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Coordination Chemistry of the Soft Chiral Lewis Acid [Cp*Ir(TsDPEN)]$^+$

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Supporting Information

ABSTRACT: The paper surveys the binding of anions to the unsaturated 16e Lewis acid [Cp*Ir(TsDPEN)]$^+$ ([**1**H]$^+$), where TsDPEN is racemic $H_2NCHPhCHPhNTs^-$. The derivatives Cp*IrX(TsDPEN) were characterized crystallographically for X^- = CN^-, Me(C═NH)S^-, NO_2^-, 2-pyridonate, and 0.5 MoS_4^{2-}. [(**1**H)$_2$(μ-CN)]$^+$ forms from [**1**H]$^+$ and **1**H(CN). Aside from 2-pyridone, amides generally add reversibly and bind to Ir through N. Thioacetamide binds irreversibly through sulfur. Compounds of the type Cp*IrX(TsDPEN) generally form diastereoselectively, although diastereomeric products were observed for the strong ligands (X = CN^-, H^- (introduced via BH_4^-), or Me(C═NH)S^-). Related experiments on the reaction (*p*-cymene)Ru(TsDPEN-H) + BH_4^- gave two diastereomers of (*p*-cymene)RuH(TsDPEN), the known hydrogenation catalyst and a second isomer that hydrogenated acetophenone more slowly. These experiment provide new insights into the enantioselectivity of these catalysts. Diastereomerization in all cases was first order in metal with modest solvent effects. The diphenyl groups are generally diequatorial for the stable diastereomers. For the 2-pyridonate adduct, axial phenyl groups are stabilized in the solid state by puckering of the IrN_2C_2 ring induced by intramolecular hydrogen-bonding. Crystallographic analysis of [Cp*Ir(TsDPEN)]$_2$(MoS_4) revealed a unique example of a κ^1,κ^1-tetrathiometallate ligand. Cp*Ir(SC(NH)Me)TsDPEN) is the first example of a κ^1-*S*-thioamidato complex.

INTRODUCTION

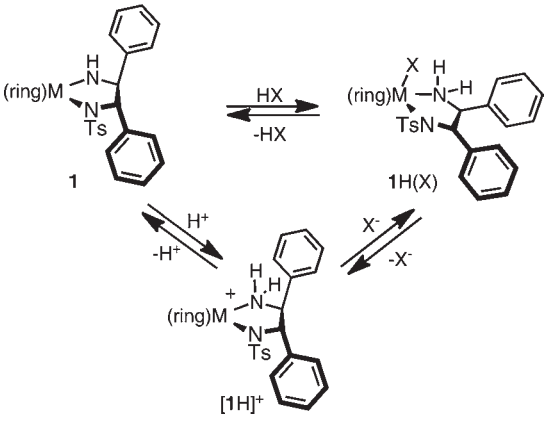
Transfer hydrogenation catalysts often exist in one of two states, an unsaturated metal center, usually stabilized by π-interactions with amido (R_2N^-) ligands, and a saturated aminohydride state.[1−5] Many such complexes are known, and a popular ligand in this area is the monoanion [H_2NCHPhCHPhNTs]$^-$ abbreviated $TsDPEN^-$. For example, (*p*-cymene)RuH(*S*,*S*-TsDPEN) is useful for the enantioselective transfer hydrogenation (TH) of ketones and imines.[6] In the catalytic cycle, this Ru(II) complex shuttles between hydro and dehydro states, (*p*-cymene)RuH(TsDPEN) and (*p*-cymene)Ru(TsDPEN-H), respectively. The present report focuses on a related complex, Cp*Ir(TsDPEN-H) (**1**), which is more amenable to detailed mechanistic studies.[7] Compound **1** is also catalytically active for TH but is more robust than the (*p*-cymene)Ru derivative.[8]

A few years ago, our group and Ikariya's, and Noyori's groups showed that a third state of the TH catalysts arises by protonation of the dehydro state of these catalysts.[9,10] Thus, protonation of **1** occurs at its NH center to afford the cation [Cp*Ir(TsDPEN)]$^+$ ([**1**H]$^+$, Scheme 1).

The cation [**1**H]$^+$ is a soft Lewis acid with distinctive properties.[11,12] It is not poisoned by water or many related oxygenic ligands, a property that is key to its reactivity toward H_2 in polar media.[13−16] Adjacent to the vacant coordination site on the 16e metal is an amine ligand, which is well positioned for hydrogen-bonding to Lewis bases. These chiral complexes add H_2 with high diastereoselectivity, reflecting the influence of the phenyl substituents on the metal.

In a previous paper, we showed that [**1**H]$^+$ and related complexes bind a wide variety of charge-neutral Lewis bases such as phosphines, CO, and ammonia.[11] The Lewis base adducts [**1**H(L)]$^+$ were found to largely exist as single diastereoisomers.

Scheme 1. Three States of Half-Sandwich Transfer Hydrogenation Catalysts



In this report, we examine the binding of anionic ligands to [**1**H]$^+$. Using a variety of anionic ligands, Ikariya and co-workers have examined other derivatives of the type **1**H(X). For example, **1** adds a variety of carbon-based ligands such as, for example, nitromethane, acetone, malonate esters, and phenylacetylene. The alkyl complexes (*p*-cymene)Ru(R)(TsDPEN) (R = Me, Et) have also been prepared, although they are thermally labile.[17] For the carboxylate derivatives **1**H(O_2CR), crystallographic analysis revealed intramolecular hydrogen-bonding between the carboxylate and the amine center.[18,19]

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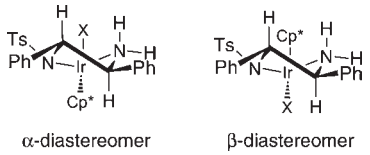
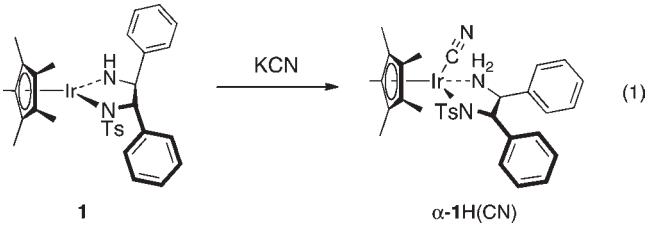


Figure 1. Structures of the α- and *β*-isomers of Cp*Ir(X)(*S,S*-TsDPEN).

In this report we describe the synthesis and characterization of a wide variety of Cp*Ir(X)(TsDPEN) adducts where X = CN^-, Me(C=NH)S^-, Me(C=O)NH^-, NO_2^-, 2-pyridonate, and MoS_4^{2-}. The diastereoselectivity of HX additions to **1** was also investigated, along with the mechanism of diastereomerization. These findings establish the versatility of $[\mathbf{1H}]^+$ as a Lewis acid. Compounds of the type Cp*Ir(X)(TsDPEN) can exist as two diastereoisomers, depending on the relative configuration of the stereogenic Ir center and the TsDPEN ligand. The stable diastereomer for all adducts features the same relative disposition of ligands at metal and substituents on the $TsDPEN^-$ ligand; this isomer is labeled α (Figure 1). The less stable diastereomer, *β*, is observed in some cases.

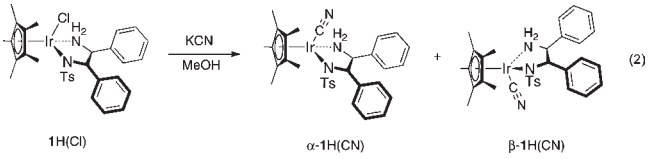
RESULTS AND DISCUSSION

Cyanide. The complex Cp*Ir(CN)(TsDPEN) (**1**H(CN)) was prepared by the reaction of **1** and KCN in methanol (eq 1). The solvent serves as the proton donor; reactions in nonacidic solvents such as MeCN also proceed but are slower. The origin of the proton from the solvent was verified by the addition of Et_4NCN to a solution of **1** in CD_3CN under anhydrous conditions, which slowly afforded **1**D(CN). The IR spectrum of Cp*Ir(CN)(TsDPEN) features ν_{CN} at 2107 cm^{-1}, which is typical for related cyanide complexes.[20,21]



(1)

Of course, **1**H(CN) can also be prepared by salt metathesis from **1**H(Cl) and KCN, but the results were surprising. First, it is important to note that solutions of **1**H(Cl) in MeOH contain significant amounts of $[\mathbf{1H}]^+$, as indicated by the red color of these solutions. In CD_3OD, the ^3J for the pair of doublets of the TsDPEN backbone (*CH*PhC*H*Ph) is 8.4 Hz versus 11.0 Hz in CD_2Cl_2. The diminished coupling is consistent with a contribution from $[\mathbf{1H}]^+$, wherein ^3J is almost 0 Hz. According to ^{1}H NMR spectroscopy, salt exchange between **1**H(Cl) and KCN afforded a 50:50 mixture of α-**1**H(CN) and the *β*-diastereomer (eq 2). Over the course of weeks, *β*-**1**H(CN) quantitatively converts to α-**1**H(CN). At room temperature, isomerization of *β*-**1**H(CN) to α-**1**H(CN) followed first order kinetics with a half-life greater than 20 days. Similar behavior was observed for the two isomers of Cp*Ir(CO)(TsDACH).[11]



(2)

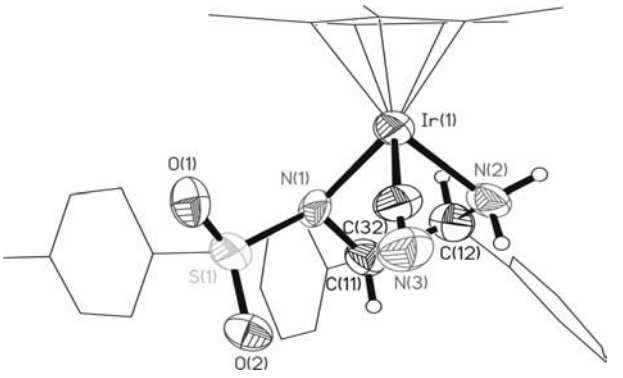
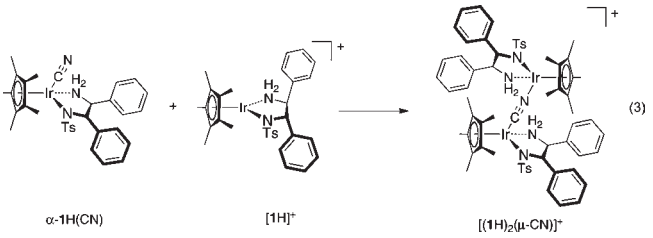


Figure 2. Structure of α-Cp*Ir(CN)(TsDPEN). Thermal ellipsoids are shown at the 50% probability level but are omitted on the Cp*, tosyl, and phenyl groups for clarity.

A cyanide-bridged bimetallic complex can be readily prepared from **1**H(CN). Thus, treatment of α-**1**H(CN) with 1 equiv of $[\mathbf{1H}]BF_4$ gave $[(\mathbf{1H})_2(\mu\text{-CN})]BF_4$. In the IR spectrum, the conversion is indicated by a shift of ν_{CN} from 2107 to 2152 cm^{-1}, which is in the region characteristic of a *μ*-CN ligand (eq 3).[22] On the basis of its ^{1}H NMR spectrum, $[(\mathbf{1H})_2(\mu\text{-CN})]BF_4$ exists mainly as a single diastereomer in CH_2Cl_2 solution. Using the mixture of *β*-**1**H(CN) and α-**1**H(CN), we generated a pair of diastereomers of $[(\mathbf{1H})_2(\mu\text{-CN})]BF_4$.



(3)

The structure of **1**H(CN) was verified crystallographically (Figure 2). The Ir(1)−C(32) distance is 1.990(8) Å, and the C(32)−N(3) distance was found to be 1.146(9) Å, both of which are typical for related complexes.[23] The Ir−C−N angle is 173.2°, tilted toward the NH_2 group on the TsDPEN backbone. Intermolecular hydrogen-bonds exist between the Ir*CN* and a neighboring *H*$_2$NIr at 2.906(8) Å and between a lattice water (H$_2$*O*) and *H*$_2$NIr at a distance of 3.062(18) Å.

Borohydride and Hydride. The synthesis of **1**H(BH_4) was attempted by treatment of **1** with $NaBH_4$ in methanolic solution. A potentially related (BINAP)Ru(H)(BH_4)(DPEN) complex had been prepared in this way by Noyori et al.[24] and Morris et al.[25] The reaction **1** + $NaBH_4$ was found, however, to afford the well-known hydride **1**H(H), the proton being derived from solvent as proposed above for the cyanation. The reaction of NBu_4BH_4 with CH_2Cl_2 solutions of **1** and of **1**H(Cl) also gave **1**H(H). Treatment of a methanol solution of **1** with the milder reducing agent $NaBH_3CN$ resulted in the formation of primarily **1**H(CN) and some **1**H(H). The transfer of CN^- from $NaBH_3CN$ to metal centers is known.[21,26,27]

The usual synthesis of **1**H(H) by treating **1** with methanol results in the formation of 0.8% of a minor isomer (298 K). The reaction of $NaBH_4$ and **1** was found to initially produce equal

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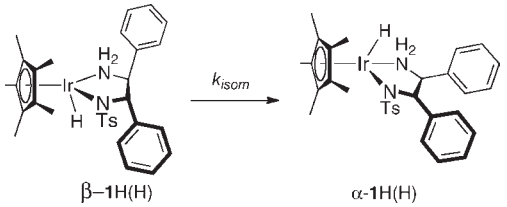
Table 1. Rate Constants and Half-Life Data for the Isomerization of the Unstable Diastereomer of 1H(H) in Several Solvents at 298 K



solvent	k_{isom} (s^{-1})	$t_{1/2}$ (h)
CD_2Cl_2	7.8×10^{-5}	2.5
CD_3CN	4.1×10^{-5}	4.7
C_6D_6	1.6×10^{-5}	12

amounts of the two diastereomers of **1**H(H). The ^{1}H NMR signals for the new isomer (β-**1**H(H)) match with those for the minor hydride observed from the preparation of **1** and methanol. Crystals of the racemic mixture were obtained, but they were featherlike and diffracted X-rays poorly. β-**1**H(H) was found to convert to the α-diastereomer with $t_{1/2}$ = 4.7 h at room temperature. The rate of isomerization was almost unaffected by solvent polarity (Table 1) as well as by the addition of PPh_3. A kinetic isotope effect of 1.2(3) was determined for the isomerizations of **1**H(H) and Cp*IrD-(D_2NCHPhCHPhNTs). The rate of isomerization was unaffected when the tosyl group was replaced by a mesyl ($MeSO_2$) group.[28] The temperature dependence of the rate constant over a range of 22 °C revealed $\Delta S^{\ddagger}$ = 138 J/mol K (see Supporting Information).

We previously found that the conformation of the diphenylethylene backbone of TsDPEN is readily analyzed by ^{1}H NMR spectroscopy by means of the coupling constants of the methine protons.[11] This analysis indicates that the phenyl groups in β-**1**H(H) are diaxial: J = 4.7 Hz for C*H*(Ph)NH_2 and a broad singlet observed for C*H*(Ph)NTs. In contrast, the phenyl groups are diequatorial in most pseudo-octahedral Cp*Ir(X)(TsDPEN) complexes,[11] including α-**1**H(H).

The reaction of (*p*-cymene)Ru(TsDPEN-H) with $NaBH_4$ was also investigated, since this compound is more widely used as a catalyst than the Cp*Ir derivative. We obtained two diastereomers of (*p*-cymene)RuH(TsDPEN) in a 6:4 (β:α) ratio. The β-isomer had previously been detected at a level of about 1% in samples of (*p*-cymene)RuH(TsDPEN).[3] To compare the reactivity of the diastereomers in transfer hydrogenation, a 6:4 diastereomeric mixture of β- and α-(*p*-cymene)RuH(*R*,*R*-TsDPEN) was treated with 3.3 equiv of acetophenone, and the consumption of hydride isomers was monitored via ^{1}H NMR. After 50 min at room temperature, we observed the consumption of 95% of the stable hydride isomer, but only 20% of the unstable isomer (Figure 3). The organic product is 1-phenylethanol. This experiment suggests that the β-hydride isomer is a less effective TH catalyst compared to the α-isomer. Since the β-isomer of (*p*-cymene)RuH(TsDPEN) is present in <1% quantity when generated by treating (*p*-cymene)Ru(TsDPEN-H) with 2-propanol, it is doubtful that this isomer has a significant role in TH catalysis.

Amides and Thioamides. Acetamide was found to add to **1** to afford the corresponding amido-amine adduct, **1**H(NHC(O)Me).

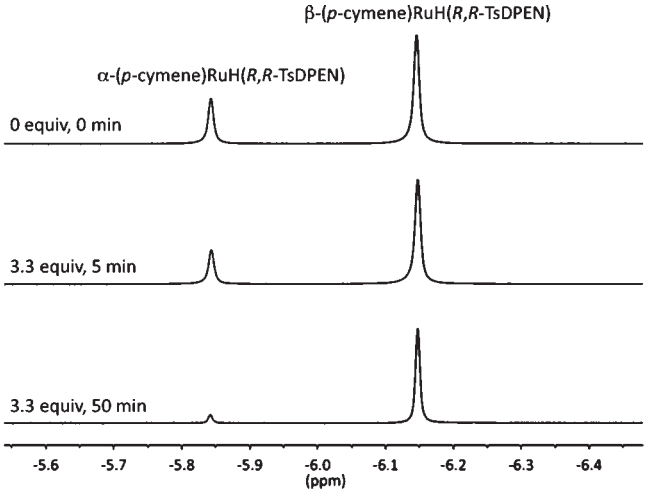
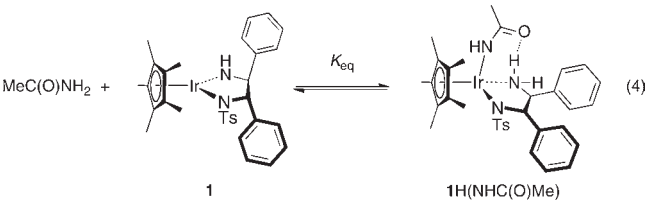


Figure 3. ^{1}H NMR spectra in the hydride region for the reaction of a mixture of α- and β-(*p*-cymene)RuH(*R*,*R*-TsDPEN) with acetophenone in CD_2Cl_2 solution at 23 °C. Equivalents of (initial) acetophenone and reaction times are indicated on the spectra.

In the absence of excess acetamide, the adduct was found to slowly revert to the precursor (eq 4).



$$K_{eq} = \frac{[\mathbf{1}\text{H(NHC(O)Me)}]}{[\mathbf{1}][\text{MeC(O)NH}_2]}$$

In CD_3CN solution at 298 K, K_{eq} is 3.3(1) × 10^2 M^{-1}. Samples of **1**H(NHC(O)Me) can be precipitated from MeCN solution but redissolve to afford a mixture of **1**, $MeC(O)NH_2$, and **1**H(NHC(O)Me). A singlet at δ5.13 (CD_3CN) is assigned to MeC(O)N*H*Ir, 0.4 ppm upfield of free acetamide. A broad triplet at δ11.24 in the ^{1}H NMR spectrum is assigned to one of the diastereomeric NH_2 groups of the $TsDPEN^-$ ligand, the low-field shift being consistent with intramolecular hydrogen-bonding to the MeC(*O*)NHIr center. Ikariya and co-workers have isolated the analogous (*p*-cymene)Ru(amidate)(MsDPEN) (amidate = NHC(O)C(CN)(CH_3)$CH_2C_6H_5$, Ms = mesyl), where the amidate NH coordinates to the Ru center. ^{1}H NMR resonances for the NH (δ6.00) and NH_2 group of MsDPEN (δ9.62) of Ikariya's complex are similar to the corresponding signals observed for **1**H(NHC(O)Me).[29] Several other compounds feature *N*-bonded iridium amides.[30−33] Qualitative tests showed that formamide and benzamide also add to **1**.

Compared to acetamide, thioacetamide was found to add more strongly to **1**. From the reaction of stoichiometric amounts of **1** and the thioamide we obtained **1**H(SC(NH)Me) in analytical purity. Crystallographic analysis confirmed the presence of the *S*-bonded tautomer (Figure 4). The imine *N* was found to engage in intermolecular hydrogen-bonding with the H_2N group of a neighboring Ir-adduct (d_{N-H_2N} = 2.925(5) Å).

Two diastereomers of **1**H(SC(NH)Me) were evident in fresh solutions, but after a few hours a single diastereomer dominates.

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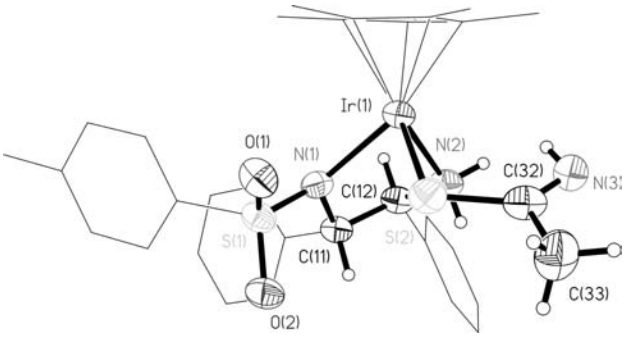
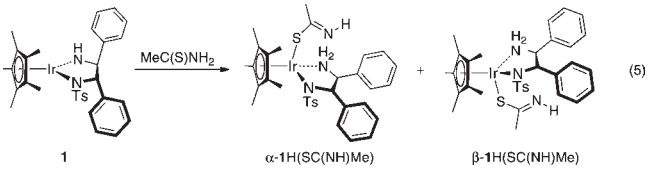


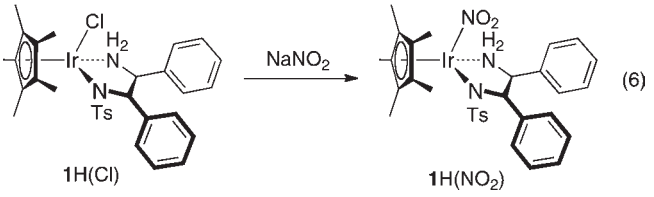
Figure 4. Structure of α-Cp*Ir(SC(NH)Me)(TsDPEN). The thermal ellipsoids are shown at 50% probability level but are omitted on the Cp* and phenyl rings for clarity.

These isomers are distinguished by imine N*H* signals at δ7.8 and 8.1 (CD_2Cl_2). One isomer exhibits sharp Cp* and TsDPEN signals, whereas the other isomer features broadened signals for the Cp* and TsDPEN. These signals remained unchanged from −30 to 40 °C. These isomers are proposed to differ with respect to coordination of the thioacetamide anion to the *R*- or *S*-face of $[\mathbf{1}H]^+$ (eq 5).



In one of the diastereomers, intramolecular hydrogen-bonding between the imine and amine is strong, as indicated by the low field ^{1}H NMR signal at δ11.30. The NH_2 group for the more stable diastereomer does not display this low-field feature (δ7.48 and 4.06). At 23 °C, **1**H(SC(NH)Me) was found to diastereomerize via a first order pathway with $k = 1.5 \times 10^{-4}$ s^{-1} ($t_{1/2} \sim$ 1.3 h), slightly faster than the rates for the isomerization of **1**H(H) and **1**H(CN).

Nitrite. The nitro complex **1**H(NO_2) was prepared via anion metathesis of **1**H(Cl) and $NaNO_2$ (eq 6).



We originally observed **1**H(NO_2) when **1**H(H) was treated with nitric oxide,[34,35] even when this reaction was conducted anaerobically.

Hydrogen-bonding between the amine of TsDPEN and the nitrito ligand is indicated by the N*H* signal in the ^{1}H NMR spectrum at δ6.65 (δ4.42 for **1**H(Cl)).[11] On the basis of the downfield shift of the N*H* signal, hydrogen-bonding in **1**H(NO_2) is similar to that for the adducts of acetamide (δ11.24) and 2-hydroxypyridine (see below), and the previously reported acetate and formate adducts (δ9.59, δ8.96).[18] The C_5Me_4H analogue of **1**H(NO_2) gave crystals suitable for X-ray diffraction. Crystallographic analysis verified the presence of a hydrogen bond between the amine proton and O(3) of the nitro ligand (2.742(3) Å) (Figure 5). The coordination sphere in **1**H(NO_2) is unexceptional, exhibiting equatorial phenyl groups. Only a single diastereomer was observed via ^{1}H NMR spectroscopy.

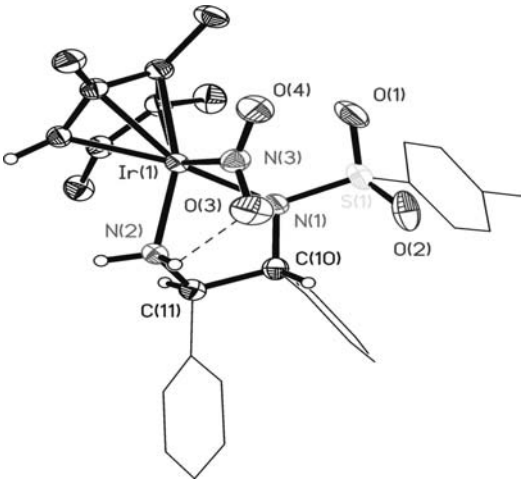


Figure 5. Structure of $(C_5Me_4H)Ir(NO_2)(TsDPEN)$. The thermal ellipsoids are shown at 50% probability level but are omitted on the phenyl and tosyl groups for clarity.

2-Pyridone. 2-Pyridone, an amide that is known to engage in strong H-bonding,[36] adds to **1** as indicated by an immediate color change from purple to yellow. 2-Pyridone is sufficiently acidic (pK_a = 8.26 in MeCN solution) relative to $[\mathbf{1}H(NCMe)]^+$ (pK_a = 21 in MeCN) that a stable adduct of type **1**H(2-pyridonate) is anticipated.[9,37] The binding is stronger than for acetamide: the reaction only required stoichiometric amounts of the pyridone, and the product did not dissociate detectably in solution. Crystallography confirmed that the pyridonate is *N*-bonded (Figure 6), as is typical for pyridonates of softer metals.[38,39] The C(32)−O(3) bond distance of 1.260(4) Å is similar to that seen in other pyridonate complexes.[40,41] Intramolecular hydrogen-bonding exists between the pyridonate carbonyl and the TsDPEN amine, with a O(3)−N(2) distance of 2.761(5) Å. The pyridonate ring is coplanar with one of the phenyl rings. Interestingly, the phenyl substituents on the TsDPEN ligand are diaxial, an orientation that had not been previously observed in pseudo-octahedral TsDPEN complexes, except for the metastable hydride described above.

Consistent with the crystallographic results, the ^{1}H NMR signals for the pyridonate CH groups appear in the region (δ6−6.5) associated with vinylic protons, as is characteristic of the pyridone tautomer.[40,42] Further evidence for a pyridonate description is evident in the ^{13}C NMR spectrum, where resonances were observed in the region for carbonyl centers at δ 172.7 and 173.3.[40] The axial proton on the amine of **1**H(2-pyridonate) exhibits a ^{1}H NMR signal at δ11.51, the downfield shift resulting from hydrogen-bonding to the carbonyl. ^{1}H NMR data obtained on crystals dissolved at −18 °C displayed signals for both diastereomers, both of which feature *equatorial* phenyl groups. ^{1}H NMR spectra revealed a 5:4 isomer ratio (20 °C), which was only slightly dependent on temperature (ΔH = 2.6 kJ/mol and ΔS = 6.8 J/mol K over a 60 °C temperature range). Indicative of the changeable isomer ratio, solutions were found to be thermochromic: cold solutions appear yellow and warm solutions are pink. No color changes were observed for solid

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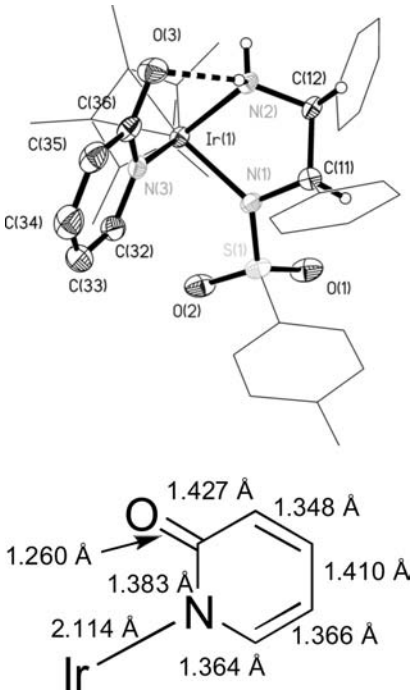
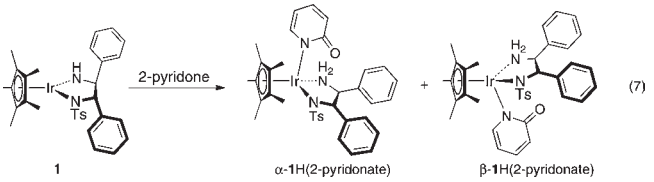
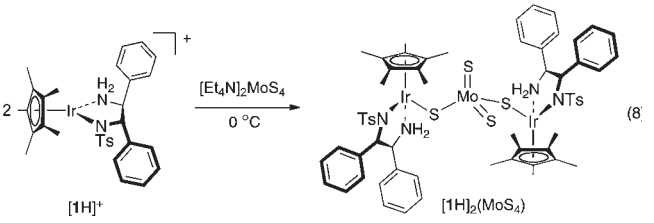


Figure 6. Structure of Cp*Ir(2-pyridonate)(TsDPEN), which crystallizes as the β-diastereomer. The thermal ellipsoids are shown at 50% probability level but are omitted on the Cp* ring, phenyl, and tosyl groups for clarity (inset: bond distances for the 2-pyridone ring).

samples over a comparable temperature range (−30 to 120 °C).[43] The second isomer is proposed to arise from the attachment of 2-pyridonate to the opposite metal face (eq 7).[11] Consistent with the crystallographic results, the ^{1}H NMR signals for the pyridonate C*H* groups appear in the vinyl region (δ6−6.5), which is characteristic of the pyridone tautomer.[40,42]



Tetrathiomolybdate. Although the thioanions MoS_4^{2-} and WS_4^{2-} have been well studied as "metalloligands",[44,45] complexes of the type $(\mu\text{-}\kappa^1,\kappa^1\text{-}MS_4)(ML_x)_2$ or esters such as $MoS_2(SR)_2$ remain unknown.[46−48] We prepared the first example of such by the reaction of $(Et_4N)_2MoS_4$ with 2 equiv of [**1**H]BF$_4$ (eq 8). Although thermally only slightly stable at room temperature, dark purple [**1**H]$_2$MoS$_4$ was characterized by NMR and IR spectroscopies, which indicated a single diastereomer. Similar results were obtained for the green WS_4^{2-} derivative.



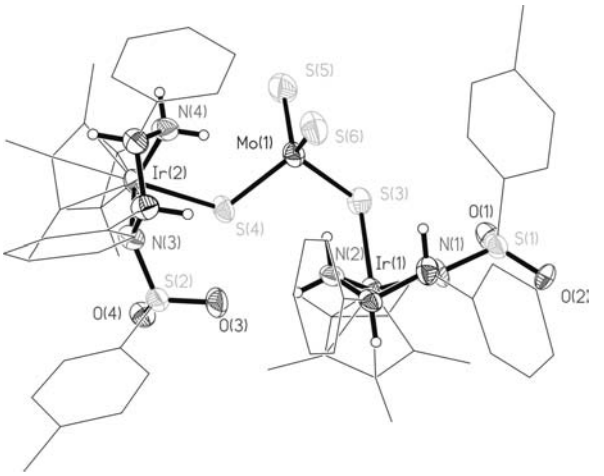


Figure 7. Structure of [Cp*Ir(TsDPEN)]$_2$MoS$_4$. The thermal ellipsoids are shown at 30% probability level but are omitted on the Cp*, phenyl, and tosyl groups.

Crystallographic analysis of [**1**H]$_2$MoS$_4$ revealed a tetrahedral Mo(VI) center linking two iridium centers. Diastereomers were not observed. Similar diastereoselectivity had been observed for $[(\mathbf{1})_2\text{dppe}]^{2+}$.[11] The Mo−S bonds are of two distinct types: the Mo−SIr distances are 2.222(4) and 2.231(4) Å, whereas Mo−$S^{terminal}$ distances are 2.130(5) and 2.170(4) Å (Figure 7, Table 2). The longer Mo−$S^{terminal}$ bond is affected by hydrogen-bonding to one amine proton on each of the Ir complexes ($d_{S\cdots NH2}$ = 3.508(8) Å). The dihedral angle between the planes generated from Ir(1)−S(3)−Mo(1) and Ir(2)−S(4)−Mo(2) is 46.5°.

CONCLUSIONS

In this work, we showed that [**1**H]$^+$ binds a wide variety of soft anionic ligands. Adducts were prepared in two ways: (i) stable anions were combined directly with [**1**H]$^+$ and (ii) for less accessible anions, the corresponding conjugate acids were added to **1**. This methodology has afforded the first derivative of the type $MoS_2(SR)_2$[46] and the first structurally characterized example of a monodentate thioacetamido complex.[49]

In general, the initial binding of anions to [**1**H]$^+$ is unselective, but the equilibrium diastereoselectivities are high. Supporting this view, basic ligands that would be expected to bind strongly generate observable amounts of the β-diastereomer. In contrast, weakly basic anions (e.g., nitrite, tetrathiomolybdate) or ligands that eliminate readily (acetamide), gave only the more stable α-isomer.

The observation of metastable diastereomers of **1**H(H) and (*p*-cymene)RuH(TsDPEN) is noteworthy because of the utility of these compounds as enantioselective catalysts for asymmetric transfer hydrogenation.[6,50] The high enantioselectivity arises because (i) the catalysts form hydrides with high diastereoselectivity from hydrogen donors (formate, alcohols, etc.) and (ii) the resulting hydrides diastereoselectively transfer H_2 to prochiral substrates. We were surprised that using BH_4^-/ROH as a source of H_2 results in almost no diastereoselection, and the resulting mixture of diastereomers is stable for many hours. The uncommon diastereomer is competent for transfer hydrogenation, but is slow. The differing rates probably arise because in the less stable hydride substrate accessibility is hindered by the diaxial phenyl groups. The diaxial orientation of the phenyl groups is proposed

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Table 2. Selected Bond Distances (Å) and Related Structural Features for New Compounds of the Type 1H(X)

compound	**1** (ref 11)	$[\mathbf{1H}]BAr^F_4$ (ref 9)	**1**H(CN)	**1**H(SC(NH)Me)	$[\mathbf{1H}]_2MoS_4$	**1**H(NO_2)	**1**H(2-pyridonate)
Ir−Cp*(centroid)	1.794(6)	1.782(6)	1.810(7)	1.818(4)	1.823(16), 1.800(14)	1.830(4)	1.803(4)
Ir−N(1)Ts	2.058(5)	1.984(4)	2.151(5)	2.174(3)	2.144(10), 2.137(10)	2.137(3)	2.168(3)
Ir−N(2)H_x (x = 1,2)	1.901(5)	2.096(5)	2.124(9)	2.112(5)	2.157(10), 2.091(11)	2.106(3)	2.116(3)
Ir−X			1.990(1)	2.361(9)	2.393(4), 2.406(4)	2.105(3)	2.114(3)
phenyl group orientation	axial	axial	equatorial	equatorial	equatorial	equatorial	axial

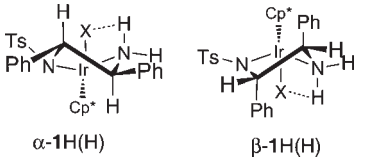


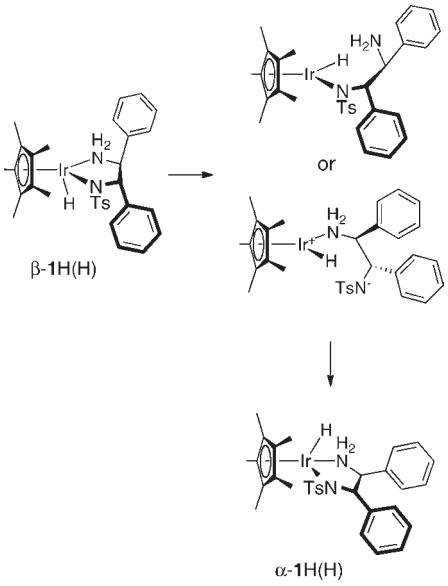
Figure 8. Proposed conformations of the α- and β-diastereomers of Cp*IrH(*S,S*-TsDPEN). Similar conformations apply also to (*p*-cymene)-RuH(TsDPEN).

to result from dihydrogen-bonding between the hydride ligand and the amine group (Figure 8).[51] Dihydrogen-bonding is observed between N−H and Ru−H in the stable isomer of (*p*-cymene)RuH(TsDPEN).[1]

Although the binding of hard Lewis bases to $[\mathbf{1H}]^+$ is usually unfavorable, binding affinities can be enhanced by intramolecular hydrogen-bonding. This additional interaction is proposed to influence the affinity of **1** for amides and 2-pyridone, even though $[\mathbf{1H}]^+$ shows no affinity for pyridine itself.[11] The influence of hydrogen-bonding in the pyridonate adduct is sufficient to stabilize the β-isomer of **1**H(2-pyridonate), at least in the solid state. The hydrogen-bonding interaction proposed to stabilize **1**H(NHC(O)-Me) is weaker than in the pyridonate complex, reflecting the reduced tendency of simple amides to engage in hydrogen-bonds.[52]

We propose that diastereomerization occurs via two pathways. For weakly basic ligands (acetamido, nitrito, chloride), only a single diastereomer is observed. For these anions, we assume that diastereomerization involves an elimination-readdition pathway, either by dissociation of the anionic ligand or its conjugate acid. More interesting is the isomerization mechanism for tightly bound, basic ligands such as cyanide and hydride. In these cases, dissociation of the anion is unlikely. A dissociative pathway for the hydride is precluded because the rate of addition of H_2 to **1** is too slow, requiring days at 1 atm of H_2. Instead, diastereomerization is proposed to involve opening of the Ir(TsDPEN) ring in a hemilabile manner. One can envision dissociation of the amine or the tosylamido ligands followed by reattachment of this group to the opposite face of the 16e-intermediate (Scheme 2).

Scheme 2. Two Pathways for the Chelate-Ring-Opening Mechanism Proposed for the Diastereomerization of 1H(H)



EXPERIMENTAL SECTION

Materials and Methods. All synthetic manipulations were performed in air unless noted. TsDPENH was prepared according Noyori and co-workers.[53] The preparations of Cp*Ir(TsDPEN-H) (**1**), [Cp*Ir(TsDPEN)]BF_4 ($[\mathbf{1H}]BF_4$), and (*p*-cymene)Ru(TsDPEN-H) have been described.[1,11,14] Other reagents were obtained from conventional commercial sources or were prepared by standard methods.[54] ^1H and ^{13}C NMR spectra were referenced to the residual solvent peaks.[55]

Cp*Ir(CN)(TsDPEN), 1H(CN). Two milliliters of a 0.072 M KCN in MeOH solution were added to 100 mg (0.144 mmol) of solid **1** (Note: Cp*Ir(TsDPEN-H) was not initially dissolved in MeOH to avoid formation of **1**H(H) via hydrogen transfer). The resulting yellow solution was allowed to stir for 5 min before solvent was removed under reduced pressure. The pale red residue was recrystallized from CH_2Cl_2 solution with hexane to afford a pale yellow solid. Slow diffusion of a CH_2Cl_2 solution of the solid into hexane gave pale yellow crystals suitable for crystallographic analysis. Yield: 68 mg (66%). IR: ν_{CN} (KBr) = 2107 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.86 (s, 15H, Cp*, β) 1.94 (s, 15H, Cp*, α), 2.20 (s, 3H, $SO_2C_6H_4$-4-CH_3, β), 2.21 (s, 3H, $SO_2C_6H_4$-4-CH_3, α), 3.60 (ddd, 2.5, 10.8, 13.0 Hz, 1H, $H_2NCHPhCHPhNTs$, α), 3.84 (br m, 1H, $H_2NCHPhCHPhNTs$, β), 4.01 (br s, 4.13, $HHNCHPhCHPhNTs$, α), 4.19 (d, 1H, 11.0 Hz, H_2N-$CHPhCHPhNTs$, α), 4.39 (br m, 1H, $HHNCHPhCHPhNTs$, β), 4.58 (br m, 1H, $HHNCHPhCHPhNTs$, β), 4.60 (d, 9.0 Hz, $H_2NCHPhCH$-$PhNTs$, β), 4.84 (br m, 1H, $HHNCHPhCHPhNTs$, α), 6.62−7.46 (m, 28H, phenyl). The same compound was prepared by addition of 1 mL of a 0.14 M KCN in MeOH solution that was 0.028 M in **1**H(Cl). Yield: 75 mg (74%). When **1** is treated with Et_4NCN in CD_3CN the signal at δ 3.60 appears as a doublet assigned to the $HDNCH(Ph)$ proton. Anal. Calcd for $C_{31}H_{36}IrN_3O_4S\cdot CH_2Cl_2\cdot 0.75H_2O$: C, 48.49; H, 4.87; N, 5.14. Found: C, 48.29; H, 4.69; N, 4.98.

[Cp*$_2$Ir$_2$(TsDPEN)$_2$(μ-CN)]BF_4. A 6.4 mL aliquot of a 0.016 M solution of [Cp*Ir(TsDPEN)]BF_4 in CH_2Cl_2 was added to 11 mL of a 0.01 M solution of Cp*Ir(CN)(TsDPEN) in CH_2Cl_2. The resulting pale red solution was allowed to stir for 5 min before the solvent was removed under reduced pressure. The red residue was recrystallized from a minimum volume of CH_2Cl_2 by the addition of hexane, affording a pale yellow solid. Yield: 126 mg (81%). IR (KBr): ν_{CN} = 2152 cm^{-1}. ^1H

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NMR (500 MHz, CD_2Cl_2): δ 1.91 (s, 15H, Cp*), 2.00 (s, 15H, Cp*), 2.177 (s, 3H, $SO_2C_6H_4$-4-CH_3), 2.18 (s, 3H, $SO_2C_6H_4$-4-CH_3), 3.68 (ddd, 2.7, 11.2, 13.2 Hz, 1H, H_2NCHPhCHPhNTs), 3.75 (ddd, 2.7, 11.2, 13.2, 1H, H_2NCHPhCHPhNTs), 4.54 (d, 11.2 Hz, 1H, $H_2NCHPhCH$PhNTs), 4.79 (d, 11.2 Hz, 1H, $H_2NCHPhCH$PhNTs), 6.54−7.40 (m, 28 H).

Cp*IrH(TsDPEN) Isomers. Under an atmosphere of Ar, 0.5 g (0.72 mmol) of **1** was treated with 68 mg (1.8 mmol) of $NaBH_4$ in 5 mL of MeOH. After 2 min, solvent was removed from the yellow mixture under reduced pressure. The remaining residue was extracted into 3 × 10 mL of CH_2Cl_2. The combined extracts concentrated under reduced pressure to afford a yellow solid. Yield: 330 mg (66%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ −11.49 (s, 1H, Ir−H, β), −10.12 (s, 1H, Ir−H, α), 1.63 (s, 15H, Cp*, β), 1.89 (s, 15H, Cp*, α), 2.28 (s, 3H, $SO_2C_6H_4$-4-CH_3, β), 2.35 (s, 3H, $SO_2C_6H_4$-4-CH_3, α), 3.36 (d, 11 Hz, 1H, *H*HNCHPhCHPhNTs, β), 3.58 (d, 10.2 Hz, 1H, *H*HNCHPhCHPhNTs, α), 3.69 (ddd, 3.2, 9.6, 12.6 Hz, 1H, H_2NCHPhCHPhNTs, α), 3.77 (d, 4.7 Hz, 1H, H_2NCHPhCHPhNTs, β), 4.10 (t, 11.5 Hz, 1H, H*H*NCHPhCHPhNTs, α), 4.16 (d, 9.6 Hz, 1H, $H_2NCHPhCH$PhNTs, α), 4.71 (s, 1H, $H_2NCHPhCH$PhNTs, β), 4.73 (br s, 1H, H*H*NCHPhCHPhNTs, β), 6.80−7.75 (m, 28H). ^{1}H NMR (500 MHz, CD_3CN): δ −11.75 (s, 1H, Ir−H, β), −10.74 (s, 1H, Ir−H, α), 1.64 (s, 15H, Cp*, β), 1.87 (d, 0.8 Hz, 15H, Cp*, α), 2.28 (s, 3H, $SO_2C_6H_4$-4-CH_3, β), 2.38 (s, 3H, $SO_2C_6H_4$-4-CH_3, α), 3.68 (ddd, 3.6, 9.2, 12.1 Hz, 1H, H_2NCHPhCHPhNTs, α), 3.73 (m, 1H, H_2NCHPhCHPhNTs, β), 3.91 (d, 11.1 Hz, 1H, *H*HNCHPhCHPhNTs, β), 4.15 (d, 9.2 Hz, 1H, $H_2NCHPhCH$PhNTs, α), 4.24 (t, 11.2 Hz, 1H, *H*HNCHPhCHPhNTs, α), 4.40 (d, 10.6 Hz, 1H, H*H*NCHPhCHPhNTs, α), 4.57 (s, 1H, $H_2NCHPhCH$PhNTs, β), 4.91 (d, 8.7 Hz, 1H, H*H*NCHPhCHPhNTs, β), 6.85−7.74 (m, 28H).

(*p*-Cymene)RuH(*R*,*R*-TsDPEN) Isomers. The preparation followed the procedure for α- and β-**1**H(H) (preceding procedure) starting with 100 mg (0.17 mmol) of (*p*-cymene)Ru(*R*,*R*-TsDPEN-H) to afford a mixture of (*p*-cymene)RuH(*R*,*R*-TsDPEN) α and β isomers as a brown solid. Yield: 28 mg (28%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ −6.13 (s, 1H, Ru−H, β), −5.82 (s, 1H, Ru−H, α), 1.27 (d, 6.6 Hz, 3H, $CH(CH_3)_2$, β), 1.29 (d, 6.9 Hz, 3H, $CH(CH_3)_2$, α), 1.29 (d, 6.9 Hz, 3H, $CH(CH_3)_2$, β), 1.34 (d, 6.9 Hz, 3H, $CH(CH_3)_2$, α), 1.95 (s, 3H, CH_3 cymene, β), 2.30 (s, 3H, $SO_2C_6H_4$-4-CH_3, β), 2.33 (s, 3H, CH_3 cymene, α), 2.37 (s, 3H, $SO_2C_6H_4$-4-CH_3, α), 2.61 (m, 1H, $CH(CH_3)_2$, β), 2.71 (m, 1H, $CH(CH_3)_2$, α), 3.22 (t, 12.1 Hz, 1H, *H*HNCHPhCHPhNTs, α), 3.31 (m, 1H, *H*HNCHPhCHPhNTs, β), 3.51−3.60 (m, 2H, H*H*NCHPhCHPhNTs, $\alpha + \beta$), 3.72 (m, 1H, H_2NCHPhCHPhNTs, β), 3.81 (d, 9.8 Hz, 1H, $H_2NCHPhCH$PhNTs, α), 4.06 (ddd, 3.1, 9.9, 12.9 Hz, 1H, H_2NCHPhCHPhNTs, α), 4.37 (dd, 1.0, 5.8 Hz, 1H, C_6H_4 cymene, β), 4.73 (d, 3.6 Hz, 1H, H_2NCHPhCHPhNTs, β), 4.82 (dd, 0.8, 5.8 Hz, 1H, C_6H_4 cymene, α), 4.86 (d, 5.7 Hz, 1H, C_6H_4 cymene, β), 5.00 (dd, 1.0, 5.7 Hz, 1H, C_6H_4 cymene, α), 5.26 (d, 5.7 Hz, 1H, C_6H_4 cymene, β), 5.34 (d, 5.7 Hz, 1H, C_6H_4 cymene, α), 5.41−5.44 (m, 2H, C_6H_4 cymene, $\alpha + \beta$), 6.75−7.48 (m, 28H).

Cp*Ir(NH(CO)Me)(TsDPEN), 1H(NH(CO)Me). A MeCN solution of acetamide (1.2 mL, 0.14 M) was added to a flask containing 100 mg (0.14 mmol) of solid **1**. The purple solution was allowed to stir overnight, affording a yellow precipitate. The precipitate was filtered off and washed with hexane. Yield: 50 mg (46%). ^{1}H NMR (500 MHz, CD_3CN): δ 1.73 (s, 15H, Cp*), 1.98 (s, 3H, $H_3CCONHIr$), 2.18 (s, 3H, $SO_2C_6H_4$-4-CH_3), 3.61 (ddd, 3.4, 11.4, 12.5 Hz, 1H, H_2NCHPhCHPhNTs), 4.17 (br d, 1H, *H*HNCHPhCHPhNTs), 4.26 (d, 11.2 Hz, 1H, $H_2NCHPhCH$PhNTs), 5.12 (br s, 1H, $H_3CCONHIr$), 6.59−7.62 (m, 14H), 11.24 (br t, 11 Hz, 1H, H*H*NCHPhCHPhNTs). Upon dissolving the sample in CD_3CN, the yellow solution turned purple concomitant with the appearance of signals for **1** in the ^{1}H NMR spectrum.

Cp*Ir(SC(NH)Me)(TsDPEN), 1H(SC(NH)Me). Under an atmosphere of Ar, 1.6 mL of a 0.09 M MeCN solution of thioacetamide was added to 5 mL of a 0.03 M MeCN solution of **1**. The resulting yellow solution was allowed to stir for 5 min before removing the solvent under reduced pressure. The resulting yellow solid was recrystallized from CH_2Cl_2 solution by the addition of hexane to afford a deep yellow solid. The resulting solid is air sensitive and will degrade upon exposure to water. Slow diffusion of a CH_2Cl_2 solution of the solid into hexane resulted in light yellow crystals suitable for crystallographic analysis. Yield: 78 mg (71%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.76 (s, 15H, Cp*, β), 1.81 (s, 15H, Cp*, α), 2.19 (s, 3H, β), 2.23 (s, 3H, α), 2.35 (s, 3H, β), 2.73 (d, 0.9 Hz, 3H, β), 3.22 (br d, 1H, *H*HNCHPhCHPhNTs, β), 3.60 (m, 2H, H_2NCHPhCHPhNTs, $\alpha + \beta$), 4.06 (br d, 1H, *H*HNCHPhCHPhNTs, α), 4.20 (d, 11.1 Hz, 1H, $H_2NCHPhCH$PhNTs, α), 4.26 (d, 10.8 Hz, 1H, $H_2NCHPhCH$PhNTs, β), 6.53−7.33 (m, 28H, phenyl), 8.02 (br s, 1H, *H*HNCHPhCHPhNTs, α), 7.48 (br t, 1H, H*H*NCHPhCHPhNTs, α), 7.84 (s, 1H, SC(N*H*)Me, β), 8.06 (s, 1H, SC(N*H*)Me, α), 11.30 (br t, 1H, H*H*NCHPhCHPhNTs, β). The ^{1}H NMR spectrum was invariant from −30 to 40 °C. Anal. Calcd for $C_{33}H_{40}IrN_3O_2S_2 \cdot CH_2Cl_2$: C, 47.93; H, 4.96; N, 4.93. Found: C, 47.66; H, 4.83; N, 4.87.

Cp*Ir(NO$_2$)(TsDPEN), 1H(NO$_2$). Nitric oxide was bubbled through a solution of 120 mg (0.18 mmol) of **1** in 10 mL of MeCN. An immediate color change from pale orange to brown was observed. A tan solid was obtained upon recrystallization from CH_2Cl_2/hexane. **1**H(NO_2) can also be prepared from a CD_3CN solution of **1**H(Cl) and $NaNO_2$. Nitric oxide was purified by passage through a saturated aqueous NaOH solution. Yield: 75 mg (56%). ^{1}H NMR (500 MHz, CD_3CN): δ 1.78 (s, 15H, Cp*), 2.25 (s, 3H, $SO_2C_6H_4$-4-*Me*), 3.72 (ddd, 1 H, H_2NCHPhCHPhNTs), 4.23 (d, 1H, $H_2NCHPhCH$PhNTs), 5.18 (br d, 1H, H*H*NCHPhCHPhNTs), 6.65 (br t, 1H, *H*HNCHPhCHPhNTs), 6.70−7.23 (m, 14H). Anal. Calcd for $C_{31}H_{36}IrN_3O_4S$: C, 50.39; H, 4.91; N, 5.69. Found: C, 50.07; H, 5.09; N, 5.43. FD-MS: m/z = 693 (MH^+). The Cp* system tended to form long needles that did not diffract well. The related (C_5Me_4H)Ir(NO_2)(TsDPEN) was prepared as described above (55% yield) and readily crystallized as the CH_2Cl_2 solvate. ^{1}H NMR (500 MHz, CD_3CN): δ 1.76 (s, 3H, C_5Me_4H), 1.80 (s, 3H, C_5Me_4H), 1.83 (s, 3H, C_5Me_4H), 1.91 (s, 3H, C_5Me_4H), 2.25 (s, 3H, $SO_2C_6H_4$-4-*Me*), 3.84 (ddd, 3.3, 11, 12.7 Hz, 1 H, H_2NCHPhCHPhNTs), 4.36 (d, 11 Hz, 1H, $H_2NCHPhCH$PhNTs), 4.84 (br d, 7 Hz, 1H, H*H*NCHPhCHPhNTs), 6.47 (br t, 10 Hz, 1H, *H*HNCHPhCHPhNTs), 6.70−7.23 (m, 14H).

Cp*Ir(2-pyridonate)(TsDPEN), 1H(2-pyridonate). A solution of 0.14 g (0.21 mmol) of **1** in 10 mL of MeCN was treated with 5 mL of 0.041 M (0.21 mmol) MeCN solution of 2-hydroxypyridine. The addition resulted in an instantaneous color change from reddish-purple to yellow-orange. The solution was stirred for 5 min, and the solvent was removed under reduced pressure. The yellow solid was recrystallized by dissolution in 2 mL of MeCN followed by the addition of 30 mL of Et_2O. Yield: 73.3 mg (44%). ^{1}H NMR (500 MHz, CD_3CN): δ 1.61 (s, 15H, Cp*), 1.63 (s, 15H, Cp*), 2.16 (s, 3H, $SO_2C_6H_4$-4-CH_3), 2.21 (s, 3H, $SO_2C_6H_4$-4-CH_3), 3.57 (dt, 6.0, 11.3 Hz, 1 H, H_2NCHPhCHPhNTs), 3.73 (ddd, 4.6, 10.9, 15.9 Hz, 1 H, H_2NCHPhCHPhNTs), 3.79 (d, 11 Hz, 1H, $H_2NCHPhCH$PhNTs), 3.98 (br t, 9.7 Hz, 1H, H*H*NCHPhCHPhNTs), 4.36 (d, 11 Hz, 1H, $H_2NCHPhCH$PhNTs), 4.68 (br dd, 5.0, 10.9 Hz, 1H, H*H*NCHPhCHPhNTs), 6.10−6.15 (m, 2H, pyridone ring), 6.20 (dd, 1.3, 8.6 Hz, 1H, pyridone ring), 6.35 (dt, 1.5, 6.5 Hz, 1H, pyridone ring), 6.37−6.56 (m, 9 H), 6.58 (tt, 1.3, 7.2 Hz, 1H, pyridone ring), 6.66 (m, 1H), 6.68 (d, 7.8 Hz, 1H, $SO_2C_6H_4$-4-Me), 6.80 (d, 8.4 Hz, 1H, $SO_2C_6H_4$-4-Me), 6.69−7.25 (m, 18H), 7.26 (ddd, 2.2, 6.6, 8.7 Hz, 1H, pyridone ring), 7.32 (ddd, 2.2, 6.6, 8.7 Hz, 1H, pyridone ring), 8.52 (dd, 2.2, 6.1 Hz, 1H, pyridone ring), 8.76 (dd, 2.0, 6.1 Hz, 1H, pyridone ring), 9.79 (br t, 7.8 Hz, 1H, *H*HNCHPhCHPhNTs), 11.51 (br t, 11.1 Hz, 1H, *H*HNCHPhCHPhNTs). ^{13}C NMR (500 MHz, CD_3CN): δ 9.29, 9.67, 68.92, 72.03, 72.99, 73.88, 87.12, 87.43, 108.52, 108.96, 117.78, 118.20, 127.21, 127.22, 127.44, 127.66, 127.99, 128.01,

128.40, 128.88, 128.95, 128.97, 129.02, 129.55, 130.75, 131.09, 138.80, 138.85, 138.87, 138.88, 140.15, 140.32, 140.95, 141.74, 144.00, 144.54, 153.61, 155.60, 172.72, 173.34, 175.85. Anal. Calcd for $C_{31}H_{36}IrN_3O_4S$: C, 50.39; H, 4.91; N, 5.69. Found: C, 50.07; H, 5.09; N, 5.43.

[Cp*Ir(TsDPEN)]$_2$(MoS$_4$), [1H]$_2$MoS$_4$. Five milliliters of a 0.01 M (50 mmol) solution of $(Et_4N)_2MoS_4$ in MeCN was added to 71 mg (100 mmol) of [Cp*Ir(TsDPEN)]BF_4 in 10 mL of MeCN at 0 °C. The color changed instantly from pale yellow to a dark purple. The solution was stirred for 5 min before removing the solvent under reduced pressure. The product was recrystallized by diffusion of 60 mL of Et_2O into a solution of the purple residue in 2 mL of acetone at −20 °C. Large colorless crystals of Et_4NBF_4 were removed manually, leaving a purple solid. Yield: 71 mg (88%). ^{1}H NMR (500 MHz, CD_3CN): δ 1.80 (s, 30H, Cp*), 2.29 (s, 6H, $SO_2C_6H_4$-4-CH_3), 3.86 (br t, 13 Hz, 2H, H_2NC*H*PhCHPhNTs), 4.02 (d, 11 Hz, 2H, H_2NCHPhC*H*PhNTs), 5.10 (br s, 2H, H*H*NCHPhCHPhNTs), 5.82 (br t, 13 Hz, 2H, *H*HNCHPhCHPhNTs), 6.60−7.43 (m, 28H, phenyl). UV−vis (MeCN): 463 (ε = 1.06 × 10^4 M^{-1} cm^{-1}), and 500 nm (ε = 1.11 × 10^4 M^{-1}cm^{-1}).

The synthesis of [**1**H]$_2$MoS$_4$ was also achieved by the reaction of 2 equiv of **1**H(Cl) and $(Et_4N)_2MoS_4$. Above 0 °C, solutions degraded over the course of a day as evidenced by precipitation of a black solid and observation of free HTsDPEN by ^{1}H NMR spectroscopy. Solid samples degraded after several hours at room temperature.

[Cp*Ir(TsDPEN)]$_2$(WS$_4$). A green product was obtained using the preceding procedure but using $(Et_4N)_2WS_4$ in place of $(Et_4N)_2MoS_4$. [**1**H]$_2$WS$_4$ was found to degrade at room temperature, but more slowly than the MoS_4 derivative. Yield: 71 mg (94%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.79 (s, 30H, Cp*), 2.15 (s, 6H, $SO_2C_6H_4$-4-CH_3), 3.75 (br t, 11.8 Hz, 2H, H_2NC*H*PhCHPhNTs), 4.20 (br d, 2H, H_2NCHPhC*H*PhNTs), 6.00 (br s, 2H, H*H*NCHPhCHPhNTs), 6.60−7.45 (m, 30H, phenyl). UV−vis (MeCN): 405 (ε = 3.01 × 10^4 M^{-1} cm^{-1}).

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra, kinetic measurements for the isomerization of **1**H(CN), **1**H(H), and **1**H(SC(NH)Me), Eyring and van't Hoff plots for the isomerization of **1**H(H), details for acetophenone hydrogenation by (*p*-cymene)RuH(*R*,*R*-TsDPEN), calculation of K_{eq} for **1**H(NHC(O)Me), variable temperature data and van't Hoff plot for the isomerization of **1**H(2-pyridonate) and crystallographic information files (cif) for **1**H(CN), **1**H(SC(NH)Me), (C_5Me_4H)Ir(NO_2)(TsDPEN), [**1**H]$_2$MoS$_4$, and **1**H(2-pyridonate). This material is available free of charge via the Internet at http://pubs.acs.org.

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