Solid-State Induced Control of Kinetically Unstable Stereoisomers

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Abstract: Arene complexes of the form TpM(π-acid)(L)(η^2-arene) (Tp = hydridotris(pyrazolyl)borate, M = Re, Mo, or W, π-acid = CO or NO, L = 1-alkylimidazole, pyridine, PMe$_3$, arene is prochiral) exist as a dynamic equilibrium of coordination diastereomers in solution. In both crystalline and amorphous solid states, however, only one diastereomer is present. Reactions on the bound arenes in these complexes have been performed stereoselectively, by exploiting the homomorphic nature of the solid phase.

The need to control the stereochemistry of chemical reactions is among the fundamental issues faced in organic synthesis. Systems that undergo low-energy isomerization processes, most typically conformational isomerizations, present a particularly interesting challenge.[1] Consider the Winstein–Holness equation below,[2] where A and B represent two isomers of a reactant and C and D represent products, each one uniquely originating from one reactant. In cases where isomerization of the reactants A

$$C \xleftarrow{k_C} A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B \xrightarrow{k_D} D \qquad (1)$$

and B occurs much faster than formation of the products C or D, the Curtin–Hammett principle dictates that selectivity for one product can be obtained provided that the difference in rate constants k_c and k_d is sufficiently large.[3,4] In the other limit, often referred to as "kinetically quenched", the chemical reaction is sufficiently fast relative to the isomerization that equilibrium of A and B is not maintained and the ratio of products C:D is determined from the initial ratio of reactant isomers (A:B). An example of such a reaction is the protonation of a cyclic amine by strong acid. In this example, the rate of protonation is diffusion controlled and is much faster than conversion of the two dominant conformational isomers.[5] Now, consider such a system in which the ratio of reactants A and B is "frozen", far from the equilibrium ratio found in solution, by crystal packing forces or other intermolecular interactions. Numerous examples have been cited in which one conformer or isomer is selectively trapped in the solid state, usually through a process of slow-growth crystallization (vide infra). Such a process has taken several names in the literature, but is most commonly referred to as crystallization-induced asymmetric transformation (CIAT
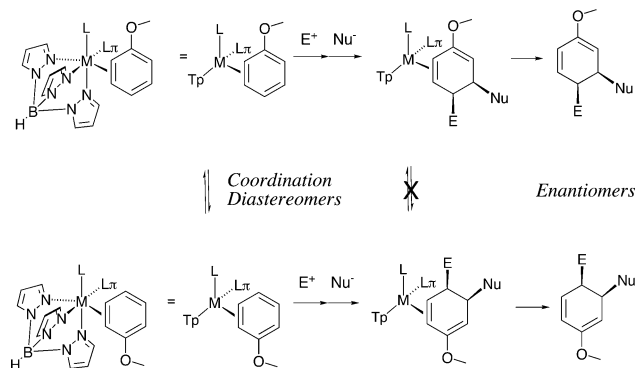
or AT)[6,7] or dynamic resolution (CIDR).[8,9] If this sample is allowed to react under kinetically quenched conditions (i.e., where a chemical reaction can occur much faster than reequilibration), then it is possible that a high degree of product stereoselectivity can be achieved, arising from the reactant ratio carrying over from the solid state. In this regard, the solid state can be used to select for a single, kinetically unstable diastereomer, to be used in a subsequent chemical reaction, as was first suggested some 40 years ago.[10] Herein, we provide a demonstration of this strategy for controlling the stereoselectivity of reactions in the context of transition-metal promoted electrophilic addition to arenes.

Coordination to π-basic metal fragments has been established as an effective strategy for both the activation and dearomatization of aromatic species.[11,12] With the advent of chiral {TpM-(π-acid)(L)} metal fragments (Tp = hydridotris(pyrazolyl)-borate, M = Re, Mo, or W, π-acid = CO or NO, L = 1-alkylimidazole, pyridine, PMe$_3$),[13–18] the opportunity exists to perform efficient dearomatization sequences with control of absolute stereochemistry, provided that the arene is prochiral.[19] Integral to effectively performing these asymmetric reactions

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Scheme 1

*Scheme 2*

is the ability to control the diastereoselectivity of arene coordination. Complexes of {TpM(π-acid)(L)} metal fragments and prochiral arenes are typically observed as mixtures of two coordination diastereomers, each having the coordinated C═C bond oriented orthogonally to the bond axis of the π-acid, with the bulk of the arene or aromatic heterocycle placed over this ligand (see Scheme 1).[15,16] Electrophiles and nucleophiles that react with the aromatic ligand of TpM(π-acid)(L)(η^2-aromatic) complexes are known to approach from the unbound face,[19,20] so the stereochemistry of the newly formed stereocenter(s) is directly related to the coordination diastereoselectivity (shown for anisole in Scheme 1). Given that the rate constants for the electrophilic addition of the two coordination diastereomers are similar (vide infra), controlling the ratio of coordination diastereomers is critical to the formation of products in high diastereomeric excess. However, equilibrium ratios are typically low (<5:1), and the associated isomerization barriers, ranging from 10 to 23 kcal/mol,[21] are too small to make any solution-based separation of diastereomers practical. It is in this context that the highly ordered nature of the solid state can be exploited.

In the presence of a suitable promoter, many TpM(π-acid)-(L)(η^2-arene) complexes add to carbon electrophiles to give arenium complexes in which the cationic ligand is stabilized by electron donation from the highly π-basic {TpM(π-acid)-(L)} fragment.[19] For example, TpRe(CO)(BuIm)(η^2-anisole) (**1**) adds to cyclopentenone at −40 °C in the presence of a moderately active proton source to give a 4*H*-anisolium complex (**2**; Scheme 2).[22] The coordination diastereoselectivity (**2A**:**2B** ratio) of the anisolium product varies significantly depending on how the initial sample of **1** is introduced to the reaction. TpRe(CO)(BuIm)(η^2-anisole) (**1**) is observed as a 2:1 ratio of coordination diastereomers at 25 °C having the methoxy group directed toward (**1A**) or away from (**1B**) the imidazole group. The isomerization barrier for these two forms of the closely related 1-methylimidazole analogue (**4**) was measured to be $\Delta G^\ddagger$ =17.2 kcal/mol (20 °C) ($t_{1/2} \sim$ 0.5 s @ 25 °C).[21] When the solid sample of **1** (0.10 g) was dissolved in CH$_3$CN (5.0 g) at ambient temperature, chilled to −40 °C, and then combined with the other reagents, the product ratio (**2A**:**2B**) was 4:1. If a comparable volume of solvent was used to dissolve the sample of **1** at −40 °C *in the presence of the other reagents*, the product ratio became 11:1. Finally, when a smaller solvent volume was
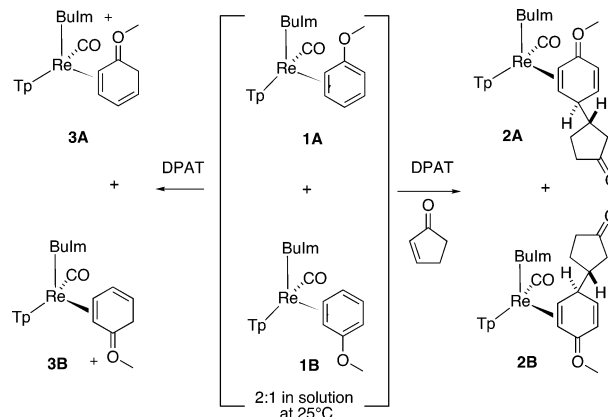
used (0.5 g of acetonitrile/0.10 g of **1**) at −40 °C, the product ratio rose to >20:1.

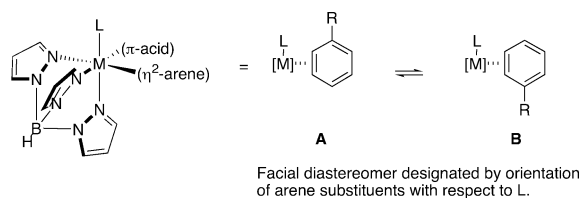Such discrepancies in arenium product ratios were also observed in protonation experiments of TpM(π-acid)(L)(η^2-arene) complexes. When solvated samples of **1** were exposed to diphenylammonium triflate (DPAT; p$K_a \sim$ 1), the anisolium product ratios (**3A**:**3B**) reflected the initial 2:1 ratio of the solvated complex. However, when **1** was dissolved at −60 °C in the presence of the acid, the **3A**:**3B** ratio of the protonation products was >20:1. These observations led to the hypothesis that the solid sample of **1** utilized had a much higher diastereomeric ratio than was observed in solution under equilibrium control. Confirmation of this hypothesis was obtained through a series of ^{1}H NMR experiments recorded at sufficiently low temperature as to inhibit interconversion between coordination isomers. A solution of **1** in CD$_2$Cl$_2$ (acid-free) was prepared at −60 °C, taking care to ensure that the solvent was at this temperature *before* the solute was added. Subsequent observation by ^{1}H NMR (−60 °C) showed a 14:1 ratio of **1A** to **1B**, indicating that the solid state was enriched in **1A** to at least this degree. Upon warming to 20 °C, the diastereomer ratio (**1A**: **1B**) dropped to 2:1. This ratio remained at 2:1 when the sample was cooled back to −60 °C, even after 3 h. Repeating this experiment at −80 °C indicated that the **1A**:**1B** ratio in the solid state was >20:1.

Under a variety of conditions, observations comparable to those described above were made for a series of {TpM(π-acid)-(L)} complexes of prochiral arenes (Table 1), all of which were prepared by their precipitation from a solution containing equilibrium ratios of coordination diastereomers. Where complete solvation at low temperature was possible (for all samples except **4** and **5**), the complexes could be monitored at temperatures sufficiently low that isomerization was not observed. Therefore, the observed diastereomer ratio is considered indicative of the solid state. Once TpM(π-acid)(L)(η^2-arene) complexes are protonated, heterofacial isomerization becomes sufficiently slow at room temperature such that no conversion is observed over many hours in solution. Evidence of a high degree of homomorphism in the solid state can therefore be observed indirectly, by trapping the arene complexes as their conjugate acids, even at room temperature. Remarkably, these TpM(π-acid)(L)(η^2-arene) complexes appear to have a uniformly homomorphic solid state, even when samples are prepared by simple precipitation from solution (induced by addition of hexanes to the solution, in accord with published proce-

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Table 1.[a]

Facial diastereomer designated by orientation
of arene substituents with respect to L.

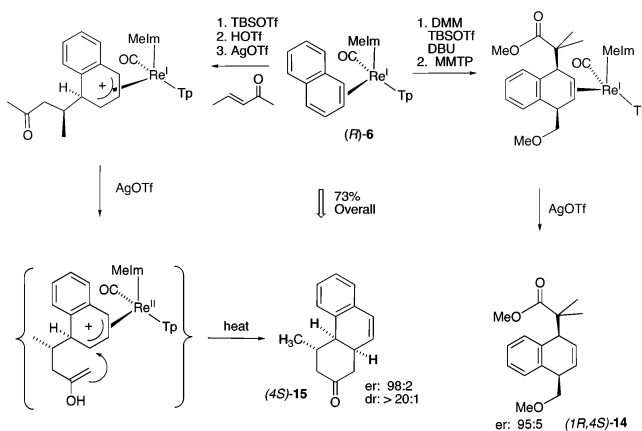| complex	equilibrium A:B[b]	initial A:B[c]	protonated A:B[d]	crystal structure isomer	crystal structure space group
[MeImMRe]-anisole (**4**)	2:1	2:1[e]	<20:1	A	*P*2(1)/*n*
MeImRe]-3-methylanisole (**5**)	2:1	2:1[e]	<1:20		
[MeImRe]-naphthalene (**6**)	4.5:1	>20:1[f]	>20:1	A	*P*2(1)/*n*
[BuImRe]-anisole (**1**)	2:1	>20:1[g]	>20:1	A	*P*-1 (No. 2)
[BuImRe]-3-methylanisole (**7**)	2:1	12:1[h]	>20:1	A	*P*-1
[BuImRe]-4-methylanisole (**8**)	1:2	1:12[g]	1:6	A	*P*-1
[BuImRe]-naphthalene (**9**)	3.5:1	>20:1[i]	>20:1		
[PyRe]-naphthalene (**10**)	3:1	>20:1[g]	10:1	A	*C*2/*c* (No. 15)
[PMe₃Re]-naphthalene (**11**)	<1:20	<1:20[j]	<1:20		
[MeImMo]-naphthalene (**12**)	4:1	>20:1[g]	>20:1	A	*P*2(1)/*n*
PMe₃W]-anisole (**13**)	3.5:1	>20:1[g]	>20:1	A	*P*2(1)/*c*

[a] [M] = {TpM(π-acid)}, [MeImRe] = {TpRe(CO)(MeIm)}, [BuImRe] = {TpRe(CO)(BuIm)}, [PyRe] = {TpRe(CO)(Py)}, [PMe₃Re] = {TpRe(CO)(PMe₃)}, [MeImMo] = {TpMo(NO)(MeIm)}, [PMe₃W] = {TpW(NO)(PMe₃)}. [b] Ratio of coordination diastereomers observed in equilibrated solutions at ambient temperature. [c] Highest ratio of coordination diastereomers observed. [d] Highest ratio of protonated coordination diastereomers observed.[33] [e] Complete solvation could not be effected at low temperature. [f] Acid-free CD₂Cl₂ at −20 °C. [g] Acid-free CD₂Cl₂ at −80 °C. [h] Acetone-*d₆* at −60 °C. [i] Acetone-*d₆* at ambient temperature. [j] Acetonitrile-*d₃* at ambient temperature.

dures[13,14,16,17]). These solids are often *amorphous* in that they do not show sufficient long-range order to diffract X-rays. Alternatively, crystals can be grown from solution by layering hexanes over a THF or diethyl ether solution. In most cases (Table 1), the only coordination isomer present, according to the X-ray structure determination,[23] was that found in the powder sample prepared from precipitation. However, in the case of the BuIm-(4-methylanisole) case (**8**), different diastereomers were found for the precipitated and re-crystallized solids.

Table 1 illustrates how even minor changes in molecular structure can influence the morphology of the solid state. For example, complexes **4** and **5** differ only by the addition of a methyl group at C3 of the anisole ligand, a location well removed from any possible intramolecular steric interaction with the metal complex. As expected, in solution, the A:B ratios are identical. Yet, the dominant diastereomer in the solid state is **A** for anisole and **B** for 3-methylanisole. Complexes **5** and **7** differ only by the alkyl group attached to the ancillary imidazole ligand. Where L = 1-methylimidazole (**5**), diastereomer **B** dominates the solid state, while for L = 1-butylimidazole, only isomer **A** is present. In solution, the observed A:B ratio is again 2:1 for both complexes. In all, high homomorphism in the solid is observed for three different metals, four different auxiliary ligands, and four different arenes in this study.

A solid sample prepared by CIAT can selectively supply a kinetically unstable diastereomer for a chemical transformation, provided that the reaction is carried out on a time scale that is faster than isomerization.[24] To demonstrate the utility of this approach in controlling stereochemistry, CIAT was applied to two reaction sequences currently being investigated in our laboratories utilizing the naphthalene complex TpRe(CO)-(MeIm)(3,4-η²-naphthalene) (**6**), which has an intrafacial isomer-

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Scheme 3

ization barrier of $\Delta G^{\ddagger} = 22.5$ kcal/mol (343 K) ($t_{1/2} \sim 1$ h @ 25 °C). Samples of this complex were resolved with 97% ee α-pinene (er = 99:1)[20] and incorporated in both a 1,4-tandem addition and a Michael−enol cyclization sequence, as shown in Scheme 3. In each case, the complex was exposed to the electrophile under conditions such that the chemical reaction was anticipated to occur faster than interconversion of the coordination diastereomers. The details for these organic reactions are described elsewhere.[25] Germane to this study, however, is that the final organic products were obtained with er's of 95:5 and 98:2, respectively. When the identical reaction sequences were performed, except that the naphthalene complex was allowed to dissolve and stand (1.5 h) in solution *prior to addition of the electrophile,* the er's of the recovered products were 3:1 and 8:1, respectively, ratios similar to the 4.5:1 ratio found for **6** in solution at equilibrium. Similar experiments have also shown that the origin of the high enantiomer ratio previously reported[20] for the preparation of 2-(1,2-dihydro-

(25) Ding, F.; Valahovic, M. T.; Keane, J. M.; Anstey, M. R.; Sabat, M.; Trindle, C. O.; Harman, W. D. Submitted for publication.

naphthalen-2-yl)-2-methylpropionic acid methyl ester by our group can also be attributed to CIAT.[26]

The observation that a compound forms a homomorphic solid phase as a racemic mixture does not guarantee the same result for the corresponding enantioenriched material. If the racemate organizes in a centrosymmetric space group in the solid, this state will not be possible for the enantioenriched form. Consider complex **1**, which despite its 2:1 equilibrium ratio precipitates in hexanes to form a solid containing >95% diastereomer **A** (Table 1). When an enantioenriched sample of **1** was precipitated in the same manner, protonation experiments showed the resulting solid to contain only a 3:1 ratio of A:B.

Ever since Pasteur first demonstrated that the solid state could be utilized to separate enantiomers, crystallization has been a valuable tool for controlling the configurations of chiral samples.[27,28] Many examples have since been reported in which solid-state interactions have provided access to solution state samples of conformers,[10,29−33] stereoisomers,[8,34−38] and regio-isomers[39,40] in nonequilibrium ratios, and this strategy has been used to control the stereochemistry of reactions. It is even possible to carry out stereoselective reactions directly in the solid state, either by light[41] or at the gas/solid interface.[42]

It is now possible to predict through calculations the most stable polymorph for simple organic compounds.[43,44] However, there are few reports using CIAT as a means to deliver a kinetically unstable diastereomer for a chemical reaction. This strategy has three requirements: (1) the diastereomers (e.g., conformational or coordination diastereomers) must interconvert on a time scale that is faster than formation of the solid, enabling the material to funnel effectively into one form as the precipitation or crystallization process occurs. (2) A single type of diastereomer must be present in the solid. (3) The synthetic reaction that is utilized must be fast, relative to the rate of isomerization. Dynamic processes that have isomerization barriers similar to the TpM(π-acid)(L)(arene) systems discussed herein include cyclohexyl ring chair/chair isomerizations, amide C−N rotations, atropisomerization in biphenyls, and allyl

rearrangements on metals.[1,45,46] With isomerization barriers in the 17−23 kcal/mol range, it has been demonstrated herein that aldol and Michael reactions, two of the most significant reactions of organic synthesis, can successfully compete against a rapid stereoisomerization. Given that a broad range of organic molecules show dynamic processes that occur on similar time scales ($t_{1/2} \sim$ 10 ms to 1 h), the current results may have implications for effecting stereoselective reactions with other systems of rapidly interconverting diastereomers (e.g., conformers).

Experimental Details

General Methods. NMR spectra were obtained on a 300 or 500 MHz Varian INOVA spectrometer. Samples were prepared under a dry nitrogen atmosphere. Unless otherwise noted, deuterated solvents were used as received from Cambridge Isotopes. Alumina (Al_2O_3) was activated by storing it in a lab oven at $\sim$165 °C for $\sim$12 h. Diphenylammonium triflate was obtained by collecting the precipitate resulting from slow addition of triflic acid to a methylene chloride solution of diphenylamine. The syntheses of compounds **4**,[16] **6**,[16] **10**,[16] **11**,[16] and **12**[17] have been previously reported as have compounds **14** and **15**.[25] Syntheses and characterization of compounds **1**, **7**−**9**, and **13** will be reported elsewhere[22,23] but are available as Supporting Information.

The kinetic ratios of TpM(π-acid)(L)(η^2-arene) complexes and {TpM(π-acid)(L)} arenium triflates reported in Table 1 were observed as follows. Where applicable, chemical shifts are reported for the peaks from which the reported ratios were derived. In all other cases, either no peaks indicative of corresponding diastereomers were observed or those that were observed were present in trace amounts (visually estimated at <1:20) and due to excessive overlap were not suitable for rigorous integration.

Selected characterization data (see Supporting Information for complete experimental details).

[TpRe(CO)(BuIm)(5,6-η^2-(2H-anisolium))](OTf) (2H-1) and [TpRe-(CO)(BuIm)(5,6-η^2-(4H-anisolium))](OTf) (4H-1). ^{1}H NMR (acetone-d_6, ambient temperature, δ): (**2H-1B**) 8.12 (2H, d, $J = 2.5$, 2x Tp 3,5), 8.07 (1H, d, $J = 2.0$, Tp 3,5), 7.82 (1H, dd, $J = 2.5,1.0$, Tp 3,5), 7.51 (1H, d, $J = 2.0$, Tp 3,5), 7.34 (1H, t, $J = 1.5$, Im), 7.29 (1H, d, $J = 2.0$ Tp 3,5), 6.65 (1H, buried, H4), 6.59 (1H, t, $J = 2.0$, Tp 4), 6.43 (1H, t, $J = 2.0$, Tp 4), 6.17 (1H, t, $J = 2.0$, Tp 4), 5.17 (1H, dt, $J = 9.5, 3.0$, H3), 5.06 (1H, bs, H5), 4.15 (2H, t, $J = 7.0$, NCH$_2$), 3.90 (1H, d, $J = 6.5$, H6), 3.38 (1H, d, $J = 26.0$, H2), 3.18 (3H, s, OCH$_3$), 3.03 (1H, d, $J = 24.5$, H2), 1.76 (2H, m, NCH$_2$CH_2), 1.24 (2H, m, CH_2CH$_3$), 0.88 (3H, t, $J = 7.5$, CH$_2$CH_3), (2 × Im buried or indiscernible from minor resonances; BH not observed); (**2H-1A**) 8.24 (1H, d, $J = 2.0$, Tp 3,5), 8.16 (1H, d, $J = 2.0$, Tp 3,5), 7.96 (1H, dd, $J = 2.0, 0.5$, Tp 3,5), 7.88 (1H, d, $J = 2.0$, Tp 3,5), 7.86 (1H, dd, $J = 2.5, 0.5$, Tp 3,5), 7.41 (1H, d, $J = 2.0$ Tp 3,5), 7.37 (1H, bs, Im), 6.76 (1H, ddd, $J = 9.0, 5.0, 2.5$, H4), 6.56 (1H, t, $J = 2.0$, Tp 4), 6.33 (1H, t, $J = 2.0$, Tp 4), 6.18 (1H, t, $J = 2.0$, Tp 4), 5.24 (1H, dt, $J = 9.5, 3.0$, H3), 4.80 (1H, d, $J = 6.5$, H6), 4.19 (2H, t, $J = 7.0$, NCH$_2$), 4.12 (1H, bs, H5), 3.74 (3H, s, OCH$_3$), 3.50 (1H, d, $J = 21.5$, H2), 3.12 (1H, d, $J = 27.0$, H2), 1.76 (2H, m, NCH$_2$CH_2), 1.24 (2H, m, CH_2CH$_3$), 0.88 (3H, t, $J = 7.5$, CH$_2$CH_3), (2 × Im buried or indiscernible from minor resonances; BH not observed); (**4H-1B**, select resonances) 7.02 (1H, m, H3), 6.50 (1H, d, $J = 1.8$, H2), 4.90 (1H, m, H5), 3.61 (1H, buried, H6), 3.08 (3H, s, OCH$_3$); (**4H-1A**, select resonances) 7.17 (1H, m, H3), 4.44 (1H, d, $J = 7.5$, H6), 4.04 (1H, t, $J = 7.5$, H5), 3.59 (3H, s, OCH$_3$). ^{13}C NMR (acetone-d_6, −20 °C, δ): (**2H-1A**) 196.0 (C1), 194.8

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(CO), 145.3 (Tp 3,5), 143.9 (Tp 3,5), 142.6 (Tp 3,5), 138.0 (Tp 3,5), 137.7 (Tp 3,5), 136.3 (Tp 3,5), 135.5 (C4), 130.2, 122.1 (Im), 115.9 (C3), 108.0 (Tp 4), 107.3 (Tp 4), 107.6 (Tp 4), 64.2 (C5), 61.2 (C6), 59.2 (OCH$_3$), 48.2 (NCH$_2$), 34.0 (C2), 33.2 (NCH$_2$CH$_2$), 19.9 (CH$_2$-CH$_3$), 13.6 (CH$_2$CH$_3$), (2 × Im indiscernible from minor resonances). IR ν_{CO} = 1855 cm^{-1} (vs), ν_{BH} = 2493 cm^{-1} (w). CV: $E_{p,a}$ = +1.12 V (II/I). Anal. Calcd for C$_{25}$H$_{31}$BF$_3$N$_8$O$_5$ReS: C, 37.09; H, 3.86; N, 13.84. Found: C, 36.99; H, 3.83; N, 13.93.

[TpW(NO)(PMe$_3$)(5,6-η^2-(2*H*-anisolium))](OTf) (2*H*-13). ^{1}H NMR (acetone-*d$_6$*, −80 °C, δ): (**2*H*-13A**) 8.35 (1H, d, J = 2.0, Tp 3,5), 8.32 (1H, d, J = 2.0, Tp 3,5), 8.29 (1H, d, J = 2.0, Tp 3,5), 8.27 (1H, d, J = 2.0, Tp 3,5), 8.09 (1H, d, J = 2.0, Tp 3,5), 7.90 (1H, d, J = 2.0 Tp 3,5), 6.68 (1H, m, H4), 6.62 (1H, t, J = 2.5, Tp 4), 6.58 (1H, t, J = 2.5, Tp 4), 6.38 (1H, t, J = 2.5, Tp 4), 4.93 (1H, dt, J = 9.0, 4.5, H3), 4.80 (1H, m, H6), 4.65 (3H, s, OCH$_3$), 4.29 (1H, d, J = 27.0, H2), 3.46 (1H, d, J = 27.5, H2), 2.78 (1H, t, J = 11.5, H5), 1.15 (9H, d, J = 9.0, PMe$_3$), (BH not observed); (**2*H*-13B**, ambient temperature) 8.31 (1H, d, J = 2.1, Tp 3,5), 8.24 (1H, d, J = 2.1, Tp 3,5), 8.22 (1H, d, J = 2.1, Tp 3,5), 8.12 (1H, d, J = 2.4, Tp 3,5), 8.09 (1H, d, J = 2.4, Tp 3,5), 7.58 (1H, d, J = 2.1 Tp 3,5), 6.62 (1H, t, J = 2.4, Tp 4), 6.55 (1H, buried, H4), 6.53 (1H, t, J = 2.4, Tp 4), 6.44 (1H, t, J = 2.4, Tp 4), 4.97 (1H, m, H3), 4.7 (1H, very broad, BH), 4.61 (1H, m, H5), 3.74 (1H, d, J = 23.7, H2), 3.46 (2H, buried, H2 and H6), 3.42 (3H, s, OCH$_3$), 3.38 (1H, d, J = 26.0, H2), 3.18 (3H, s, OCH$_3$), 1.39 (9H, d, J = 9.9, PMe$_3$). ^{13}C NMR (acetone-*d$_6$*, −20 °C, δ): (**2*H*-13A**) 205.5 (C1), 144.7 (Tp 3,5), 143.3 (Tp 3,5), 143.1 (Tp 3,5), 139.0 (Tp 3,5), 138.5 (Tp 3,5), 137.6 (Tp 3,5), 132.9 (C4), 111.1 (C3), 108.6 (Tp 4), 108.1 (Tp 4), 106.9 (Tp 4), 68.4 (C5), 63.7 (C6), 60.2 (OCH$_3$), 32.8 (C2), 11.7 (d, J = 30.2, PMe$_3$); (**2*H*-13B**) 195.5 (C1), 146.3 (Tp 3,5), 142.8 (Tp 3,5), 142.7 (Tp 3,5), 139.6 (Tp 3,5), 139.2 (Tp 3,5), 139.0 (Tp 3,5), 128.1 (C4), 113.4 (C3), 108.6 (Tp 4), 108.5 (Tp 4), 108.0 (Tp 4), 70.2 (d, J = 13.7, C5), 63.7 (C6), 58.5 (OCH$_3$), 33.0 (C2), 12.9 (d, J = 32.1, PMe$_3$). IR ν_{NO} = 1622 cm^{-1} (vs), ν_{BH} = 2510 cm^{-1} (w). CV (CH$_3$CN): $E_{p,a}$ = +1.39 V (II/I). Anal. Calcd for C$_{20}$H$_{28}$-BF$_3$N$_7$O$_5$PSW: C, 31.56; H, 3.71; N, 12.88. Found: C, 30.92; H, 3.64; N, 12.81.

4-Methyl-3,4,4a,10a-tetrahydro-1*H*-phenanthren-2-one (15). To a mixture of α-pinene complex and resolved naphthalene complex (50 mg, 0.0390 mmol complex (*R*)-**6**) was added a solution of 3-penten-2-one (30 mg, 0.23 mmol) and TBSOTf (21 mg, 0.080 mmol) in 0.5 g of CH$_3$CN d at −40 °C. The resulting mixture was allowed to sit for 12 min. A separate solution of HOTf (18 mg, 0.12 mmol) in 0.5 g of MeOH was cooled to −40 °C, added to the above solution, and allowed to sit for 0.5 h. The solution was then warmed to 20 °C and allowed to stand another 0.5 h before AgOTf (20 mg, 0.080 mmol) was added. After 15 min, the reaction mixture was placed in a 75 °C oil bath for 1.0 h. After returning the solution to 20 °C, the solvents were evaporated and 1 mL of water was added to the oil-like residue. The water layer was extracted with 50 mL of ether, which was then washed with 2 mL of brine and dried over Na$_2$SO$_4$. After the evaporation of ether, the elution of 10% ethyl acetate in hexanes from a preparatory TLC silica plate yielded the product (6 mg, 73%) as slightly yellow oil (R_f = 0.32). The ee was determined as 95% by HPLC (chiral OD-H column, 2% 2-propanol in hexanes as eluents, 0.1 mL/min; minor, t_R = 72.8 min; major, t_R = 78.7 min). ^{1}H NMR (CDCl$_3$) δ 7.08−7.28 (4H, m, β ring), 6.64 (1H, dd, J = 9.5, 3.0, H4), 5.71 (1H, dd, J = 9.5, 3.0, H3), 3.28 (1H, m, H2), 2.69 (1H, dd, J = 13.5, 6.0, COCH$_2$CH), 2.62 (1H, dd, J = 9.5, 6.4, H1), 2.46 (1H, m, COCH$_2$CH), 2.40 (1H, m, COCH$_2$-CH(CH$_3$)CH), 2.33 (1H, m, CH), 2.19 (1H, dd, J = 13.0, 5.5, COCH$_2$-CH(CH$_3$)CH), 0.88 (3H, d, J = 6.0, CH$_3$). ^{13}C NMR (CDCl$_3$) δ 137.11, 133.05, 129.10, 127.39, 127.03, 126.84 (β ring), 131.05 (C3), 128.53 (C4), 49.35 (COCH$_2$CH(CH$_3$)CH), 46.34 (C1), 45.35 (COCH$_2$CH), 37.91 (C2), 32.35 (CH), 20.99 (CH$_3$). HRMS calcd for C$_{15}$H$_{17}$O$^+$, 213.1279, found 213.1279. Purity (^{1}H NMR): >95%.

Supporting Information Available: Experimental preparations and characterizations for compounds not previously reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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