Mononuclear Indoline Complexes. 2. Synthesis, Structure, and Reactivity of [(Cymene)Ru(η^1-*N*-indoline)(CH_3CN)$_2$](OTf)$_2$

Lisa D. Vasquez, B. C. Noll, and M. Rakowski DuBois*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

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The complex [(cymene)Ru(η^1-indoline)(CH_3CN)$_2$](OTf)$_2$, **1**, has been synthesized by the reaction of [(cymene)Ru(OTf)$_2$]$_x$ with indoline in acid solution and characterized by an X-ray diffraction study. Bond distances for the indoline ligand are compared to those reported recently for other η^1- and η^6-indoline complexes. Complex **1** rearranged to [(cymene)Ru(η^6-indoline)](OTf)$_2$ when heated in dichloromethane solution. The titration of an aqueous solution of **1** has been carried out, and the pK_a of the coordinated ligand was determined to be 5.2. The value is similar to that reported for the indolinium ion. Ligand-exchange reactions of **1** have been studied. Deprotonation of the η^1-indoline ligand in **1** results in dehydrogenation of the ligand to form free indole and ruthenium hydride products. The deprotonation of **1** in the presence of an alkene has been found to result in a hydrogen-transfer reaction to form alkane. Characteristics of the hydrogen-transfer reactions are discussed.

Introduction

The hydrotreating of petroleum feedstocks is a catalytic process for removing heteroatom impurities from crude hydrocarbons.[1] Although reactions of many metal thiophene complexes have been studied as potential models for the hydrodesulfurization reaction,[2] the possible pathways for the activation of aromatic nitrogen heterocycles on the catalyst surfaces are less well-understood. In the hydrodenitrogenation of indole over heterogeneous metal catalysts, the partially hydrogenated indoline molecule was found to form prior to the denitrogenation step.[3] The mechanism by which the metal surface activates the indoline molecule toward further ring-opening reactions has not been established. Although relatively few discrete transition-metal complexes containing the indoline ligand have been synthesized,[4−8] a study of these types of derivatives may help to establish the possible modes of activation of this heterocycle by transition metals. We have recently reported the synthesis and characterization of [(cymene)Ru(η^6-indoline)](OTf)$_2$ and have begun to examine its reactivity.[8] In this paper, we report the synthesis and characterization of the η^1-bonded indoline complex, [(cymene)Ru(η^1-N-indoline)(CH_3CN)$_2$](OTf)$_2$, **1**, and some related derivatives. The complex permits the direct comparison of the σ- and π-bonded indoline ligands to the same metal fragment, and we have compared the relative stabilities of the bonding modes, the pK_a values for the coordinated ligands, and the reactivity of the heterocycles.

Results and Discussion

Synthesis and Characterization of 1. The reaction of [(cymene)Ru(OTf)$_2$]$_x$ with aromatic heterocycles has been used to prepare a number of π-coordinated sandwich-type complexes, including [(cymene)Ru(tetramethylthiophene)](OTf)$_2$,[9] [(cymene)Ru(tetramethylpyrrolyl)]OTf,[10] [(cymene)Ru(η^6-indole)](OTf)$_2$,[11] and [(cymene)Ru(η^6-1-Me-indoline)](OTf)$_2$.[8] However, we have reported that the reaction of the ruthenium starting material with the unsubstituted indoline led to a mixture of products which did not include the η^6-indoline derivative. σ-Coordination of the indoline nitrogen was presumed to be a competing process in this reaction, but the product mixture was not completely characterized at that time. The target complex of that study, [(cymene)Ru(η^6-indoline)](OTf)$_2$, was successfully synthesized by an alternate route that involved hydrogenation of the corresponding η^6-indole complex over a Rh/C catalyst.

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(2) See, for example: (a) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801. (b) Angelici, R. J. *Bull Soc. Chim. Belg.* **1995**, *104*, 265. (c) Angelici, R. J. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York, 1994; Vol. III, p 1433. (d) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.
(3) (a) Massoth, F. E.; Balusami, K.; Shabtai, J. *J. Catal.* **1990**, *122*, 256. (b) Olive, J. L.; Biyoko, S.; Moulinas, C.; Geneste, P. *Appl. Catal.* **1985**, *19*, 165. (c) Odebunmi, E. O.; Ollis, D. F. *J. Catal.* **1983**, *80*, 76.
(4) (a) Semmelhack, M. F.; Wulff, W.; Garcia, J. L. *J. Organomet. Chem.* **1982**, *240*, C5.
(5) Kabir, S. E.; Kolwaite, D. S.; Rosenberg, E.; Scott, L. G.; McPhillips, R.; Dugue, R.; Day, M.; Hardcastle, K. I. *Organometallics* **1996**, *15*, 1979.
(6) Johnson T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 3182.
(7) Fox, P. A.; Gray, S. D.; Bruck, M. A.; Wigley, D. *Inorg. Chem.* **1996**, *35*, 6027.
(8) Chen, S.; Vasquez, L.; Noll, B. C.; Rakowski DuBois, M. *Organometallics* **1997**, *16*, 1757.
(9) (a) Ganja, E. A.; Rauchfuss, T. B.; Stern, C. L. *Organometalllics* **1991**, *10*, 270. (b) Krautscheid, H.; Feng, Q.; Rauchfuss, T. B. *Organometallics* **1993**, *12*, 3273.
(10) Kvietok, F.; Allured, V.; Carperos, V.; Rakowski DuBois, M. *Organometallics* **1994**, *13*, 60.
(11) Chen, S.; Carperos, V.; Noll, B.; Swope, R. J.; Rakowski DuBois, M. *Organometallics* **1995**, *14*, 1221.

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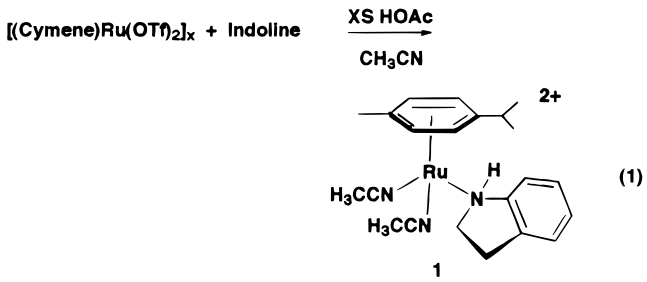
More recently, we found that the reaction of [(cymene)-$Ru(OTf)_2]_x$ with indoline proceeded to give a single yellow product in high yield in the presence of excess acetic acid. This product was isolated in 78% yield and found to have the formulation [(cymene)Ru(η^1-indoline)$(CH_3CN)_2$](OTf)$_2$, **1**, eq 1. Acetic acid has been used



previously to promote the reaction of (cymene)Ru dimers with arenes to form sandwich structures [(η^6-cymene)-Ru(η^6-arene)]$^{2+}$. The acid was proposed to protonate and labilize the anion in the reacting dimer.[12]

In the ^{1}H NMR spectrum of **1**, the hydrogens of the cymene ring occur as four doublets in the region of δ 5.4−6.0. These are shifted upfield relative to the cymene resonances of the η^6-indoline complex, which occur in the range δ 6.5−6.7. In addition to the aromatic resonances of the indoline ligand near δ 7.3, four complex multiplets are observed for the inequivalent hydrogens of the saturated heterocycle at δ 3.8, 3.6, 3.4, and 3.2. Two methyl resonances for the inequivalent acetonitrile ligands in the asymmetric complex are observed at δ 2.62 and 2.55 in CD_3CN. Although the nitrile signals overlap the septet of the C*H*Me$_2$ hydrogen on the cymene ligand, the decrease in intensity of the nitrile methyl resonances could still be observed over a period of hours as the ligands exchanged with the deuterated solvent. The pseudo-first-order rate constant for this process at room temperature was estimated to be 2×10^{-4} s^{-1}. The value is somewhat larger than the rate constant for the exchange of acetonitrile in (η^6-C_6H_6)Ru$(CH_3CN)_3]^{2+}$, which has been reported to be 3.9×10^{-5} s^{-1} at 298 K.[13] Evidence was not observed in the spectrum of **1** for displacement of the indoline ligand by the acetonitrile solvent over this time period to form [(cymene)Ru$(CH_3CN)_3]^{2+}$. After 20 h, only the resonances for [(cymene)Ru(indoline)$(CD_3CN)_2]^{2+}$ were observed in the spectrum.

A broadened resonance in the ^{1}H NMR spectrum of **1** at δ 6.90 was assigned to the N−H proton, and an N−H stretch in the infrared spectrum was observed at 3127 cm^{-1}. The presence of two triflate anions in the product was also confirmed by the elemental analysis data. The FAB$^+$ mass spectrum of **1** showed an envelope of peaks at m/e = 593, which corresponds to the parent cation plus one triflate anion.

Single crystals of **1** were obtained from a hexane/acetonitrile solution and were characterized by an X-ray diffraction study. The asymmetric unit consists of two dications and four triflate ions. The two ruthenium complexes are very similar, and a perspective drawing of one of these is shown in Figure 1. Selected bond distances and angles for one dication are given in Table 1. The Ru−N bond distance to the indoline ligand, 2.179(7) Å, is similar to that of the Ru−N bond in (cymene)Ru$(NH_2Ar)Cl_2$, which has been characterized recently.[14] The Ru−indoline bond is significantly longer

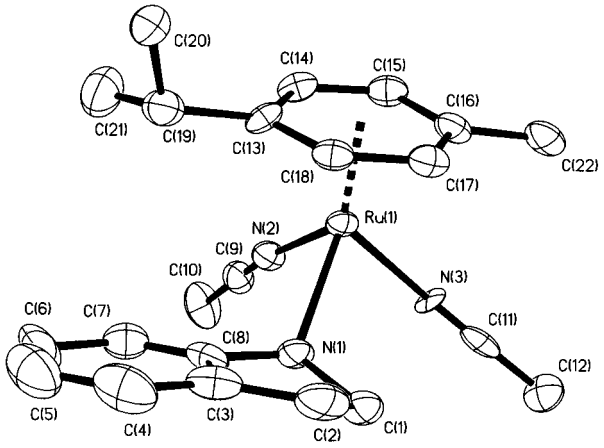


Figure 1. Perspective drawing and numbering scheme for [(Cymene)Ru(σ-indoline)$(CH_3CN)_2$](OTf)$_2$, **1**. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [(cymene)Ru(σ-indoline)$(CH_3CN)_2$]-(OTf)$_2$, 1

Ru(1)−N(1)	2.179 (7)	Ru(1)−N(2)	2.083 (7)
Ru(1)−N(3)	2.040 (6)	N(1)−C(1)	1.515 (11)
C(1)−C(2)	1.536 (14)	C(2)−C(3)	1.488 (15)
N(1)−C(8)	1.439 (12)	N(2)−C(9)	1.122 (11)
N(3)−C(11)	1.140 (11)	Ru(1)−C(14)	2.198 (8)
Ru(1)−C(15)	2.226 (8)	Ru(1)−C(16)	2.212 (8)
Ru(1)−C(17)	2.189 (8)	Ru(1)−C(18)	2.183 (8)
N(1)−Ru(1)-N(2)	83.7 (3)	N(1)−Ru(1)-N(3)	81.4 (3)
N(2)−Ru(1)-N(3)	84.2 (3)	C(1)−N(1)-Ru(1)	115.3 (5)
C(1)−N(1)-C(8)	103.6 (7)	C(8)−N(1)-Ru(1)	117.0 (5)
N(1)−C(1)-C(2)	105.4 (8)		

Table 2. Crystal Data for [(cymene)Ru(σ-indoline)$(CH_3CN)_2$](OTf)$_2$, 1

formula	$C_{24}H_{29}F_6N_3O_6RuS_2$
fw (amu)	734.69
cryst syst	triclinic
unit cell dimens	
a (Å)	12.109(3)
b (Å)	14.402(4)
c (Å)	18.261(5)
α (deg)	94.290(7)
β (deg)	107.996(6)
γ (deg)	90.122(6)
volume (Å^3)	3019(2)
space group	$P\bar{1}$
Z	4
density, calcd (g/cm^3)	1.616
λ(Mo Kα) (Å)	0.710 73
temp (K)	149(2)
scan type	0.3° ω scans
θ range	1.18−25.00
no. of indep reflns	10 605
no. of reflns obsd	8327
abs coeff	semiempirical from ψ-scans
R^a	0.1052
$R_w{}^b$	0.2397
GOF	1.034
largest peak in final diff map (e$^-$/Å^3)	5.794, −1.290

^{a} $R = R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

(12) (a) Rubinskaya, M. I.; Kudinov, A. R.; Kaganovich, V. S. *J. Organomet. Chem.* **1983**, *246*, 279. (b) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87.

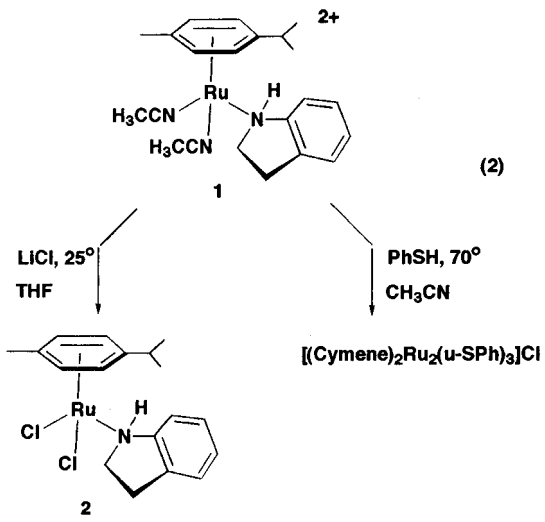
(13) Luginbuhl, W.; Zbinden, P.; Pittet, P. A.; Armbruster, T.; Burgi, H. B.; Merbach, A. E.; Ludi, A. *Inorg. Chem.* **1991**, *30*, 2350.

than the Ru−N bonds of the nitrile ligands (2.061(7) Å). The latter bonds each involve an sp hybrid on nitrogen with less spatial extension than the sp^3 hybrid of the indoline nitrogen. The five-membered ring of the indoline ligand is nonplanar, with C(1) displaced by 0.422 Å from the plane of the carbocyclic ring. The bond distances in the coordinated indoline ligand in **1** have been compared with those of [(cymene)Ru(η^6-indoline)]$^{2+}$ reported previously.[8] The only distance that shows a significant difference is the N−C(carbocycle), e.g., N−C(8), distance, which appears to be slightly lengthened in the Ru σ complex (1.447(12) Å, average of two cations), compared to that in the π-coordinated derivative (1.353(11) Å). Only one other structural study of a complex with a σ-coordinated indoline ligand has been reported, that of $(Cl)_2(PPh_3)Pd(\sigma$-*N*-indoline).[8] The N−C(carbocycle) distance in this structure, 1.444(5) Å, was very similar to that observed in this study for the σ-indoline ligand in **1**. The lengthening of a bond in a σ-coordinated heterocycle has been observed previously in benzothiophene derivatives and has been related to the activation of the ligand toward ring opening. For example, in the complex $Cp(CO)_2Re(\eta^1$-(*S*)-3-Me-benzothiophene), the S−C2 bond was lengthened by 0.2 Å relative to the distance in the free ligand.[15] However, in the present indoline complex, it is the heteroatom bond to the carbocycle which shows an increase in the bond distance.

Acidity of Coordinated Indoline Ligands. The coordination of a +2 metal ion to the indoline ligand should significantly increase its acidity. Complex **1** was titrated in aqueous solution with NaOH, and the titration curve was used to determine the pK_a value for **1** of 5.2. This value is similar to that reported for the indolinium ion[16] and suggests that coordination by the cymene−Ru fragment has a similar effect on the acidity of indoline as a protonation reaction. The pK_a for the σ-coordinated indoline ligand is much smaller than the value of 9.7 determined for the η^6-ligand in [(cymene)-Ru(η^6-indoline)](OTf)$_2$.[8] The value for the π-coordinated ligand is in turn significantly smaller than that expected for the free indoline molecule.[17] The deprotonated indolinyl complex [(cymene)Ru(η^1-indolinyl)$(CH_3CN)_2$]-(OTf) has also been generated by reactions with other bases in nonaqueous solvents, but the complex has not been characterized in detail because it undergoes a further reaction in solution which is described below.

Thermal Stability of 1 and Ligand-Exchange Reactions. When **1** was heated in dichloromethane, the formation of the η^6-indoline complex, [cymene)Ru-(η^6-indoline)](OTf)$_2$, was observed. Similar isomerizations from η^1-*N*- to η^6-coordination have been characterized for other nitrogen heterocycles, such as pyridine and quinoline, in ruthenium complexes of the formula [Cp′Ru$(CH_3CN)_2$(heterocycle)]$^+$, Cp′ = Cp, Cp*.[18] In the CpRu systems, the rate-limiting step was proposed to be the dissociation of the first acetonitrile ligand.

Ligand-exchange reactions with **1** have also been carried out, eq 2. For example, the reaction of **1** with



LiCl in THF solution at room temperature resulted in the formation of the neutral complex (cymene)Ru$(Cl)_2$-(indoline), which was isolated and characterized spectroscopically. Ligand substitution reactions were also attempted in acetonitrile solvent in an effort to preferentially exchange the indoline ligand with other neutral donors. For example, the addition of thiophenol to an acetonitrile solution of **1** was monitored by NMR spectroscopy at room temperature. No evidence was observed for the mononuclear derivative [cymeneRu-$(CH_3CN)_2(HSPh)]^{2+}$. After several days, approximately 70% of the starting reagent remained and a 30% yield of a new product was observed, which did not incorporate indoline. Complete conversion to this product was achieved in refluxing acetonitrile, and the complex was isolated and identified as the known derivative $[(cymene)_2Ru_2(\mu\text{-}SPh)_3]^+$.[19]

Hydrogen-Transfer Reactivity. Earlier studies by Fish and co-workers have shown that derivatives of the formula $[CpM(CH_3CN)_2(\eta^1$-N-quinoline)$]^{n+}$, where M = Ru or Rh, are intermediates in the hydrogenation of the unsaturatured nitrogen heterocycle ligand.[20] The reaction of **1** with hydrogen was also investigated. We wished to determine, for example, whether hydrogen addition to **1** might lead to hydrogenolysis of a C−N bond of the indoline ligand. Reaction of **1** with ca. 3 atm of H_2 proceeded at room temperature in chloroform or THF, but no discrete products could be identified in the very complex NMR spectrum of the resulting solutions, suggesting that decomposition had occurred.

When the same reaction was repeated in the presence of 1 equiv of NEt_3 in dichloromethane, the NMR spectrum was still quite complex but one product that could be identified was the dehydrogenation product, free indole. The product was formed over about a 24 h period with a final yield of ca. 60%. Although our initial observations were made with 1 atm of hydrogen present, the dehydrogenation of the indoline ligand in **1** proceeded in the same way under 1 atm of nitrogen or in an evacuated NMR tube. Many resonances were ob-

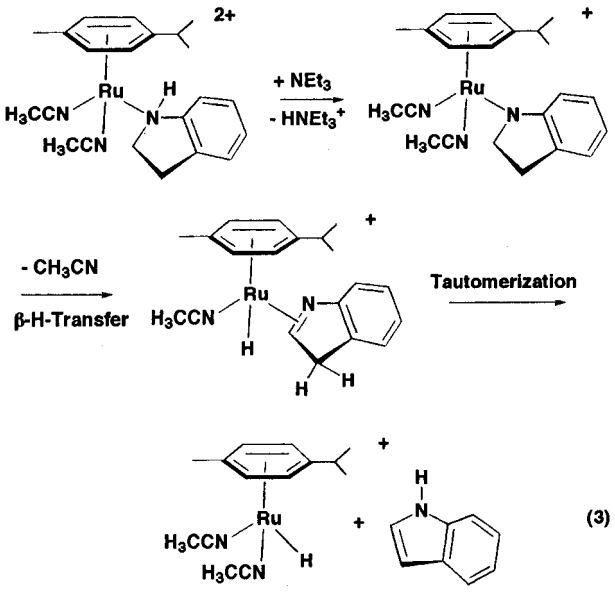
(14) Burrell, A. K.; Steedman, A. J. *Organometallics* **1997**, *16*, 1203.
(15) Choi, M.-G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328.
(16) Ho, T. C. *Catal. Rev.-Sci. Eng.* **1988**, *30*, 117.
(17) Although we have not found a report of the pK_a of indoline, it is expected to have a value similar to aniline, ca. 25.
(18) (a) Fish, R. H.; Kim, H.-S.; Fong, R. H. *Organometallics* **1991**, *10*, 770. (b) Fish, R. H.; Fong, R. H.; Tran, A.; Baralt, E. *Organometallics* **1991**, *10*, 1208.
(19) Mashima, K.; Mikami, A.; Nakamura, A. *Chem. Lett.* **1992**, 1795.
(20) Baralt, E.; Smith, S. J.; Hurwitz, J.; Horvath, I. T.; Fish, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5187.

served in the cymene and indoline regions of the NMR spectrum during the course of the reaction, and detailed assignments could not be made. However, resonances that were tentatively assigned to the deprotonated complex [(cymene)Ru(indolinyl)$(CH_3CN)_x$]OTf disappeared over a period of 1 day, while indole peaks increased in intensity. Evidence for free acetonitrile was also observed in the initial spectra.

New ruthenium hydride resonances were present in the NMR spectrum during the dehydrogenation reaction. One major product displayed a hydride singlet at δ −5.8, but this signal disappeared shortly after the indole formation was completed. The chemical shift of this resonance is similar to those observed for other mononuclear (cymene)Ru(II) hydride derivatives.[21] Several other resonances in the region from δ −8 to −15 were also observed throughout the reaction. The major hydride product that is ultimately formed after several days is characterized by two doublets at δ −13.28 and −14.84 (J = 3 Hz). These chemical shifts are consistent with inequivalent bridging hydrides in a dinuclear structure,[22]but the product has not yet been identified.

One equivalent of base, which deprotonated the indoline ligand, was required to initiate the reaction. In addition to triethylamine, we have used sodium methoxide or pyrrolidine to generate the indolinyl complex. One important effect of the deprotonation reaction is the labilization of a coordinated nitrile ligand in the resulting monocation, as mentioned above. The deprotonation of **1** in CD_3CN was also monitored by NMR spectroscopy and compared to the reaction in dichloromethane. In CD_3CN, the deprotonated form of **1** was also tentatively identified and exchange of the coordinated nitrile ligands in this derivative with the deuterated solvent was complete in less than 20 min. The ligand-exchange rate is much faster than that observed for **1**. This is consistent with the related observation that the monocation $[CpRu(AN)_3]^+$ shows a much higher rate of nitrile exchange than does the dication $[(cymene)Ru(AN)_3]^{2+}$.[13] Indole formation proceeded at a somewhat slower initial rate in CD_3CN (30% after 5 h) compared to the reaction in CD_2Cl_2 (47% after 3 h). Our observations are consistent with the proposal that dissociation of acetonitrile is an initial step in the dehydrogenation sequence.

Dissociation of a nitrile ligand from **1** is expected to permit a facile β-hydrogen elimination from the indolinyl ligand, as shown in eq 3. Dissociation and tautomerization of the resulting π-coordinated ligand would provide a pathway for the generation of indole. This mechanism for dehydrogenation includes features consistent with the reverse pathway proposed for the hydrogenation of related unsaturated nitrogen heterocycles catalyzed by $[Cp^*Rh(CH_3CN)_3]^{2+}$.[20] For example, in the hydrogenation of quinoline, an intermediate with an η^2-coordination of the C−N bond of the heterocycle has been proposed. Because of the complex mixture of products formed in this reaction, we were not able to correlate structures proposed for ruthenium−hydride intermediates to specific hydride resonances in the NMR spectrum.



A different type of dehydrogenation pathway for primary and secondary amines coordinated to Ru(II) or Ru(III) has been characterized in earlier work.[23,24] These reactions involved an oxidation of the metal center to Ru(IV) followed by intramolecular electron transfer and proton loss to give the oxidized ligand. In contrast, the driving force of aromatization in the dehydrogenation of indoline permits this reaction to proceed through nonoxidized ruthenium(II) hydride intermediates.

Transfer Hydrogenation of Alkenes. Indoline has been used previously as a hydrogen donor in the transfer hydrogenation of unsaturated molecules catalyzed by transition-metal complexes.[25] In particular, $Rh(PPh_3)_3Cl$ has been found to be an effective catalyst for hydrogen transfer from indoline to olefins.[26] However, no information on how indoline interacts with the metal complex in the hydrogen-transfer process was determined in earlier mechanistic studies of that system. The dehydrogenation pathway for the ruthenium indoline complex, which depends on the deprotonation of a σ-indoline ligand, may also be extended to hydrogenation of a substrate. When the deprotonation of **1** was carried out in dichloromethane in the presence of an alkene (cycloheptene or t-Bu-ethene), we observed a hydrogen-transfer reaction and the formation of the corresponding alkane (cycloheptane or t-Bu-ethane). This reaction was also carried out in a stepwise sequence and monitored by NMR spectroscopy. The hydride resonance at δ −5.8 was first generated by the addition of triethylamine to **1**, and then 1 equiv of cycloheptene was added to the solution. The hydride resonance disappeared, and the formation of cycloheptane was observed in the spectrum. Insertion of the alkene into the Ru−H bond of a mononuclear interme-

(21) See, for example: Trabesinger, G.; Albinati, A.; Feiken, N.; Kunz, R. W.; Pregosin, P. S.; Tschoerner, M. *J. Am. Chem. Soc.* **1997**, *119*, 6315.

(22) Jahncke, M.; Meister, G.; Rheinwald, G.; Stoeckli-Evans, H.; Suss-Fink, G. *Organometallics* **1997**, *16*, 1137.

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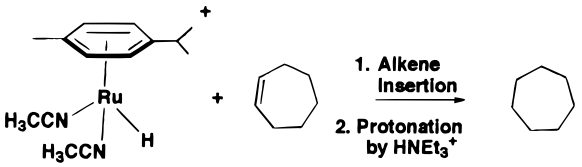
(24) (a) Keene, F. R.; Ridd, M. J.; Snow, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 7075. (b) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 1884. (c) Diamond, S. E.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 2661.

(25) Johnstone, R. A. W.; Wilby, A. H.; Entwhistle, I. D. *Chem. Rev.* **1985**, *85*, 129.

(26) (a) Nishiguchi, T.; Tachi, K.; Fukuzumi, K. *J. Org. Chem.* **1975**, *40*, 237. (b) Nishiguchi, T.; Tachi, K.; Fukuzumi, K. *J. Org. Chem.* **1975**, *40*, 240.

diate is proposed to be followed by protonation of the resulting Ru−alkyl complex by $HNEt_3^+$ to give the observed hydrogenated product, eq 4. In contrast, when



+ "CymeneRu$(CH_3CN)_2^{2+}$" (4)

the alkene was added to the solution later in the reaction, when the resonance at δ −5.8 was no longer present, no alkane formation was observed during a 24 h period.

Hydrogen transfer from indoline to cycloheptene in the presence of **1** does not appear to be catalytic. When a 10-fold excess of the two reagents was added to **1**, less than 1 equiv (ca. 0.6 equiv) of alkane was formed. We believe that regeneration of the ruthenium−indoline or −indolinyl complex is not efficiently achieved under these basic reaction conditions. As described above, the synthesis of **1** was best accomplished in the presence of excess acid. The competing reactions to form multiple ruthenium hydride derivatives can also be expected to limit the alkane yield.

Summary and Conclusions

The neutral indoline ligand can serve as a σ or π donor to (cymene)Ru(II). In earlier work, we established that the indoline ligand in [(cymene)Ru(η^6-indoline)]$^{2+}$ had a pK_a of 9.7 in aqueous solution. The deprotonated η^6-indolinyl complex was isolated and identified by ^{1}H NMR data. No evidence for a further dehydrogenation reaction to form [(cymene)Ru(η^6-indole)]$^{2+}$ or free indole was observed with this system. In this work, we have shown that the σ-*N*-bonded indoline derivative **1** is significantly more acidic than the π derivative (pK_a = 5.2), and it is also the less stable form, undergoing a rearrangement to the π complex under thermal conditions.

Deprotonation of **1** results in a significant destabilization of the complex; the resulting σ-indolinyl complex undergoes dehydrogenation of the indoline ligand to form free indole and ruthenium hydride derivatives. When the deprotonation is carried out in the presence of an alkene, a hydrogen transfer is observed to form the alkane. The reaction of the deprotonated form of **1** is proposed to proceed by nitrile dissociation, followed by a β-hydrogen elimination from the indolinyl ligand, which undergoes further tautomerization and dissociation to produce indole. Insertion of the alkene into a coordinatively unsaturated ruthenium hydride derivative and protonation of the ruthenium alkyl intermediate by triethylammonium ion are thought to complete the reaction sequence.

Experimental Section

Materials. [(Cymene)Ru$(Cl)_2]_2$ and [(cymene)Ru$(OTf)_2]_x$ were synthesized by published procedures.[9a,27] Indoline, cycloheptene, and 3,3-dimethylbutene were purchased from Aldrich and used without further purification. Dichloromethane and acetonitrile were distilled from CaH_2 prior to use. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone before use. Reactions were carried out under nitrogen using standard Schlenk line and glovebox techniques. Elemental analyses were carried out by Desert Analytical Laboratory, Tucson, AZ.

Synthesis of [(cymene)Ru(η^1-*N*-indoline)$(CH_3CN)_2$]$(OTf)_2$, 1. [(Cymene)Ru$(OTf)_2]_x$ was prepared from [(cymene)-$RuCl_2]_2$ (0.930 g, 1.52 mmol) and AgOTf (1.809 g, 7.041 mmol) in 2 mL of dichloromethane and 10 mL of acetonitrile. The solution was stirred for 18 h under N_2 and filtered over Celite. Indoline (0.40 mL) and glacial acetic acid (0.50 mL) were then added to the degassed filtrate. After 6 h, the brown oil was washed with 2 × 10 mL of diethyl ether to remove any excess indoline and then dissolved in 5 mL of tetrahydrofuran. After several minutes of stirring, a bright yellow solid precipitated out of solution. The yellow solid was rinsed with diethyl ether to remove any residual tetahydrofuran and dried in vacuo. Yield: 1.63 g, 73%. ^{1}H NMR (CD_3CN): δ 6.90 (br, 1 H, NH), 5.91, 5.76, 5.66, 5.36 (4 d, 1 H each, J = 6 Hz, cym), 7.45, 7.24 (2 m, 1 H each, H7, H4), 7.31 (m, 2 H, H5, H6), 3.79, 3.65 (2 m, 1H each, NCH_2), 3.40, 3.22 (2 m, 1 H each, NCH_2CH_2), 2.56 (sept, 1 H, C*H*Me_2), 1.88 (s, 3 H, cym-CH_3), 1.23, 1.17 (2d, 6 H, J = 7 Hz, CH*Me*$_2$), 2.62, 2.53 (2 s, 3 H each, CH_3CN). ^{13}C (CD_2Cl_2): δ 162.35 (OTf), 150.32, 133.85 (quart indoline C), 128.71, 127.85, 126.32, 118.04 (indoline methine C's), 122.33, 119.79 ($NCCH_3$), 109.54, 103.19 (quart cym C's), 87.06, 86.45, 86.01, 84.37 (cym methine C's), 57.48 (NCH_2), 31.44 (NCH_2CH_2), 30.30 (*C*HMe)$_2$), 22.56, 21.77 (CH*Me*$_2$), 18.08 (PhCH_3), 5.00, 4.77 (CH_3CN). MS (FAB$^+$): *m*/*z* 593 (P cation + OTf). IR (KBr, cm^{-1}): 3127 (m, br, ν_{N-H}), 2300 (m, ν_{RCN}). Analysis was obtained on a sample isolated from deuterated acetonitrile. Anal. Calcd for $C_{24}H_{23}D_6F_6N_3O_6S_2Ru$: C, 38.92; H, 3.92. Found: C, 38.61; H, 3.74.

X-ray Diffraction Study of 1. Crystals were examined under Exxon Paratone-N oil. The selected crystal was mounted in the 146 K cryostream of a Siemens SMART CCD diffractometer equipped with a LT-2A low-temperature apparatus. Unit cell constants were determined on indexing three roughy orthogonal sets of 20 frames and refined using 8192 reflections with $I > 10\sigma(I)$ chosen from the data collection. Nearly a full sphere of data was collected at 30 s per 0.3° (ω) scan to achieve adequate redundancy for a semiempirical absorption correction. All data were corrected for Lorentz and polarization effects. The space group was determined from cell metrics and intensity data. Le Pages's utility MISSYM was used as implemented in Spek's PLATON[28] to verify the absence of higher symmetry.

Structure solution via direct methods revealed the entire non-hydrogen structure of the cation and most atoms of the anions. Subsequent cycles of least-squares refinement followed by calculation of difference Fourier maps identified the remaining atoms. The asymmetric unit consists of two cations and four triflate anions. Disorder is evident in the anions. Interatomic distances for all triflate anions were set to average values collected from the Cambridge Structural Database. One anion was modeled at two positions with refined site occupancies of 0.626(9) and 0.374(9). Much of the residual electron density is clustered about the remaining triflates, although these peaks are not sufficiently organized to warrant modeling. The largest peaks in the final difference map are near the Ru positions and are likely to be artifacts from absorption. Hydrogen atoms were generated at ideal positions that were allowed to ride on the position of the parent atom.

Thermal Stability of Complex 1. When complex **1** (0.730 g, 0.994 mmols) was refluxed in dichloromethane for 66 h,

(27) Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth*. **1982**, *21*, 74.

(28) Spek, A. L. *Acta Crystallogr*. **1990**, *A46*, C34.

[(cymene)Ru(η^6-indoline)](OTf)$_2$[6] was formed in 83% yield. The product was isolated and identified by ^{1}H NMR spectroscopy.

Synthesis of (Cymene)Ru(η^1-indoline)Cl$_2$, 2. Complex **1** (0.199 g, 0.271 mmol) was dissolved in 15 mL of tetrahydrofuran, and LiCl (0.0620 g, 1.46 mmol) was then added to the solution. The solution immediately turned orange and was stirred under N_2 for 1 h. After the solvent was removed in vacuo, the orange solid was redissolved in dichloromethane and filtered through Celite. The filtrate was evaporated to give the product as an orange solid. The complex was recrystallized by slow vapor diffusion of ether into a dichloromethane solution of the compound. Yield: 0.101 g (88%). ^{1}H NMR ($CDCl_3$): δ 7.83, 7.32 (d, 1H, J = 7 Hz, C4,7), 7.18 (m, 2H C5,6), 5.24 (2d, 1H each, J = 7 Hz, cymene), 4.98, 4.48 (d, 1H each, J = 6 Hz, cymene), 5.06 (br, 1H, N*H*), 4.18, 3.54, 3.28, 3.10 (m, 1H each, NCH_2CH_2), 2.90 (sept, 1H, C*H*Me$_2$), 1.98 (s, 3H, cym-C*H*$_3$), 1.28, 1.19 (2d, 3H each, J = 7 Hz, CH-(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 151.76, 132.30, 126.16, 117.86 (quart C's), 127.61, 125.05, 104.81, 96.65 (indoline arene C's), 84.18, 82.61, 79.77, 75.52 (cymene C's), 54.89 (NCH_2), 30.59 (NCH_2CH_2), 29.24 (*C*HMe$_2$), 22.86 20.91 (CH*Me*$_2$), 17.87 (cymene-Me). MS (ES): m/z 426 (P^+). Anal. Calcd for $C_{18}H_{23}Cl_2NRu$: C, 50.83; H, 5.45. Found: C, 50.66; H, 5.73.

Reaction of 1 with Thiophenol. Complex **1** (0.104 g, 0.142 mmols) was dissolved in 35 mL of acetonitrile, and thiophenol (0.0162 g, 0.147 mmols) was then added. After refluxing for 1 day, the solvent was removed in vacuo and the orange oil was washed with 2 × 20 mL of diethyl ether. The orange solid was then recrystallized by layering dichloromethane and diethyl ether overnight to give the known complex [(cymene)$_2$Ru$_2$(μ-SPh)$_3$](OTf),[19] which was identified by ^{1}H NMR and mass spectroscopy.

Reaction of 1 with Hydrogen. Tetrahydrofuran (10 mL) was added to **1** (0.063 g, 0.086 mmol) in a 25 mL Schlenk tube. The tube was cooled to −196 °C, charged with 0.79 atm of H_2, and warmed to room temperature. After 23 h of stirring, the color of the solution changed from yellow to dark orange. The solution was dried in vacuo. The ^{1}H NMR spectrum (acetone-d_6) of the crude brown oil was very complex with the presence of four or five cymene-containing products. These were not identified.

Reaction of 1 with Hydrogen and Triethylamine. The same reaction as above was repeated with **1** (0.087 g, 0.12 mmol) and triethylamine (0.0116 g, 0.115 mmol). After 19.5 h of stirring, the solvent was removed in vacuo, leaving a dark brown oil. The ^{1}H NMR spectrum (acetone-d_6) showed free indole and an unidentified ruthenium hydride derivative with hydride resonances at −13.13 and −14.67 ppm. Attempts to isolate the pure hydride product by column chromatography on alumina were unsuccessful.

Reaction of 1 with Triethylamine. In an NMR Schlenk tube, triethylamine (0.0044 g, 0.043 mmol) was added to **1** (0.033 g, 0.044 mmol) in dichloromethane-d^2 (1 mL). Nitromethane (mL, 0.028 mmol) was added as an internal standard. The solution was cooled to −196 °C and put under vacuum for 30 min and the reaction tube was sealed. The reaction was monitored at room temperature by ^{1}H NMR spectroscopy. Within 15 min, resonances were observed for indole, and these resonances continued to increase for about 26 h. Many new resonances were observed in the cymene and indoline regions, and signals for [(cymene)Ru(η^1-indolinyl)($CH_3CN)_x$]$^+$ could not be assigned in detail. However, new triplets observed at δ 3.52 and 4.56 were tentatively assigned to the indolinyl methylene hydrogens. These signals decreased in intensity as indole was formed. New ruthenium hydride resonances were observed at δ −5.83 (s), −7.86 (s), −9.03 (s), and −13.33 and −14.83 (2 d, J = 3 Hz). After 1 day, the hydride resonance at δ −5.83 had disappeared and only those between δ −7.9 and −15 remained.

The same reactants were monitored in CD_3CN solution. A spectrum recorded after 20 min indicated that the nitrile ligands had completely exchanged with solvent. Resonances tentatively assigned to [(cymene)Ru(η^1-indolinyl)($CD_3CN)_x$]$^+$ were observed: δ 7.46, 7.25, 6.95, 6.81 (4 m, arene H's of indolinyl), 6.03, 5.64 (2 d, cymene), 3.43, 2.92 (2 t, NCH_2CH_2), 1.69 (cymene-Me), 2.74 (sept, $CHMe_2$), 1.2 (d, $CHMe_2$ obscured by NEt_3). Other unidentified resonances were also observed in the spectrum, including multiplets at δ 7.02, 6.45, 5.48, and 4.08, and resonances for free indoline may also be present in low intensity. Resonances for indole were observed to grow over a period of 24 h to give a yield of ca. 60%, while resonances attributed to the indolinyl complex decreased. No new cymene-containing ruthenium products were observed at the end of the reaction, and no ruthenium hydride signals were detected. In two separate experiments in CD_3CN, sodium methoxide supported on alumina and pyrrolidine were substituted for triethylamine. Similar formation of indole was observed, but the nature of the ruthenium products varied with the identity of the base.

Reaction of 1 with Triethylamine in the Presence of an Alkene. To a solution of **1** (0.029 g, 0.036 mmol) in dichloromethane-d_2, 3,3-dimethylbutene (0.0034 g, 0.040 mmol) and triethylamine (0.0046 g, 0.046 mmol) were added. The tube was cooled to −196 °C, put under vacuum for 30 min, and sealed. After the solution was thawed to room temperature, the reaction was monitored by ^{1}H NMR spectroscopy. There was an immediate color change from bright yellow to dark red-orange. Resonances were observed for free indole, 2,2-dimethylbutane, and unidentified ruthenium hydride derivatives with hydride resonances between −5.88 and −10 ppm. After 15 h, 20% of the alkene had converted to the alkane. After 7 days, ca. 25% of the alkene was converted. Reactions with excess alkene gave higher alkane yields (see below). The same reaction was repeated with cycloheptene, resulting in formation of cycloheptane; however, the results were not quantified.

Reaction of Cycloheptene with a Catalytic Amount of 1. In a NMR Schlenk tube, dichloromethane-d_2 was added to **1** (0.410 g, 0.0559 mmol). Under N_2 flow, indoline (0.0670 g, 0.562 mmol), cycloheptene (0.0536 g, 0.557 mmol), and triethylamine (0.0058 g, 0.058 mmol) were added to the Schlenk tube. The tube was cooled to −196 °C, put under vacuum, and sealed. The reaction was monitored at room temperature by ^{1}H NMR spectroscopy. There was an immediate color change to dark brown with formation of free indole. The alkane yield after 5 min was approximately 3%, and after 18 h it was 6%. The yield did not increase significantly after the first day. After 7 days, ca. 7% of the alkene (or 70% based on Ru complex) had converted to the alkane.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond distances, bond angles, anisotropic displacement parameters, and hydrogen coordinates for **1** (16 pages). Ordering information is given on any current masthead page.

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