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Platinum(II) Olefin Hydroarylation Catalysts: Tuning Selectivity for the anti-Markovnikov Product

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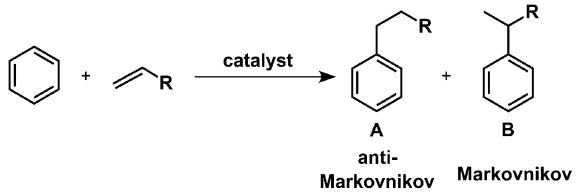
Abstract: Pt^{II} complexes containing unsymmetrical (pyridyl)pyrrolide ligands are shown to catalyze the hydroarylation of unactivated alkenes with selectivity for the anti-Markovnikov product. Substitution on the pyrrolide portion of the ligand allows effective tuning of the selectivity to anti-Markovnikov alkylarene products, whereas substitution on the pyridyl portion can promote competitive alkenylarene production.

Efficient catalytic anti-Markovnikov hydroarylation of olefins would provide an atom efficient route to linear alkyl benzenes directly from terminal olefins and benzene (**A**, Scheme 1).[1] Traditional Friedel–Crafts catalysts (e.g., $AlCl_3$ or HF) produce the branched Markovnikov alkylarene products (**B**, Scheme 1).[2] Recently, several homogeneous transition-metal catalysts that demonstrate moderate selectivity to the linear alkyl anti-Markovnikov products (**A**) have been reported.[3,4]

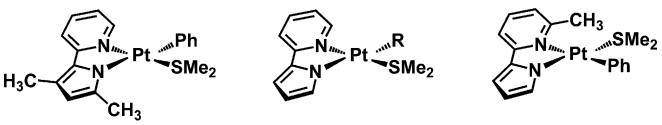
Studies of anti-Markovnikov/Markovnikov (**A**/**B**) selectivity in hydroarylation reactions of unactivated alkenes have been reported primarily using propylene and benzene as substrates with Ir, Ru, or Pt catalysts.[5] The Ir^{III} complexes [Ir(acac–O,O)$_2$(R)(L)] (R = (acac–C^3) or Ph, L = H_2O or pyridine, and acac = acetylacetonate) favored the anti-Markovnikov product with an **A**/**B** ratio of 61:39.[3] A similar ratio was obtained with the Ru^{II} system [Ru(CO)(NCMe)(Ph)Tp] (Tp = trispyrazolylborate).[4] In contrast, reported Pt^{II}-based catalysts for olefin hydroarylation have produced much lower selectivities with respect to anti-Markovnikov products. With the Pt^{II}–bipy cationic complex [Pt(Ph)(*t*bpy)(THF)][BAr′$_4$] (*t*bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl, Ar′ = 3,5-bis (trifluoromethyl)phenyl) as a precatalyst, a ratio of 34:66 **A**/**B** was found favoring the Markovnikov product.[6a] When 1-pentene was used as the olefin, a similar selectivity of 32:68 for **A**/**B** was observed.[6b] Optimization of the Pt–bipyridyl system through modification of the ligand was of limited success. The related Pt^{II} complex [Pt(dpm)(Ph)(THF)][BAr′$_4$] (dpm = 2,2′-dipyridylmethane) gave a higher turnover number (TON) for ethylbenzene production, but showed reduced activity for hydroarylation of longer chain α-olefins than the [Pt(Ph)(*t*bpy)(THF)][BAr′$_4$] precatalyst.[7] The [Pt(dpm)(Ph)(THF)][BAr′$_4$] system also underperformed with respect to selectivity for the anti-Markovnikov product with propylene and benzene (**A**/**B** 23:77).[6b]



Scheme 1.

Similarly, an **A**/**B** ratio in favor of the Markovnikov product (15:85) was reported when the neutral Pt^{II} complex [PtPh(py^{Me2}pyr)(SMe$_2$)] (py^{Me2}pyr = 3,5-dimethyl-2-(2-pyridyl)pyrrolide (**1**)) was used as a precatalyst for propylene hydroarylation with benzene.[8] However, we report herein that modification of the precatalyst through varying substituents on the unsymmetrical (pyridyl)pyrrolide[9] ligands is highly effective in tuning the **A**/**B** ratio in these neutral Pt^{II} systems. The Pt^{II} complexes shown in Scheme 2 were employed as precatalysts for the reaction of a range of olefins and benzene to produce alkylarenes. Significant differences were observed in the ratio of anti-Markovnikov (**A**) to Markovnikov (**B**) products depending on the precatalyst used. Additionally, the amount of alkylarene product generated versus a side reaction leading to an alkenylarene product was dependent on the substituents on the (pyridyl)pyrrolide ligand.

Complex **1**, previously shown to be a competent precatalyst for olefin hydroarylation,[8] was recently characterized by X-ray crystallography (XRD) (Figure 1).[10] It is notable that the SMe$_2$



(1) (2) R = CH_3 (3) R = Ph (4)

Scheme 2. Precatalyst structures.

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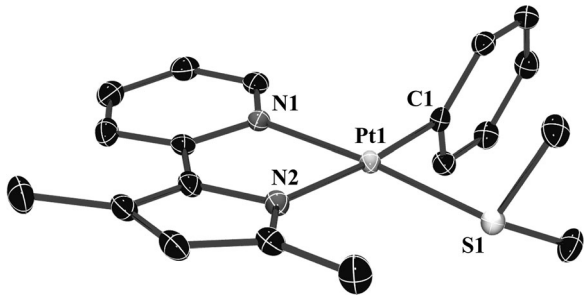


Figure 1. X-ray structure, thermal ellipsoid diagram (created with POV-Ray) of **1** at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **1**: C1–Pt1 2.0131(17), N1–Pt1 2.0538(15), N2–Pt1 2.0888(15), S1–Pt1 2.2606(6); C1-Pt1-N1 93.12(6), C1-Pt1-N2 172.74(6), C1-Pt1-S1 90.51(5), N1-Pt1-N2 79.63(6), N1-Pt1-S1 174.99(4), N2-Pt1-S1 96.75(4).

ligand is located *trans* to the pyridyl group in the square planar configuration of **1**. This geometrical arrangement is significant because the regioselectivity of the hydroarylation product (Markovnikov or anti-Markovnikov) is determined by the migration of the phenyl group to the olefin (see below). Substitution of SMe_2 by the olefin substrate should place the olefin *trans* to the pyridyl group and *cis* to the pyrrolide.[11]

It is reasonable to hypothesize that the methyl group on the pyrrolide could be influencing the regioselectivity of the migratory insertion step. Thus, we sought to investigate a similar complex with an unsubstituted pyrrolide group, pypyr = 2-(2-pyridyl)pyrrolide, complex **3** (Figure 2). Significant differences were noted in the attempted synthesis of **3** by a route similar to that used to prepare **1**. In the preparation of **1**, the reaction of the platinum dimer $[PtMe_2(SMe_2)]_2$[12] with $py^{Me2}pyr$–H resulted in N–H bond cleavage and release of methane. C–H activation of the benzene solvent also occurred in this reaction and within 30 min at room temperature, **1** was produced along with a second equivalent of methane. When the same procedure was followed with pypyr–H, C–H activation of the benzene solvent was either not observed at all or did not proceed to completion. Depending on the reaction conditions, the Pt^{II} methyl complex $[PtMe(pypyr)(SMe_2)]$ (**2**) or a mixture of **2** and the Pt^{II} phenyl complex $[PtPh(pypyr)(SMe_2)]$ (**3**) were formed.[10] Complex **2** was characterized by a singlet in the ^1H NMR spectrum attributed to the Pt–Me group at $\delta = 1.33$ ppm ($^2J_{PtH} = 79.7$ Hz). Mild heating of a benzene solution of **2** did not result in full conversion to **3**, and accessing temperatures above 60 °C resulted in formation of Pt black.

Complex **3**, the direct Pt^{II} phenyl analogue of **1** bearing the pypyr ligand, was instead prepared by the reaction of pypyr–H with the Pt^{II} phenyl starting material $[PtPh_2(SMe_2)]_2$.[13] The ^1H NMR spectrum of $[PtPh(pypyr)(SMe_2)]$ (**3**) in C_6D_6 showed a singlet at $\delta = 2.30$ ppm ($^3J_{PtH} = 59.6$ Hz) assigned to the dimethyl sulfide group bound to platinum. An XRD study on a single crystal of **3** revealed a square planar Pt^{II} complex, with the phenyl ligand again positioned *trans* to the pyrrole group, as was observed for **1** (Figure 2). The bond lengths and bond angles within **1** and **3** are similar.[10]

The influence of a methyl group in the *ortho* position of the pyridyl ring of the ligand was also examined. Reaction of $[PtPh_2(SMe_2)]_2$ with 6-methyl-2-(1H-pyrrol-2-yl)pyridine (^{Me}pypyr–H) led to clean formation of $[PtPh(^{Me}pypyr)(SMe_2)]$ (**4**). The ^1H NMR spectrum of **4** in C_6D_6 showed upfield singlets at $\delta = 2.30$ ppm ($^3J_{PtH} = 50.1$ Hz) and 2.32 ppm assigned to the platinum-bound dimethyl sulfide and the methyl group attached to the pyridine ring, respectively. An XRD study revealed that, in contrast to the structures of **1** and **3**, the phenyl ligand in **4** is situated *trans* to the pyridyl moiety (Figure 3). Close proximity of the pyridyl ring to the dimethyl sulfide was corroborated by 1D NOE NMR spectroscopy, indicating that the solution structure is similar to that found in the solid state.[10]

Thermolysis of **4** in C_6D_6 for up to 200 h at 100 °C did not result in any isomerization to the isomer with the phenyl group *trans* to the pyrrolide moiety.[10] In contrast, heating a solution of **1** in C_6D_6 at 100 °C resulted in partial conversion to the isomer with the phenyl group *trans* to the pyridyl ring. A ratio of more than 2:1 favoring the isomerized species after

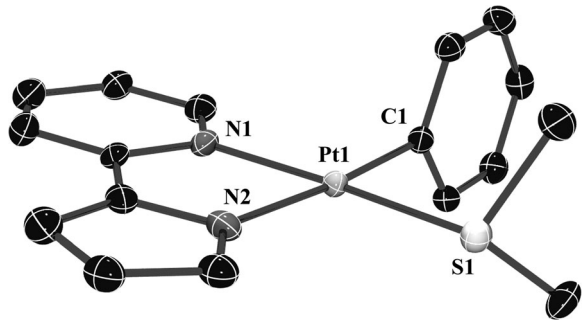


Figure 2. X-ray structure, thermal ellipsoid diagram (created with POV-Ray) of **3** at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **3**: C1–Pt1 2.015(2), N1–Pt1 2.047(2), N2–Pt1 2.068(2), S1–Pt1 2.2490(6); C1-Pt1-N1 94.44(9), C1-Pt1-N2 173.81(9), C1-Pt1-S1 93.32(7), N1-Pt1-N2 79.48(8), N1-Pt1-S1 172.07(6), N2-Pt1-S1 92.72(6).

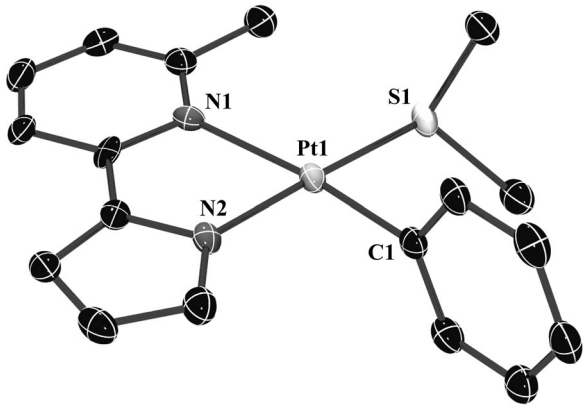


Figure 3. X-ray structure, thermal ellipsoid diagram (created with POV-Ray) of **4** at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **4**: C1–Pt1 1.994(5), N1–Pt1 2.220(4), N2–Pt1 2.002(4), S1–Pt1 2.2736(13); C1-Pt1-N1 168.98(17), C1-Pt1-N2 90.47(18), C1-Pt1-S1 89.37(14), N1-Pt1-N2 78.81(16), N1-Pt1-S1 101.44(11), N2-Pt1-S1 177.76(12).

133 h was observed.[8] Similarly, heating **3** in C_6D_6 for up to 200 h at 100 °C produced a mixture of isomers in a ratio of 1.23:1 favoring the isomer with the Pt–phenyl *trans* to the pyridyl group.

The four complexes (**1**–**4**) were tested as pre-catalysts for hydroarylation with propylene, 1-hexene, and neohexene (3,3-dimethyl-1-butene) at 100 °C. Reactions were monitored in situ by ^{1}H NMR spectroscopy with yields and TON determined after either 120 or 240 h by using gas chromatography (Table 1).

Table 1. Hydroarylation TON and ratio of products.[a,b]

Entry	Pre-catalyst	Olefin	M/olefin	TON[c]	**A**/**B**/**C**[d,e]
1	**1**	propylene	0.54	17.9 (0.9)	13:84:3
2	**2**	propylene	0.54	10.4 (0.7)	48:52:0
3	**3**	propylene	0.26	9.3 (0.8)	47:53:0
4	**3**	propylene	0.54	10.7 (0.9)	48:52:0
5	**3**	propylene	0.80	15.5 (0.3)	49:51:0
6	**4**	propylene	0.54	2.7 (0.1)	3:17:80[g]
7	**1**	1-hexene	0.51	11.8 (1.1)	16:83:1
8	**3**	1-hexene	0.51	8.4 (0.2)	57:43:0
9	**3**	1-hexene	0.51[f]	11.7 (0.8)	57:43:0
10	**3**	1-hexene	1.6	9.0 (1.5)	59:41:0
11	**3**	1-hexene	1.6[f]	10.5 (0.6)	58:42:0
12	**1**	neohexene	0.51	2.5 (0.2)	15:48:37
13	**3**	neohexene	0.51	3.1 (0.1)	85:5:10
14	**3**	neohexene	2.6	11.8 (0.2)	90:9:1

[a] Experimental conditions: 0.1–1.0 mmol olefin, 1.3 mol% catalyst, excess C_6H_6, 100 °C, 120 h, unless otherwise noted. [b] Experiments were conducted 2–4 times and averaged. [c] Standard deviation noted in parentheses. [d] C = product of branched β-hydride elimination. [e] Standard deviations for these values were all less than 1 and averaged 0.4. [f] Reaction time of 240 h. [g] A large amount of disubstituted product (**D**) was observed. A ratio of **A**/**B**/**C**/**D** 1:10:45:44 was calculated. TON is for monosubstituted product.

As can be seen by comparing entries 1, 2, and 4 in Table 1, the removal of the methyl groups from the pyrrolide portion of the ligand led to a striking change in the anti-Markovnikov (**A**) to Markovnikov (**B**) selectivity for the hydroarylation of propylene. With the original complex **1**, the Markovnikov product was strongly favored (**A**/**B** ratio of 15:85). Utilizing complexes **2** or **3** under the same reaction conditions, the products **A** and **B** were formed in a 48:52 ratio, representing a significant increase in the anti-Markovnikov selectivity. Monitoring the hydroarylation reactions for *n*-propylbenzene by ^{1}H NMR spectroscopy revealed that the selectivity (**A**/**B** ratio) was conserved over time when complexes **1**, **2**, or **3** were used as precatalysts.[14]

Although removing the methyl group on the pyrrolide ring led to a significant increase in the selectivity for the anti-Markovnikov product, it also resulted in approximately 40% lower TON (entries 1 and 4). This difference may be related to the decreased electron density at platinum leading to a lower propensity for oxidative addition of the arene C–H bond. This would be consistent with the catalyst synthesis results, in which the phenyl complex **1** was formed directly from the reaction of $py^{Me2}pyr$–H with $[PtMe_2(SMe_2)]_2$ in benzene, but the corresponding reaction with pypyr–H primarily gave only the Pt–Me complex **2**. However, it could also be an indication of reduced catalyst lifetime of **3** compared to **1**.

Remarkably, increasing the propylene concentration increased the TON to a level that was comparable to that observed when precatalyst **1** was used in place of precatalyst **3**. As shown in Table 1, entries 3–5, increasing the propylene concentration resulted in higher TON for the hydroarylation reaction with precatalyst **3**. The reactions shown for entries 3–5 were monitored by ^{1}H NMR spectroscopy, and the similar initial slopes in the plots of TON versus time suggests that the increased TON with increased olefin concentration results in large part from greater catalyst longevity. As shown in Figure 4, the TON begins to plateau at longer reaction times with higher olefin concentration.

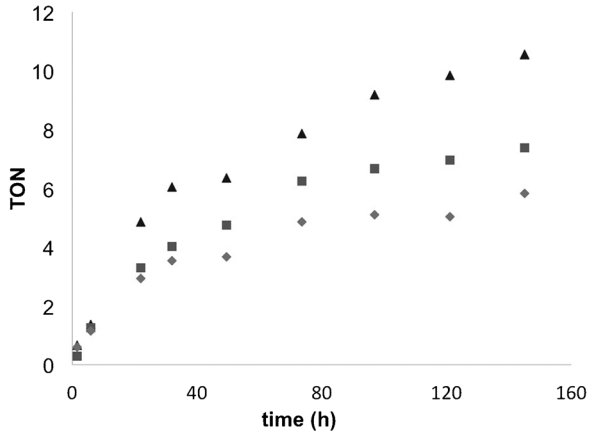


Figure 4. Plot of TON for the total products generated by using **1** at different concentrations of propylene. Experimental conditions: 0.5–2.6 M olefin, 1.3 mol% catalyst, excess C_6H_6, 100 °C. ▲ = 0.80 M propylene; ■ = 0.54 M propylene; ◆ = 0.26 M propylene.

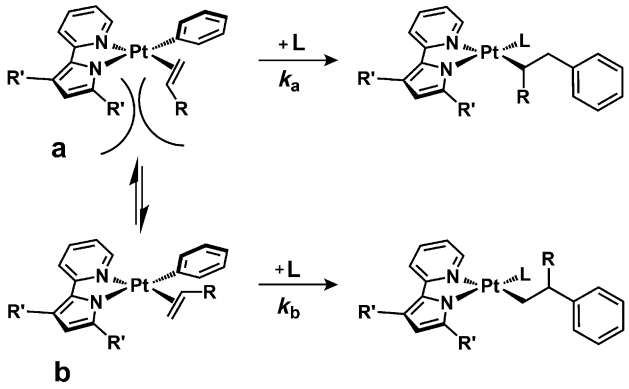
When 1-hexene was used as the substrate for the hydroarylation reaction, a comparable product ratio (16:83 for **A**/**B**, entry 7) to that obtained with propylene was observed with complex **1** as the precatalyst. In contrast, with catalyst **3** (entry 8), the anti-Markovnikov selectivity is enhanced to the extent that it becomes the favored product with an **A**/**B** ratio of 57:43. With 1-hexene, increasing the olefin concentration past 0.5 M had little effect on the TON. For example, when a threefold increase to 1.6 M was employed with complex **3** as the precatalyst, a similar TON was measured (entries 8 and 11).

When the significantly bulkier olefin neohexene was used as the substrate, selectivity for the anti-Markovnikov product drastically increased to a ratio of almost 85:5 for **A**/**B** by using **3** (entry 13). An additional product, the branched β-hydride elimination product (**C**), which in this case was α-*tert*-butylstyrene, was also observed comprising 10% of the hydroarylated product. Unfortunately, while selectivity for the anti-Markovnikov product was high, the TON was quite limited. However, increasing the olefin concentration by fivefold (from 0.5 M to 2.6 M, entries 13 and 14) led to a fourfold increase in TON. The β-hydride elimination pathway was also inhibited under these conditions and the **A**/**B** selectivity was measured at 90:9.

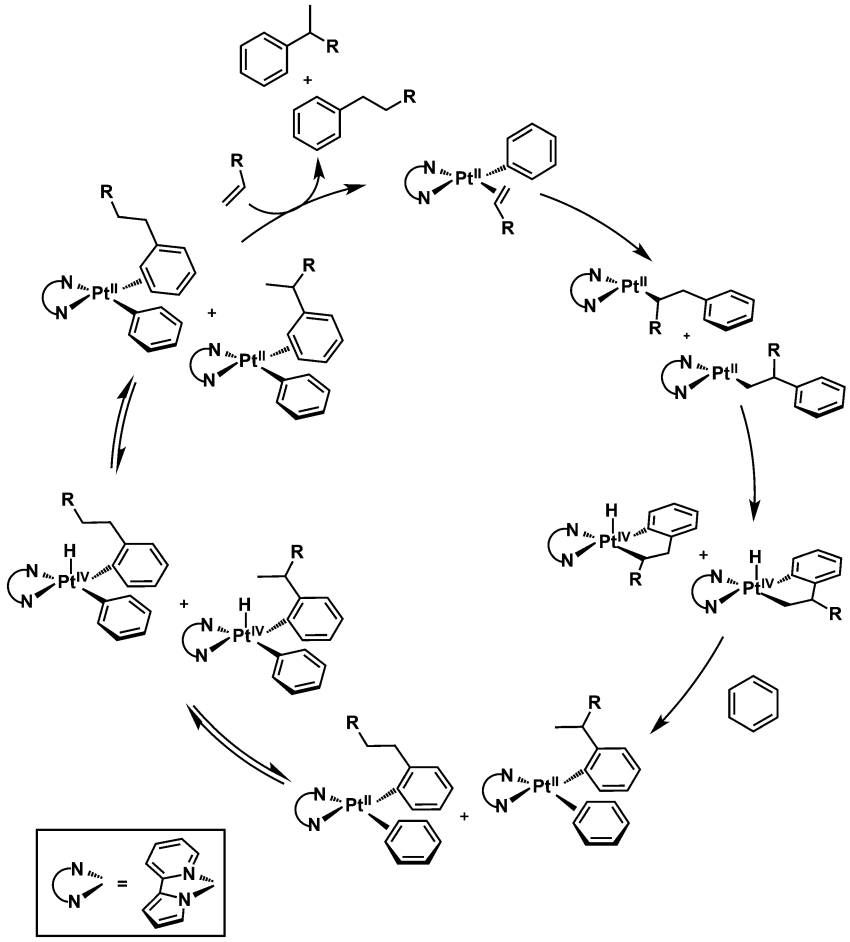
Because decreasing the steric bulk on the pyrrolide side of the ligand had such a significant influence on selectivity of olefin hydroarylation, the effect of a methyl group on the pyridyl side was also examined. Notably, this small ligand variation changed the major product of the propylene reaction from alkylarene to α-methyl styrene[15] (80% of the monosubstituted arene product). Di-substituted products **D** were also observed in this reaction and accounted for approximately 44% of the total hydroarylation products by GC analysis.[10] A low TON for monosubstituted products of 2.7 was recorded for this reaction.

Several mechanisms have been proposed for Pt^{II}-catalyzed olefin hydroarylation reactions.[8,16,17] Our results with catalysts **1**–**3** and olefin substrates ethylene, propylene, 1-hexene, and neohexene are consistent with the catalytic cycle shown in Scheme 3. Migration of the phenyl group to the olefin generates an alkyl arene ligand and an open site at the metal center. Previously reported deuterium-labeling studies in the hydroarylation of ethylene with the [PtPh(py^{Me2}pyr)(SMe_2)] system[8] indicate that an intramolecular C–H activation of the arene ring occurs next, followed by alkyl C–H reductive elimination.[8] Intermolecular C–H activation of arene solvent[18] is then followed by reductive coupling to generate the coordinated alkylarene product. Substitution of the coordinated alkylarene with olefin then closes the cycle.[8]

As depicted in Scheme 3, migration of the phenyl group to the olefin is proposed as the Markovnikov/anti-Markovnikov selectivity determining step. To allow proper orbital overlap for this migration, the two carbons of the olefin need to be in the plane of the square planar Pt^{II} complex. As shown in Scheme 4,



Scheme 4. Steric interaction of olefin and ligand in the catalyst active site. R = H, CH_3, C_5H_{11}, *t*Bu, R′ = H, CH_3.



Scheme 3. Proposed catalytic cycle for olefin hydroarylation.

there are two possible rotamers for this configuration. A methyl group at the fifth position of the pyrrolide ring (precatalyst **1**) should sterically favor rotamer **b** over rotamer **a**. The methyl group on the pyrrolide ring could also affect the relative insertion barriers (k_b vs. k_a). If the rotamers are interconverting rapidly, the reaction leading to either the branched or linear product would be under Curtin–Hammett conditions with the **A**/**B** ratio equal to $K_{a/b}(k_a/k_b)$. Thus, with precatalyst **1** and propylene, the sterics of the 5-Me group on the pyrrolide favor the branched product, whereas with precatalyst **3** and propylene, approximately equal amounts of **A** and **B** are observed. When the steric of the olefin increases (propylene < hexene ≪ neohexene), the effects on the relative energetics of the rotamers and the relative insertion barriers result in higher amounts of anti-Markovnikov product when precatalyst **3** is used. Notably, steric crowding of the *n*-alkyl chain or *t*Bu group with the phenyl

group on Pt may favor rotamer **a**, but the steric interactions are also likely to inhibit phenyl migration to the more substituted carbon. An alternative explanation for olefin hydroarylation selectivity was offered with respect to a related Pt^{II} system bearing a symmetric bipyridyl ligand.[6b] Reversible migratory insertion of the phenyl group and the olefin was proposed to be followed by irreversible intermolecular C–H activation to give the branched and linear products. A similar explanation may also be applicable herein, and computational studies are planned.

When **4** was used as the precatalyst for the reaction of propylene with benzene, α-methyl styrene was the primary product rather than alkylarenes. A notable difference between **4** and the precatalysts **1** and **3** is the position of the Ph group. The phenyl group is *trans* to the pyrrolide in **1** and **3** and *trans* to the pyridyl group in **4**. Migratory insertion of the phenyl group to an olefin residing in the place of the SMe_2 group would then give an alkylaryl moiety *trans* to the pyrrolide for **4**. β-Hydride elimination may then be favored over C–H activation from this configuration leading to α-methyl styrene. It is also possible that the three-coordinate species formed after phenyl migration isomerizes and the methyl group in the sixth position on the pyridyl ring inhibits approach of the arene. In this case, β-hydride formation could be kinetically favored over intramolecular arene C–H activation.

In summary, the unsymmetrical nature of the (pyridyl)pyrrolide ligands on Pt^{II} has allowed productive tuning of the regioselectivity in homogeneous olefin hydroarylation reactions. Because two sites at the metal center are required for olefin hydroarylation—one for arene C–H activation and one for olefin coordination—a strategy in which the two sites have different steric and electronic environments was demonstrated to provide significant advantage in increasing selectivity of the catalytic system. A selectivity of 57:43 favoring the anti-Markovnikov product was obtained with benzene and 1-hexene by using an optimized catalyst. Even more dramatic, an **A**/**B** ratio of 94:6 again favoring the anti-Markovnikov product was obtained by using benzene and neohexene. Notably, 10% of the alkenylarene product **C** was obtained in this reaction, such that the **A**/**B**/**C** ratio was 85:5:10. In addition to the high selectivities for the anti-Markovnikov products, it is notable that these unsymmetrical neutral Pt^{II} systems were not inhibited by excess olefin, as was previously observed for the closely related symmetric bipyridyl Pt^{II} systems.[16] Significantly, it was shown that with propylene as the substrate, higher olefin concentrations resulted in increased catalyst lifetimes. Further study and optimization of olefin hydroarylation reactions with other unsymmetrical ligands are continuing in our laboratories.

Acknowledgements

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Keywords: C–H activation · hydroarylation · olefins · platinum · (pyridyl)pyrrolide

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Synthetic Methods

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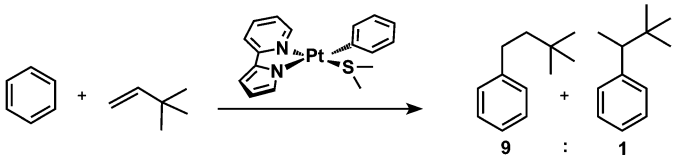
Platinum(II) Olefin Hydroarylation Catalysts: Tuning Selectivity for the anti-Markovnikov Product



Platinum plays favorites: Pt^{II} complexes containing unsymmetrical (pyridyl)pyrrolide ligands are shown to catalyze the hydroarylation of unactivated alkenes with selectivity for the anti-Markovnikov product (see scheme). Substitution on the pyrrolide portion of the ligand allows effective tuning of the selectivity to anti-Markovnikov alkylarene products, whereas substitution on the pyridyl portion can promote competitive alkenylarene production.