of (2*S*,6*S*)-**3b** versus (2*S*,6*R*)-**3b** ($k_{(S,S)}/k_{(S,R)} \approx 13/1$) and (2*R*,6*S*)-**3b** versus (2*R*,6*R*)-**3b** ($k_{(R,S)}/k_{(R,R)} \approx 20/1$).

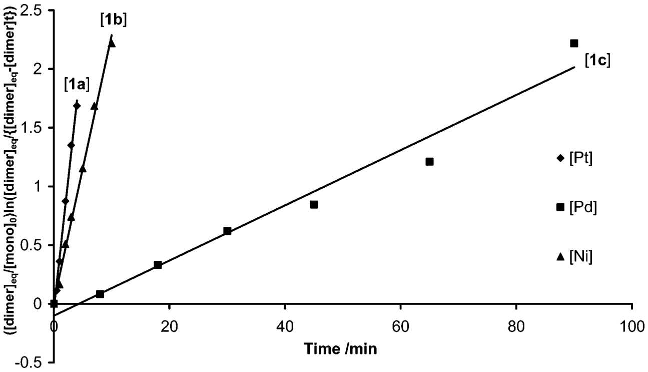

Figure 3. Reversible first-order analysis for the dimerization of 4-chloro-α-methylstyrene in dichloromethane at room temperature.

Reasoning that the catalyst-dependent distribution of α-hydroxy esters **2b**, **3b**, and **6b** obtained for the reaction between 4-chloro-α-methylstyrene and ethyl trifluoropyruvate reflects the relative rates of dimerization versus ene reactivity, the variation in composition with respect to time for the dimerization of 4-chloro-α-methylstyrene was monitored for each catalyst **1a**−**c** to obtain an order of activity. Analysis of a dichloromethane solution of 4-chloro-α-methylstyrene and catalyst **1a** revealed that dimer **5b** gradually increases at the expense of the monomer until equilibrium is reached after approximately 10 min. Qualitatively the palladium- and nickel-based systems also show a similar variation of product with time, but the former approaches equilibrium much more slowly (ca. 2 h), while the latter reaches equilibrium within 12 min. Analysis of the data reveals that the process obeys reversible first-order relaxation kinetics, and Figure 3 shows the reversible first-order analysis of the dimerization using the integrated rate expression for a standard reversible first-order process (A ↔ B).[22] The first-order rate constants, k_1, of 0.445 mol^{-1} dm^3 min^{-1} (**1a**), 0.227 mol^{-1} dm^3 min^{-1} (**1c**), and 0.023 mol^{-1} dm^3 min^{-1} (**1b**) reveal that the platinum- and nickel-based Lewis acids catalyze the dimerization (and retrodimerization) of 4-chloro-α-methylstyrene significantly faster than their palladium counterpart. Thus, efficient retrodimerization of **5b** by catalysts **1a** and **1c** accounts for the formation of **2b** and **3b** as the major products from the ene reaction between **5b** and ethyl trifluoropyruvate, whereas retrodimerization with catalyst **1b** is significantly slower, and in this case α-hydroxy ester **6b** is formed as the major product. By analogy, vastly disparate rates for alkene dimerization also account for the significant amount of Friedel−Crafts alkylation product **4a** obtained from the reaction between α-methylstyrene and ethyl trifluoropyruvate in the presence of catalysts **1a**/**1c** and the exclusive ene selectivity obtained with **1b**. In this regard, since we have previously shown that platinum-based Lewis acids are more active ene catalysts than their palladium counterparts, the high ene selectivity obtained with catalyst **1b** must be due to the markedly lower rate of dimerization compared with **1a**/**1c**.

Conclusions

Platinum group metal complexes of the type [M(diphosphine)]$^{2+}$ (M = Pt, Pd, Ni) are a potentially versatile class of Lewis acid catalyst with properties and reactivity patterns that complement their more conventional counterparts. However, the high carbophilicity of these catalysts can lead to competing reaction pathways, and in this note we have shown that alkene dimerization and Friedel−Crafts alkylation compete with the carbonyl-ene reaction and that the relative contribution from each pathway depends on the metal center. In this case, the platinum-based Lewis acid catalyzes dimerization, Friedel−Crafts alkylation, and the carbonyl-ene reaction to give a mixture of products; its palladium counterpart is entirely selective for the ene reaction, while the corresponding nickel catalyst shows platinum-like behavior. Kinetic studies revealed that each member of the triad catalyzes alkene dimerization with first-order rate constants decreasing in the order Pt > Ni ≫ Pd. Since platinum-based catalysts are generally more active than their palladium counterparts for the carbonyl-ene reaction, the product distribution obtained with [M{(*R*)-BINAP}]$^{2+}$ must reflect the vastly disparate rates of dimerization. Thus, the high carbophilicity of platinum (and nickel) renders dimerization/retrodimer-

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(21) Full details of the analysis have been provided in the Supporting Information.

(22) ([B]$_{eq}$/[A]$_0$) ln([B]$_{eq}$/([B]$_{eq}$ − [B]$_t$)) = kt. Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987.

ization and Friedel−Crafts alkylation highly favorable such that these pathways compete with the desired reaction, whereas the lower carbophilicity of palladium ensures that carbonyl-ene reactivity is dominant by virtue of a significantly lower rate of dimerization. Although the choice of metal is critical to achieving high selectivity, it should be possible to use a single catalyst to develop tandem reaction sequences for the construction of complex organic architectures provided the Lewis acidity and carbophilicity can be fine-tuned. Although promising, further studies are clearly required to determine the extent of the platinum-like reactivity of nickel, particularly with respect to rearrangement of intermediates and alternative pathways for M−C bond cleavage.

Experimental Section

General Comments. All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Dichloromethane and dioxane were distilled from calcium hydride under an atmosphere of nitrogen. Ethyl trifluoropyruvate, α-methyl styrene, 4-chloro-α-methylstyrene, and (*R*)-BINAP were purchased from commercial suppliers and used without further purification. [{(*R*)-BINAP}MCl$_2$] (M = Pt, Pd) was prepared from [M(cycloocta-1,5-diene)Cl$_2$] (M = Pd, Pt),[23] and [{(*R*)-BINAP}NiCl$_2$][24] was prepared as previously described. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL LAMBDA 500 or a Bruker AMX 300 instrument. Optical rotations were measured on a Optical Activity PolAAr 2001 digital polarimeter with a sodium lamp and are reported as follows: $[\alpha]_D^{20}$ (*c* g/100 mL, solvent). Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60F 254, and column chromatography was performed using Merck Kieselgel 60. Gas chromatography was performed on a Shimadzu 2010 series gas chromatograph equipped with a split-mode capillary injection system and flame ionization detection using a Supelco Beta DEX column, and analytical high-performance liquid chromatography (HPLC) was performed on an Agilent 110 Series HPLC equipped with a variable-wavelength detector using a Chiralpak AD-H column.

General Procedure for the Carbonyl-Ene Reaction between Styrene Derivatives and Ethyl Trifluoropyruvate. A flame-dried Schlenk flask charged with [M{(*R*)-BINAP}Cl$_2$] (0.02 mmol), AgSbF$_6$ (15.0 mg, 0.044 mmol), and CH$_2$Cl$_2$ (2.0 mL) was stirred at room temperature for 30 min, after which time ethyl trifluoropyruvate (80.0 μL, 0.6 mmol) was added followed by the styrene derivative (0.4 mmol). The resulting mixture was stirred for a further 60 min, after which time the solution was flushed through a short plug of silica with CH$_2$Cl$_2$, the solvent removed, and the resulting residue purified by column chromatography, eluting with hexane/CH$_2$Cl$_2$. The products were analyzed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis, and the enantiomeric excess was determined by chiral GC or HPLC.

Kinetic Studies. In a typical experiment, a flame-dried Schlenk flask charged with [M{(*R*)-BINAP}Cl$_2$] (0.04 mmol), AgSbF$_6$ (0.030 g, 0.088 mmol), and CH$_2$Cl$_2$ (4.0 mL) was stirred at room temperature for 30 min, after which time 4-chloro-α-methylstyrene (0.115 mL, 0.8 mmol) was added. Aliquots were removed at regular time intervals, flushed through a short plug of silica with CH$_2$Cl$_2$, and analyzed by ^{1}H NMR spectroscopy to determine the extent of dimerization. The resulting data were analyzed using reversible first-order kinetic analysis to obtain the rate constants, details of which are provided in the Supporting Information.

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Supporting Information Available: Full details of experimental procedures and characterization data for compounds **2a**,**b**, **3a**,**b**, **4a**, **5b**, and **6b**, graphs showing variation in concentration with time for the dimerization of 4-chloro-α-methylstyrene catalyzed by **1a**−**c**, and for **3a** and **3b** details of crystal data, structure solution and refinement, atomic coordinates, bond distances, bond angles, and anisotropic displacement 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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