Synthesis and Characterization of Mononuclear Indoline Complexes. Studies of σ and π Bonding Modes

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

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

Received August 27, 1996[⊗]

The dication [(cymene)Ru(η^6-1-Me-indoline)]$^{2+}$, **1a**, has been synthesized either by the hydrogenation of [(cymene)Ru(1-Me-indole)]$^{2+}$ or by the reaction of [(cymene)Ru(OTf)$_2$]$_x$ with 1-Me-indoline and has been isolated as the triflate or tetraphenylborate salt. Other [(arene)-Ru(indoline)]$^{2+}$ derivatives have also been prepared by similar methods. [**1a**](BPh$_4$)$_2$ crystallized in the space group $P\bar{1}$ with a = 10.9308(3) Å, b = 14.1874(4) Å, c = 18.4139(5) Å, α = 81.800(1)°, β = 75.17°, γ = 89.50°, V = 2731.19(13) Å^3, and Z = 2. The sandwich structure is slightly bent with an angle between the ruthenium ion and the center of each η^6-ligand of 174.3°. Complexes with η^1-N-coordinated indoline ligands have also been characterized. The reaction of indoline with Pd(Cl)$_2$(PPh$_3$)(CH$_3$CN) in refluxing dichloromethane resulted in the formation of (Cl)$_2$(PPh$_3$)Pd(η^1-indoline), **2**, which was isolated and characterized by spectroscopic methods. Complex **2** crystallized in the space group $P\bar{1}$ with a = 9.703(2) Å, b = 10.148(2) Å, c = 13.920(2) Å, α = 99.650(10)°, β = 99.230(10)°, γ = 94.560(10)°, V = 1325.8(3) Å^3, and Z = 2. The indoline ligand is tilted with respect to the metal−ligand plane, and the five-membered ring of the ligand assumes an envelope-type conformation.

Introduction

The hydrodenitrogenation (HDN) of indole over heterogeneous metal sulfide catalysts is a complex multistep process. Kinetic and mechanistic studies have established that hydrogenation of the five-membered ring to produce indoline occurs prior to the key reaction of carbon−nitrogen bond cleavage.[1−4] Mechanistic features of the opening of the saturated five-membered ring in indoline under HDN conditions have not been established. The base-induced Hofmann elimination reaction is a well-characterized pathway for the cleavage of carbon−nitrogen bonds in organic molecules, and this reaction,[5] or a related nucleophilic substitution on a ring with a quarternized nitrogen center, could occur during the HDN process.[2,6] However, model studies suggest that interaction with the metal surface is likely to play an additional role in promoting the ring-opening of nitrogen heterocycles.[7−10]

Further work is necessary in order to understand the ways in which an interaction with a transition metal center might activate the indoline molecule. Few coordination complexes containing the indoline ligand have been reported previously, and studies of the reactivities of such ligands are quite limited. Semmelhack has reported that an η^6-1-Me-indoline complex of Cr(CO)$_3$ was activated toward nucleophilic addition by bulky carbanions, and further iodine oxidation of the addition products released the 4-substituted 1-methylindoline.[11] The reaction of the triosmium cluster Os$_3$-(CO)$_{10}$(NCCH$_3$)$_2$ with indoline at 60 °C resulted in activation of the C(7)−H[12 a] bonds to give isomeric products with a N,C(7)-bridged indoline ligand.[12b] Thermolysis of these products ultimately led to dehydrogenation of the indoline ring and formation of a previously characterized[12c] η^2-indole complex of the osmium cluster. RhCl(PPh$_3$)$_3$ was found to catalyze the transfer hydrogenation of olefins when indoline was the hydrogen donor, and dehydrogenation of a Rh−indoline intermediate was proposed to be the rate-determining step.[13] However, Rh−indoline complexes were not observed in this system.

Transition metal centers have also been used to promote the synthesis of indolines. For example, [Cp*Rh-(CH$_3$CN)$_3$]$^{2+}$ was found to catalyze the hydrogenation of 1-Me-indole to 1-Me-indoline under mild homogeneous conditions.[14] An η^2-indole−Rh intermediate has been proposed but not detected in this conversion. The

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) Massoth, F. E.; Balusami, K.; Shabtai, J. *J. Catal.* **1990**, *122*, 256.

(2) Olive, J. L.; Biyoko, S.; Moulinas, C.; Geneste, P. *Appl. Catal.* **1985**, *19*, 165.

(3) Odebunmi, E. O.; Ollis, D. F. *J. Catal.* **1983**, *80*, 76.

(4) Aboul-Gheit, A. K.; Abdou, I. K. *J. Inst. Pet. (London)* **1973**, *59*, 188.

(5) Although the Hofmann elimination has been proposed for six-membered heterocycles, this mechanism is not favored for the five-membered ring of an indolinium derivative because the required coplanar arrangement of the C(2)−N and the C(3)−H bonds is not energetically favorable: Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, *734*, 736.

(6) (a) Ho, T. C. *Catal. Rev.−Sci. Eng.* **1988**, *30*, 117. (b) Laine, R. M. *Catal. Rev.−Sci. Eng.* **1983**, *25*, 459.

(7) Gray, S. D.; Weller, K. J.; Bruck, M. A.; Briggs, P. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10678.

(8) Adams, R. D.; Chen, G. *Organometallics* **1992**, *11*, 3510; **1993**, *12*, 2070.

(9) Cenac, N.; Zablocka, M.; Igau, A.; Commenges, G.; Majoral, J. P.; Skowronska, A. *Organometallics* **1996**, *15*, 1208.

(10) Laine, R. M. *New J. Chem.* **1987**, *11*, 543.

(11) Semmelhack, M. F.; Wulff, W.; Garcia, J. L. *J. Organomet. Chem.* **1982**, *240*, C5.

(12) (a) The following conventional numbering scheme is used:

(b) Kabir, S. E.; Kolwaite, D. S.; Rosenberg, E.; Scott, L. G.; McPhillips, R.; Duque, R.; Day, M.; Hardcastle, K. I. *Organometallics* **1996**, *15*, 1979. (c) Hardcastle, K. I.; Minassian, H.; Arce, A. J.; DeSanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1989**, *368*, 119.

(13) Nishiguchi, T.; Tachi, K.; Fukuzumi, K. *J. Org. Chem.* **1975**, *40*, 240.

S0276-7333(96)00744-3 CCC: $14.00

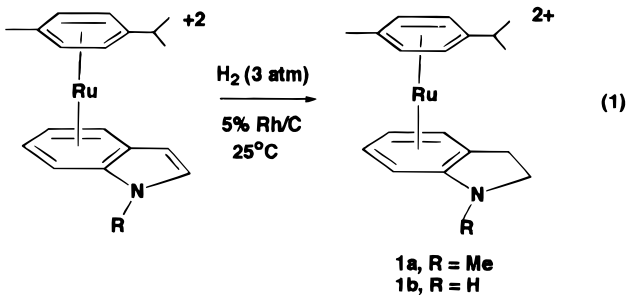
stepwise addition of electrophiles and nucleophiles to the η^1-*N*-indolyl complexes CpRe(NO)(PPh_3)(indolyl) resulted in the diastereoselective synthesis of indoline derivatives, and further ligand substitution of the complex led to the formation of free substituted indolines.[15] Applications of transition metal complexes in promoting intramolecular cyclization reactions in the construction of indolines have also been reported.[16−18]

In this paper, we report the synthesis and characterization of several new mononuclear indoline complexes of d^6 and d^8 metals, which include examples of the η^6- and η^1-coordination modes of this ligand. The acid−base properties of the coordinated ligands have been determined, and examples of the two bonding modes have been characterized for the first time by X-ray diffraction studies. The stabilities of the new complexes should permit an investigation of the reactivity of the coordinated indoline ligands, and preliminary reactivity studies are included here.

Results and Discussion

Synthesis of η^6-Indoline Complexes of Ruthenium. Two distinct approaches for the synthesis of η^6-indoline complexes of Ru(II) have been explored. The first involves the hydrogenation of η^6-indole derivatives, and the second is based on the reactions of free indoline with appropriate ruthenium reagents. In some cases, products that were not available by one method were successfully synthesized by the alternate route.

Hydrogenation of η^6-Indole Complexes of Ruthenium. The η^6-indole and 1-Me-indole complexes of the formula [(cymene)Ru(indole)]$(OTf)_2$ have been synthesized and characterized previously.[19] When a MeOH solution of the *N*−Me-indole complex was reacted under hydrogen pressure (3 atm) at room temperature in the presence of a Rh/C catalyst, hydrogenation of the five-membered ring of the indole ligand occurred to form [(cymene)Ru(η^6-1-Me-indoline)]$^{2+}$, **1a**, eq 1. The reaction was complete after a 24 h period. No hydrogenation was observed in the absence of the heterogeneous catalyst. The unsubstituted indole complex, [(cymene)-Ru(η^6-indole)]$(OTf)_2$, reacted under similar conditions in dichloromethane solution to give the triflate salt of the analogous indoline complex [(cymene)Ru(η^6-indoline)]$^{2+}$, **1b**. Both cations **1a** and **1b** were isolated as the water soluble triflate salts; anion metathesis reactions with sodium tetraphenylborate were also carried out to form the BPh_4 salts. Characterization data for the new indoline complexes are discussed below.



(1)

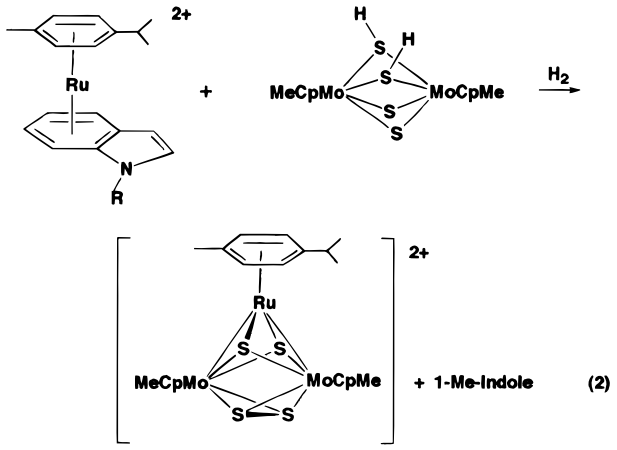
The hydrogenation of free 1-Me-indole was attempted under the same reaction conditions (3 atm of H_2, room temperature, 24 h, 1 equiv of Rh/C catalyst), and the product formation was monitored by NMR spectroscopy. Under these conditions, only 10% conversion of the substrate to 1-Me-indoline was achieved. The data suggest that the η^6-coordination of the indole molecule to the ruthenium center results in an enhancement in the rate of hydrogenation of the heterocyclic ring. The η^6-coordination of naphthalene to CpRu(II) has also been shown to activate the uncoordinated ring toward hydrogenation in the presence of a Pd/C catalyst to form CpRu(η^6-1,2,3,4-tetrahydronaphthalene)]$^+$.[20]

A homogeneous hydrogenation catalyst for the reduction of the indole complexes has been explored briefly. Previous work in our laboratory has shown that the Mo(IV) hydrosulfido complex [MeCpMo(μ-S)(μ-SH)]$_2$ can serve as a homogeneous catalyst for the reduction of various unsaturated compounds.[21] For example, the N=N bonds of azo compounds and the C=N bonds in imines and isocyanates were hydrogenated under mild conditions in the presence of the molybdenum dimer. Hydrogen transfer from the hydrosulfido ligands has been proposed to be involved in these reactions, and the transformations were suggested to be potential models for the reductive reactions catalyzed by molybdenum sulfide surfaces. The sulfido ligands in the molybdenum dimer also reacted with olefins to form dithiolate adducts, which in some activated systems could be further reduced with hydrogen.[22]

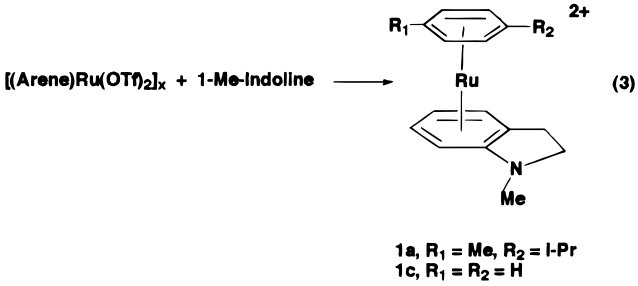
In order to determine whether this molybdenum sulfide derivative was effective in promoting the hydrogenation of the C(2)=C(3) bond in the η^6-coordinated indole ligand, [(cymene)Ru(1-Me-indole)]$(OTf)_2$ was reacted with approximately 3 atm of H_2 in the presence of ca. 1 equiv of [MeCpMo(μ-S)(μ-SH)]$_2$. No reaction was observed at room temperature, but at 50 °C, the formation of free 1-Me-indole was observed along with a mixture of other products. Chromatography of the crude product mixture resulted in the isolation of a new trinuclear product, which was formulated as [$(MeCp)_2$-Mo_2(μ-S_2)(μ-S)$_2$Ru(cymene)]$(OTf)_2$ on the basis of spectroscopic data, eq 2. The structure indicated for the product cluster is suggested by analogy to that determined for the related iron derivative [$(MeCp)_2Mo_2$(μ-S_2)(μ-S)$_2$FeCp]I, which was synthesized from a reaction of [MeCpMo(μ-S)(μ-SH)]$_2$ with $CpFe(CO)_2I$.[23] Although further studies of the Ru−Mo cluster will be carried out, these are beyond the scope of this paper. The results from this experiment did not provide any evidence for the hydrogenation of the η^6-indole complex by the homogeneous molybdenum sulfide complex.

Reactions of Indolines with Ruthenium Reagents. The 1-Me-indoline complex described above,

(14) Baralt, E.; Smith, S. J.; Hurwitz, J.; Horvath, I. T.; Fish, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5187.
(15) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 3182.
(16) Koo, K.; Hillhouse, G. L. *Organometallics* **1996**, *15*, 2669.
(17) Rahm, A.; Wulff, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 1807.
(18) Tidwell, J. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11797.
(19) Chen, S.; Carperos, V.; Noll, B.; Swope, R. J.; Rakowski DuBois, M. *Organometallics* **1995**, *14*, 1221.
(20) Suravajjala, S.; Polam, J. R.; Porter, L. C. *Organometallics* **1994**, *13*, 37.
(21) Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; Rakowski DuBois, M. *Organometallics* **1986**, *5*, 951.
(22) For example, the olefin acrylonitrile forms an adduct with the sulfido ligands in (MeCpMo(μ-S))$_2$(S_2CH_2) and the adduct reacts with H_2 in chloroform solution to form free propionitrile: McKenna, M. Ph.D. Thesis, University of Colorado, Boulder, CO, 1980.
(23) Cowans, B. A.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1987**, *6*, 995.



1a, could also be prepared by the direct reaction of $[(\text{cymene})\text{Ru}(\text{OTf})_2]_x$ with 1-Me-indoline in a dichloromethane solution, eq 3. Reaction of the same ligand



with $[(\text{benzene})\text{Ru}(\text{OTf})_2]_x$ at a higher temperature gave the analogous benzene complex [(benzene)Ru(1-Me-indoline)]$^{2+}$, **1c**. The triflate salts precipitated from the reaction solution and were separated from the side products by extraction with acetonitrile. Both complexes were characterized by ^{1}H and ^{13}C NMR and by mass spectroscopy. Reactions of these products with $NaBPh_4$ gave the tetraphenylborate salts, which were isolated as air-stable solids.

In contrast, when the reaction of $[(\text{cymene})\text{Ru}(\text{OTf})_2]_x$ with unsubstituted indoline was monitored by NMR spectroscopy, no evidence was observed for the formation of the η^6-indoline complex, **1b**, described above. The indoline ligand appears to be more prone to undergo σ interactions with metal ions than is 1-Me-indoline. This trend was observed in our studies of the Pd indoline derivatives discussed below. Competing σ-interactions may be occurring in the reaction of indoline with $[(\text{cymene})\text{Ru}(\text{OTf})_2]_x$, although discrete products were not successfully characterized.

Characterization of η^6-Indoline Complexes. The η^6-indoline complexes were characterized by fast atom bombardment (FAB) mass spectra, representative elemental analyses, and ^{1}H and ^{13}C NMR data. The FAB$^+$ spectra of the triflate salts showed patterns at m/e values expected for the parent cations, while the FAB$^-$ spectra corresponded to the parent ion of the complex plus a triflate anion. In the η^6-indoline complexes, the hydrogens of the five-membered ring are diastereotopic. For example, for the triflate salt of **1c**, ^{1}H NMR resonances for the two hydrogens at the β-position of the five-membered ring are shifted downfield relative to the free ligand, appearing as overlapping multiplets at ~3.0 ppm. The diastereotopic α-protons of the heterocyclic ring are also shifted downfield from those of free 1-methylindoline. One α-proton resonates at 3.91 ppm (ddd) with a geminal coupling constant of $J = 11$ Hz and vicinal coupling constants of 4 and 10 Hz. The other α-proton resonates at 3.62 ppm (dt) with the same geminal coupling constant and a vicinal J value of 10 Hz. A second vicinal coupling is not observed because the angle between these two protons is near 90° in the nonplanar five-membered ring (see below). Complete ^{1}H NMR data for complexes **1a**, **1b**, and **1c** are give in Table 1.

In earlier work, we have shown that the η^6-coordination of indole ligands to the (Cymene)Ru^{+2} fragment significantly decreased the basicity of the aromatic system.[19] For example, the aqueous pK_a of [(cymene)-Ru(η^6-Indole)](OTf)$_2$ was determined by a pH titration to be 7.71, while the pK_a of the free indole molecule is reported to be 16.97.[24] It is likely that the η^6-coordination of the indoline ligand also decreases the basicity of the nitrogen atom in the adjacent heterocycle, although the magnitude of this effect for an adjacent saturated ring has not been determined previously. The triflate salt of the indoline complex **1b** was soluble and stable in aqueous solution, and addition of excess NaOH formed the conjugate base, which was characterized spectroscopically (see Experimental Section). Titration of the η^6-indolinyl complex with HCl showed a single inflection point with an equivalence point at pH = 5.7. From the titration data, the pK_a of the coordinated neutral indoline molecule was determined to be 9.70. Although we have not found a literature value for the pK_a of indoline, the uncoordinated heterocycle is much less acidic than the η^6-ligand; the pK_a of free indoline is expected to be similar to the values observed for anilines, in which the amino group is also adjacent to an aromatic ring.

X-ray Diffraction Study of [(Cymene)Ru(1-Me-indoline)][BPh$_4$]$_2$. We have not found previous reports of structural data for an η^6-indoline complex. Single crystals of the BPh_4 salt of **1a** were grown by diffusion of ether into an acetonitrile solution of the compound. The complex crystallized in the space group $P\bar{1}$ with two molecules per unit cell. The structure confirms that the dication is a sandwich structure with two nearly parallel η^6-arene ligands. A disorder in the diffraction data revealed the presence of two isomers in a 54:46 ratio. The two isomers have different orientations of the indoline ligand relative to the metal cymene fragment, as a result of η^6-coordination to opposite faces of the indoline ring. In solution, the two isomers would be enantiomers, assuming free rotation of the η^6 ligands. A perspective drawing of the major isomer is shown in Figure 1, and selected bond distances and angles for this isomer, which are similar to those of the minor isomer, are given in Table 2. The five-membered ring of the indoline ligand is puckered so that the α carbon and N−Me group are both tilted away from the metal. Their displacements from the plane of the arene ring are −0.024 and −0.235 Å, respectively. The nitrogen and β-carbon atoms are displaced 0.135 and 0.269 Å out of the arene plane.

The structure of the cation **1a** can be compared to that of the closely related indole complex [(cymene)Ru(η^6-1-Me-indole)](OTf)$_2$, which we have reported previously,[19] as well as to other [(cymene)Ru(arene)]$^{2+}$ derivatives.

(24) Yagil, G. *Tetrahedron* **1967**, *23*, 2855.

Table 1. ^{1}H NMR Data for [Ru(arene)(indoline)]$^{2+}$ Complexes (Triflate Salts)[a]

	arene ring	indoline five-membered ring	other
[(Cym)Ru(1-Me-indoline)]$^{2+}$, **1a**	6.57−6.72 (m, cym), 6.49 (m, H7), 6.35−6.40 (m, H5,6), 6.12 (m, H4)	3.92 (dt, NCH), 3.69 (dt, NCH), 3.04 (t, NCH_2CH_2), 2.99 (s, NMe)	2.83 (sept, C**H**Me_2), 2.43 (s, PhMe), 1.27 (d, CH**Me**$_2$)
[(C_6H_6)Ru(1-Me-indoline)]$^{2+}$, **1c**	6.69 (s, bz), 6.42 (d, J = 6 Hz, H7), 6.35−6.42 (m, H5,6), 6.18 (d, J = 6 Hz, H4)	3.91 (ddd, J = 4, 10, 11 Hz, NCH), 3.62 (dt, J = 10, 11, Hz NCH), 2.91−3.14 (m, NCH_2CH_2), 2.91 (s, NMe)	
[(Cym)Ru(indoline)]$^{2+}$, **1b**	6.55 (m, 5H, cym + H7), 6.33 (m, 1H), 6.27 (m, 2H)	6.91 (br s, NH), 3.92 (m, NCH), 3.76 (m, NCH), 3.04 (m, NCH_2CH_2)	2.85 (sept, C**H**Me_2), 2.37 (s, PhMe), 1.25, 1.24 (2 d, CH**Me**$_2$)

[a] Chemical shifts are reported in ppm in CD_3CN. Assignments were made on the basis of COSY spectra recorded in CD_3CN, unless otherwise specified. J values are reported in Hz.

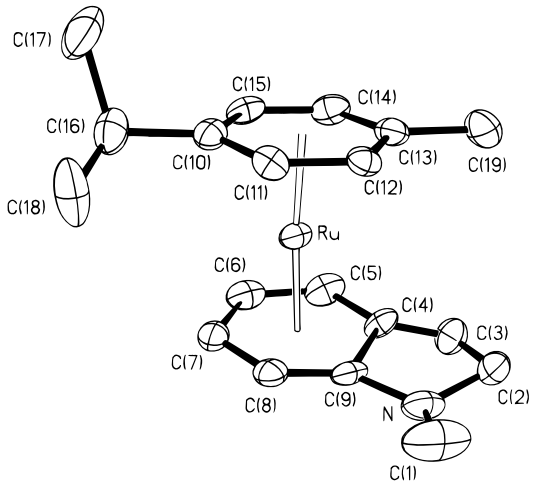


Figure 1. Perspective drawing and numbering scheme for the major isomer of [(cymene)Ru(1-Me-indoline)]$^{2+}$, **1a**. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [(cymene)Ru(1-Me-indoline)](BPh_4)$_2$

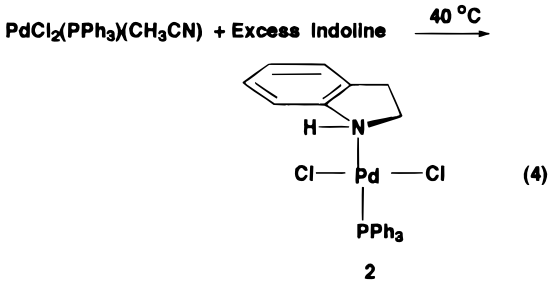
Ru−C(5)	2.269 (10)	Ru−C(11)	2.223 (2)
Ru−C(6)	2.204 (7)	Ru−C(12)	2.241 (2)
Ru−C(7)	2.200 (8)	Ru−C(14)	2.211 (2)
Ru−C(8)	2.222 (9)	Ru−C(15)	2.210 (2)
N−C(1)	1.467 (10)	N−C(9)	1.353 (11)
N−C(2)	1.472 (9)	C(5)−C(6)	1.394 (7)
C(2)−C(3)	1.529 (6)	C(6)−C(7)	1.421 (7)
C(3)−C(4)	1.233 (9)	C(8)−C(9)	1.26 (2)
C(4)−C(9)	1.58 (3)		
C(1)−N−C(9)	123.5 (14)	N−C(2)−C(3)	131.5 (5)
C(2)−N−C(9)	110.3 (12)	N−C(8)−C(9)	76.1 (6)
C(1)−N−C(2)	120.1 (7)	C(3)−C(4)−C(5)	128.7 (8)
C(2)−C(3)−C(4)	105.6 (5)	C(3)−C(4)−C(9)	112.5 (8)
C(5)−C(4)−C(9)	117.1 (7)		

In the indoline complex **1a**, the angle between ruthenium and the center of each ring is 174.3°, smaller than the 178.9° angle in the indole derivative. In addition, the distances between the ruthenium ion and the center of each η^6-ring in **1a** are greater than those in the indole complex. For example, the distances between the metal ion and the center of the cymene ring are 1.706 Å for the indole derivative and 1.730 Å for **1a**. Both distances are longer than the average distance in other (cymene)-Ru(arene) derivatives (1.678 Å).[25] The fused ring ligands show longer bonding distances to the metal ion than the cymene ring. The distance between the ruthenium ion and the η^6-ring of indoline is 1.773 Å, compared to 1.761 Å for the analogous indole distance.

(25) McCormick, F. B.; Cox, D. D.; Gleason, W. B. *Organometallics* **1993**, *12*, 610 and references within.

Attempted Reactions of η^6-Indoline Complexes with Lewis Acids. In discussions of possible mechanisms that apply to the HDN process, it has been suggested that quarternization of a nitrogen center in cyclic compounds may precede C−N bond cleavage by nucleophiles.[6] The reactions of Lewis acids with the η^6-indoline complexes were explored in attempts to prepare ligands with quarternized nitrogens and to study their reactivity. However, no adduct formation was observed between the electrophiles and the η^6-indoline ligands. For example, efforts to isolate a complex with a protonated or alkylated 1-Me-indoline ligand from the reaction of **1a** with triflic acid or methyl triflate, respectively, in dichloromethane were unsuccessful. In additional studies, 1 equiv of HCl was added to **1a** or **1b** in water and each of the resulting solutions was titrated with NaOH. The titration curves were characteristic of those of strong acids with equivalence points at pH = 7. In contrast, the uncoordinated indolinium cation is reported to have a pK_a of about 5.[6a] Attempts have also been made to activate the η^6-indoline ligands in **1a** or **1b** by N(σ)-coordination of a second metal ion. However, no reactions were observed when each of the complexes was refluxed with $Cl_2Pd(PPh_3)$(nitrile) in dichloromethane for several hours. These results provide further evidence for the decreased basicity of the nitrogen atom as a result of the η^6-coordination of the indoline ligand, as discussed above.

Synthesis of an η^1-Indoline Complex. During the course of this project, in order to obtain comparative data, we have also explored the σ-coordinating ability of the free indoline ligand. Reaction of $Cl_2Pd(PPh_3)$-($NCCH_3$) with indoline (ca. 3 equiv) in refluxing dichloromethane resulted in the formation of $Cl_2Pd(PPh_3)(\eta^1$-indoline), **2**, eq 4, which has been isolated and characterized by spectroscopic methods and by an X-ray diffraction study. The infrared spectrum of **2** shows a



(4)

2

N−H stretching absorption at 3448 cm^{-1}. In the ^{1}H NMR spectrum, the resonances for the indoline six-membered ring protons (7.1−7.7 ppm) are shifted down-

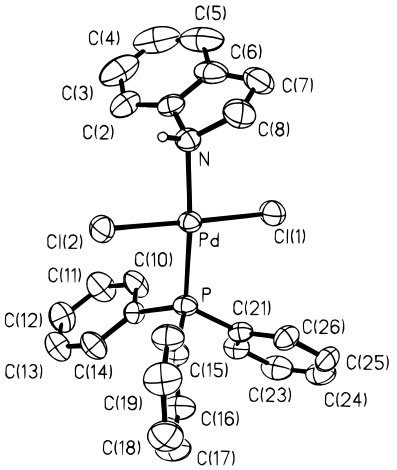


Figure 2. Perspective drawing and numbering scheme for $Pd(PPh_3)(Cl)_2$(indoline), **2**. Thermal ellipsoids are shown at the 50% probability level.

field relative to those of the free ligand.[26] The diastereotopic protons of the saturated five-membered ring resonate as four separate multiplets in the region from 3.0 to 5.8 ppm. The ^{31}P NMR spectrum displays two singlets at 30.7 and 23.9 ppm in a 5:1 ratio, which are tentatively assigned to the *trans*- and *cis*-isomers of **2**, respectively. The ^{13}C NMR, mass spectral, and microanalytical data for **2** are reported in the Experimental Section.

Attempts were also made to prepare the analogous N-coordinated 1-Me-indoline complex. When the reaction of $Cl_2Pd(PPh_3)(NCCH_3)$ with 1-Me-indoline in refluxing dichloromethane was monitored by NMR spectroscopy, no evidence was observed for coordination of the heterocycle. An alternate approach to the synthesis of this product is by the reaction of methylating agents with the anionic indolinyl derivative described below. However, such reactions with MeOTf or MeI gave a mixture of products, which were not successfully separated or characterized.

X-ray Diffraction Study of $Cl_2Pd(PPh_3)(\eta^1$-indoline), 2. Single crystals of **2** were grown by slow diffusion of diethyl ether into a dichloromethane solution. The complex crystallized in the space group $P\bar{1}$ with two molecules per unit cell. A perspective drawing of the complex is shown in Figure 2, and selected bond distances and angles are given in Table 3. The structure shows a square planar arrangement of two *trans*-chloride ligands, one triphenylphosphine, and a σ,N-bound indoline ligand. The Pd−N distance of 2.161(2) Å is somewhat longer than the average range of Pd(II)−N bonds which spans from 1.95 to 2.10 Å.[27]

The hydrogen atom on the nitrogen was located by a difference map and placed at the ideal position to give a pseudotetrahedral geometry about the nitrogen. The C(1)−N−C(8) angle of 104.7(3)° is more acute than the Pd−N−C(1) and Pd−N−C(8) angles of 114.2(2)° and 118.3(2)°, respectively. The tilt of the indoline ligand with respect to the metal−ligand plane is reflected by a dihedral angle of 64.8° between the Pd−N and the C(1)−C(2) bonds. The five-membered ring of the ligand assumes an envelope-type conformation. The dihedral angle between the N−C(1) and C(7)−C(8) bonds is 23.8°, and C(8) is displaced from the plane of the arene ring by −0.38 Å, C(7) by −0.03 Å, and N by +0.016 Å.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Pd(PPh_3)Cl_2$(indoline)

Pd−N	2.161 (2)	Pd−P	2.2525 (6)
Pd−Cl(1)	2.2835 (7)	Pd−Cl(2)	2.3118 (7)
N−C(1)	1.444 (5)	N−C(8)	1.513 (4)
C(1)−C(6)	1.399 (4)	C(1)−C(2)	1.339 (5)
C(2)−C(3)	1.405 (6)	C(3)−C(4)	1.361 (7)
C(4)−C(5)	1.350 (7)	C(5)−C(6)	1.396 (6)
C(6)−C(7)	1.472 (5)	C(7)−C(8)	1.517 (5)
N−Pd−P	174.81 (5)	N−Pd−Cl(1)	91.87 (6)
P−Pd−Cl(1)	93.17 (3)	N−Pd−Cl(2)	87.34 (6)
P−Pd−Cl(2)	87.66 (3)	Cl(1)−Pd−Cl(2)	177.99 (3)
C(1)−N−C(8)	104.7 (3)	C(1)−N−Pd	114.2 (2)
C(6)−C(7)−C(8)	103.5 (3)	C(8)−N−Pd	118.3 (2)
N−C(8)−C(7)	105.4 (4)		

Synthesis of $[Cl_2Pd(PPh_3)(\eta^1$-indolinyl)]Li, 3. The reaction of 1 equiv of indolinyl lithium with $Cl_2Pd(PPh_3)(NCCH_3)$ in THF at 0 °C resulted in the formation of a red-brown precipitate, which was isolated and identified as $[Cl_2Pd(PPh_3)(\eta^1$-indolinyl)]Li, **3**. The ^1H NMR spectrum showed resonances for two apparent isomers of **3** in a 2:1 ratio, which were tentatively assigned to the *trans*- and *cis*-isomers, respectively. By comparison with other indole and indoline complexes,[15,19] the resonance shifted farthest downfield is assigned to H7.[12a] In **3**, this resonance was shifted farther downfield to the range 8.5−8.7 ppm, and the other ring protons were shifted slightly upfield (6.4−7.2 ppm) relative to the neutral indoline complex **2**. Complete NMR data for the product are given in the Experimental Section. The same product was observed by NMR spectroscopy when **2** was reacted with BuLi for short reaction times. The reactions of **2** and **3** with areneophilic metal fragments are being explored as an additional route for accessing binuclear complexes containing the indoline ligand.

Summary and Conclusions. The initial objective of this work was to prepare relatively stable indoline complexes which would allow us to study further reactions of the coordinated ligands. The η^6-indoline derivatives $[(cymene)Ru(1\text{-Me-indoline})]^{2+}$, **1a**, $[(cymene)Ru(indoline)]^{2+}$, **1b**, and $[(benzene)Ru(1\text{-Me-indoline})]^{2+}$, **1c**, have been synthesized and characterized. In addition, an η^1-N(σ) derivative of indoline, $Cl_2Pd(PPh_3)(\eta^1$-indoline), **2**, has been synthesized and characterized by X-ray diffraction. The η^1−N-coordinating ability of the η^6-indoline ligand has been compared to that of the free ligand. For example, attempts to react $PdCl_2(PPh_3)$(nitrile) with the indoline nitrogen in $[(cymene)Ru(\eta^6$-indoline)]$^{2+}$, **1b**, were unsuccessful, and this is attributed to a decrease in the basicity of the η^6-bonded ligand. The decreased basicity has been confirmed by pH titrations of **1b** in aqueous solution.

Experimental Section

Materials. The complexes $[(p\text{-cymene})RuCl_2]_2$, $[(p\text{-cymene})Ru(OTf)_2]_x$, and $[(benzene)RuCl_2]_2$ were prepared according to the literature.[28,29] $PdCl_2(NCCH_3)_2$ and $PdCl_2(NCC_6H_5)_2$ were

(26) Downfield NMR shifts of σ-coordinated nitrogen heterocycles have been observed previously: e.g., Fish, R. H.; Baralt, E.; Kim, H. S. *Organometallics* **1991**, *10*, 1965.

(27) Barnard, C. F. J.; Russell, M. J. H. In *Comp. Coord. Chem.*, Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 5, p 1115.

(28) (a) Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74. (b) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063.

obtained from Strem, and $PdCl_2$(nitrile)(PPh_3) was prepared as described previously.[19] Indoles, indoline, 5% Rh on C, and other reagents were obtained from Aldrich and used as received. Indolyl lithium reagents were prepared by treatment of indoles with *n*-BuLi in Et_2O solution. 1-Methylindoline was prepared by the literature procedure.[30] Dichloromethane and acetonitrile were distilled from CaH_2 prior to use. Tetrahydrofuran, toluene, and diethyl ether were distilled from sodium/benzophenone. Alcohols were degassed and dried over molecular sieves. Reactions were carried out under nitrogen using standard Schlenk line and vacuum techniques. Column chromatography was carried out with Fischer Scientific neutral alumina absorption (80−200 mesh). Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ, and National Chemical Consulting, Inc., Tenafly, N.J.

[(η^6-*p*-cymene)Ru(η^6-1-methylindoline)]$^{2+}$, 1a. [Ru(cymene)$(OTf)_2]_x$ was prepared from [Ru(cymene)$Cl_2]_2$ (0.312 g, 0.510 mmol) and AgOTf (0.60 g, 2.3 mmol) in 40 mL of CH_2Cl_2. The solution was filtered, and 1-methylindoline (0.25 mL) was added to the filtrate. A brown oily solid precipitated out of solution. After the solution was stirred for 20 min, the volume was reduced to 20 mL, causing additional brown solid formation. The orange supernatant was decanted. The remaining solid was extracted with CH_3CN to form an orange solution, which was filtered and evaporated to yield **1a**$(OTf)_2$ as an orange solid. Yield: 0.680 g (27.8%). ^{1}H NMR: See Table 1. ^{13}C NMR (CD_3CN): δ 138.9 (OTf), 123.8, 119.7, 111.3, 99.6 (aromatic quat C), 93.1, 92.9, 90.6, 90.5 (cym CH), 91.5, 84.6 (indl C5,6), 90.1 (indl C7), 69.6 (indl C4), 53.9 (N**C**H_2), 33.5 (NCH_2**C**H_2), 32.1 (**C**HCH_3), 26.0 (N**C**H_3), 22.5, 22.5 (CH**C**H_3), 19.5 (Ph**C**H_3). MS (FAB$^+$): *m*/*e* 518 (M − OTf), 368 (369 calcd for M − 2OTf), 384 (M − cym − OTf). MS (FAB$^-$): *m*/*e* 666 (667 calcd for M + e), 815 (816 calcd for M + OTf).

The tetraphenylborate salt was prepared by adding 2 eq of $NaBPh_4$ to an ethanol solution of **1a**. The product precipitated out of solution as a fine off-white powder. After the mixture was stirred for 30 min, the solid was collected by filtration in air and washed with ethanol. ^{1}H NMR for **1a**$[BPh_4]_2$ (CD_3CN): δ 7.28 (m, 16 H, *o*-H of BPh_4), 6.88 (t, 16 H, *m*-H of BPh_4), 6.83 (t, 8H, *p*-H of BPh_4), 6.33−6.38 (m, 3H, cym), 6.28 (d, 1H, cym), 6.12 (m, 1H, H7), 6.03 (m, 2H, H6,5), 5.70 (m, 1H, H4), 3.82 (m, 1H, NCH), 3.57 (dt, 1H, NCH, J = 9, 12 Hz), 2.82 (s, 3H, NCH_3), 2.80 (t, 2H, NCH_2C**H**$_2$), 2.70 (sept, 1H, C**H**CH_3), 2.25 (s, 3H, PhCH_3), 1.20 (d, 6H, CHC**H**$_3$). Anal. Calcd for $C_{67}H_{65}NB_2Ru$: C, 79.92; H, 6.51; N, 1.39. Found: C, 79.57; H, 6.78; N, 1.35.

Reaction of [(cymene)Ru(1-Me-indole)](OTf)$_2$ with H_2 in the Presence of Rh/C. Methanol (15 mL) was added to 0.32 g of 5% Rh/C in a 25 mL Schlenk tube. The tube was cooled to −196 °C, charged with 0.79 atm of H_2, and warmed to 22 °C (H_2 pressure = 3.0 atm). After the mixture was stirred for 1 h to prereduce the catalyst, [(cymene)Ru(1-Me-indole)](OTf)$_2$ (0.106 g, 0.159 mmol) was added. The Schlenk tube was again charged with 3.0 atm of H_2, and the mixture was stirred at 22 °C. After 1 day, the solution was filtered and the filtrate was evaporated to give a yellow solid. This was redissolved in 1 mL of methanol, and 30 mL of Et_2O was added, forming an orange-yellow oily precipitate. The pale yellow supernatant was decanted, and the orange-yellow solid was washed with Et_2O. The ^{1}H NMR (CD_3CN) spectrum displayed resonances for the major product, [(cymene)Ru(η^6-1-methylindoline)][OTf]$_2$ (**1a**$(OTf)_2$) . There were no peaks present for the starting complex.

For comparison, 1-methylindole was hydrogenated in the presence of Rh/C under the same conditions as above (indole: Rh = 1:1, H_2 pressure = 3 atm). After 1 day, the reaction mixture was filtered and the filtrate was evaporated to give a green-yellow liquid. The liquid was dissolved in 1 mL of CD_3CN and was filtered into an NMR tube. The ^{1}H NMR displayed resonances for a mixture of 90% 1-methylindole and 10% 1-methylindoline.

Synthesis of [(Cymene)Ru(η^6-indoline)]$^{2+}$, 1b. Dichloromethane (20 mL) was added to 0.220 g of 5% Rh/C in a 70 mL Schlenk tube. The suspension was cooled to −196 °C, charged with 57 cmHg of H_2, and slowly warmed to room temperature. After a 2 h prereduction period of the catalyst, [(cymene)Ru(indole)](OTf)$_2$ (0.225 g, 0.346 mmol) was added. The mixture was cooled to −196 °C, charged with 57 mmHg of H_2, and slowly warmed to room temperature. After the mixture was stirred for 3 days, the solution was filtered over Celite and rinsed with dichloromethane and the solvent was evaporated from the filtrate to give a yellow sticky solid. The solid was then washed with tetrahydrofuran followed by diethyl ether to remove the yellow impurity, leaving a beige crystalline solid which was dried in vacuo. Yield: 0.097 g, 43%. See Table 1 for NMR data.

The tetraphenylborate salt of **1b** was prepared by the addition of $NaBPh_4$ (0.186 g, ca. 1 equiv) to an EtOH solution of **1b**$(OTf)_2$. A yellow precipitate formed immediately, and the solution was pale yellow. After 2.5 h, the supernatant was decanted and the solid was washed with EtOH, followed by Et_2O. ^{1}H NMR for **1b**$[BPh_4]_2$ (CD_3CN): δ 7.30 (br, 16H, *o*-H of BPh_4), 7.01 (t, 16H, *m*-H of BPh_4), 6.85 (t, 8H, *p*-H of BPh_4), 6.20 (m, 4H, cym), 6.10 (d, 1H, J = 6 Hz, H7), 5.93 (m, 2H, H5,6), 5.82 (d, 1H, J = 6 Hz, H4), 3.78 (m, 1H, NCH), 3.60 (m, 1H, NCH), 2.83 (m, 2H, NCH_2C**H**$_2$), 2.71 (m, 1H, C**H**CH_3), 2.19 (s, 3H, PhCH_3), 1.19 (d, 6H, CHC**H**$_3$). MS (FAB$^+$): *m*/*e* 354 (M − H − 2BPh_4).

Titration of [(cymene)Ru(η^6-indoline)](OTf)$_2$, 1b(OTf)$_2$. Complex **1b**$(OTf)_2$ proved to be too weak an acid to obtain good titration data with NaOH in aqueous solution. The product isolated after an attempted titration was formulated as [(cymene)Ru(η^6-indolinyl)]OTf and was characterized by ^{1}H NMR data. ^{1}H NMR (CD_3CN): δ 6.22, 6.17 (2 m, 2H each, cymene), 6.10, 5.99, 5.90, 5.27 (4 m 1H each, aromatic indolinyl), 2.86 (m, 1H, NCH), 2.77 (sept, 1H, C*H*Me_2), 2.68 (m, 2H, NCH_2C*H*$_2$), 2.24 (s, 3H, Me), 1.88 (m 1H, NCH), 1.24, 1.22 (2d, 6H, CH*Me*$_2$).

In a second titration attempt, 1 equiv of NaOH was added to an aqueous solution of **1b** (5.961×10^{-5} mol) and the resulting product was titrated with HCl (0.0240 M). The equivalence point was oberved after the addition of 2.63 mL of HCl at a pH of 5.70. The pK_a of the η^6-indoline ligand was determined to be 9.70.

Reaction of [Ru(cymene)(OTf)$_2]_x$ with Indoline. Indoline (0.75 mL) was dissolved in 15 mL of Et_2O, and 2 mL of this solution (0.89 mmol) was added to an ether solution of [(cymene)Ru$(OTf)_2]_x$, (0.324 mmol). After 50 min, the solution was greenish-orange with a purple-green precipitate. The supernatant was decanted from the green solid, which was washed with Et_2O. The ^{1}H NMR spectrum (CD_3CN) of the solid showed that a mixture of species was present. However, no resonances for **1b** were observed.

Synthesis of [(η^6-benzene)Ru(η^6-1-methylindoline)]$^{2+}$, 1c. [Ru(benzene)$Cl_2]_2$ (0.334 g, 0.667 mmols) and silver triflate (0.75 g, 2.9 mmol) were taken up in 40 mL of CH_2Cl_2, and the solution was refluxed at 75 °C to form [(benzene)Ru$(OTf)_2]_x$. After 3 h, 1-methylindoline (0.20 mL) was directly added to the mixture. The solution initially turned orange, then a brown precipitate formed. After the mixture was stirred for 20 min at 75 °C, the solution volume was reduced *in vacuo* to 20 mL, during which more brown solid formed. The supernatant was decanted, and the solid was extracted with 40 mL of CH_3CN to form an orange solution. The solution was filtered, and the filtrate was evaporated to give an orange-red solid. Yield: 0.729 g (89.5%). (See Table 1 for ^{1}H NMR data.) ^{13}C NMR (CD_3CN): δ 138.3 (OTf), 118.2, 100.5 (aromatic quat C), 93.1 (bz), 91.1, 84.8 (indl C5 and C6), 89.6 (indl C7), 69.5 (indl C4), 53.7 (N**C**H_2), 33.4 (NCH_2**C**H_2), 26.2 (N**C**H_3). Mass Spec (FAB$^-$): *m*/*e* 760 (M + OTf).

(29) Ganja, E. A.; Rauchfuss, T. B.; Stern, C. L. *Organometallics* **1991**, *10*, 270.
(30) Gribble, G. W.; Lord, P. D.; Skotnicki, J.; Dietz, S. E.; Eaton, J. T.; Johnson, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7812.

The tetraphenylborate salt of complex **1c** was prepared by adding $NaBPh_4$ (2 equiv) to an ethanol solution of **1c**$(OTf)_2$. The product precipitated out of solution as a flocculent tan solid. After 30 min, the solid was collected by filtration in air and washed with EtOH. ^{1}H NMR for **1c**$[BPh_4]_2$ (CD_3CN): δ 7.28 (m, 16H, *o*-H of BPh_4), 6.97 (t, 16 H, *m*-H of BPh_4), 6.84 (t, 8H, *p*-H of BPh_4), 6.39 (s, 6H, bz), 6.16 (d, 1H, H7), 6.04 (dt, 1H, H6), 5.99 (dt, 1H, H5), 5.72 (d, 1H, H4), 3.80 (m, 1H, NCH), 3.47 (dt, 1H, NCH), 2.83 (t, 2H, NCH_2CH_2), 2.80 (s, 3H, NCH_3).

Reaction of [(cymene)Ru(1-Me-indole)](OTf)$_2$ with H$_2$ in the Presence of [(MeCp)MoS(SH)]$_2$. A solution of **1a**$(OTf)_2$ (0.0826 g, 0.124 mmol) and $[(MeCp)MoS(SH)]_2$ (0.0464 g, 0.0966 mmol) was prepared in 10 mL of a $CH_3CN/CHCl_3$ solution in a 25 mL Schlenk tube. The purple solution was reacted with 3 atm of H_2 at 52 °C. After 1 day, solvent was evaporated to give a brown-crimson solid. This was redissolved in 15 mL of MeOH and filtered. (No solids were left behind during the filtration). Solvent was evaporated from the filtrate, leaving a purple-brown sticky solid. The ^{1}H NMR spectrum showed resonances for a mixture of compounds, including the starting Ru reagent, free 1-methylindole, and two cymene-containing products.

The crude product was chromatographed on neutral alumina with 1:1 CH_3CN/EtOH, which eluted a brown-yellow band. This fraction was collected and evaporated to give a brown solid, formulated as $\{[(MeCp)MoS_2]_2Ru(cym)\}[OTf]_2$. ^{1}H NMR ($CD_3CN$): δ 6.38 (m, 4H, cym), 5.96 (t, 4H, Cp), 5.86 (t, 4H, Cp), 3.20 (sept, 1H, C**H**CH_3), 2.66 (s, 3H, $PhCH_3$), 2.19 (m, 6H, $CpCH_3$), 1.41 (d, 6H, CHC**H**$_3$). MS (FAB$^+$): *m*/*e* 715 (714 calcd for M − 2OTf), 683 (682 calcd for M − 2OTf − S), 579 (580 calcd for M − 2OTf − cym). Anal. Calcd for $C_{24}H_{28}F_6O_6S_6Mo_2Ru$: C, 28.86; H, 2.89. Found: C, 28.49; H, 2.79.

The same product was prepared by the reaction of $[MeCpMo(S)(SH)]_2$ with $[(cymene)Ru(OTf)_2]_x$ in dichloromethane at room temperature.

X-ray Structural Determination of [Ru(Cym)(1-Me-indoline)][BPh$_4$]$_2$. Complex 1a$[BPh_4]_2$ was crystallized by slow diffusion of Et_2O into a CH_3CN solution of the compound. Two data collections were performed on two independent crystals. Both experiments utilized the −120 °C N_2 stream of a Siemens LT-2A low-temperature apparatus attached to a Siemens SMART CCD area detector. Data were corrected for Lorentz and polarization effects. Structure solution was by Patterson function. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were placed at calculated positions, which were allowed to ride on the position of the parent atom. Isotropic hydrogen thermal parameters were set to 1.2 times the equivalent isotropic *U* of the parent. Details on the crystal data, experimental conditions, and solution and refinement are given in Table 4.

Refinement in the centrosymmetric space group $P\bar{1}$ revealed disorder in the indoline ligand, manifested as a rotation of the ligand through approximately 60°. Site occupancy for the two forms is 0.452(4):0.548. Because this value is so close to 50%, refinement was also performed in noncentrosymmetric *P*1. Here, it appears that the structure is a racemic twin, twin ratio 0.53(3). Refinement as a twin removes any disorder. In an attempt to determine which model was more appropriate, values for C−C bond lengths were collated from the phenyl rings of the anions. These results were ambiguous.

A second cystal was carefully examined under crossed polarizing filters on a Leica MZ-8 stereomicroscope at 80× magnification. It was cut to eliminate any volumes which did not cleanly and sharply extinguish plane-polarized light. Indexing returned cell constants equivalent to those found for the first crystal. While it was expected that the final outcome would be unchanged, a hemisphere of data was collected.

Solution and refinement were again performed in both space groups. The ratios for disordered or twin components were unchanged, but space group $P\bar{1}$ showed more consistent values for phenyl C−C bonds. The uncertainty was approximately half as large as for *P*1, and the range of values was also much smaller. Based on this evidence, the centrosymmetric space group $P\bar{1}$ was selected.

Table 4. Crystal Data for Indoline Complexes 1a and 2

	1a	2
formula	$C_{69}H_{68}B_2N_2Ru$	$C_{28}H_{29}Cl_2NO_{1/2}PPd$
fw	1047.94	595.79
cryst syst	triclinic	triclinic
unit cell dimensions		
a (Å)	10.9308(3)	9.703(2)
b (Å)	14.1874(4)	10.148(2)
c (Å)	18.4139(5)	13.920(2)
α (deg)	81.8000(10)	99.650(10)
β (deg)	75.1749(2)	99.230(10)
γ (deg)	89.4977(2)	99.560(10)
volume, Å^3	2731.19(13)	1325.8(3)
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
density, calcd (g/cm^3)	1.274	1.493
λ(Mo Kα) (Å)	0.710 73	0.710 73
temp (K)	151(2)	293(2)
scan type	0.3° *ω* scans	*ω* scans
θ range (deg)	1.16−28.23	1.51−25.50
no. indep reflns	12730	4213
no. reflns obs	11411	3678
abs corr	semi-empirical from *ψ*-scans	semi-empirical from *ψ*- scans
R^a	0.0307	0.0245
Rw^b	0.0788	0.0625
GOF^c	1.036	1.015
largest peak in final diff map e$^-$/Å^3	0.830 and −0.475	0.328 and −0.352

^{a} $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]]^{1/2}$. ^{c} Goodness-of-fit $= [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$, where *M* is the niumber of reflections and *N* is the number of parameters refined.

Attempted Reaction of 1a and 1b with Cl$_2$Pd(nitrile)(PPh$_3$). Complex **1b** (0.052 g, 0.080 mmol) and $Cl_2Pd(NCC_6H_5)(PPh_3)$ (0.051 g, 0.094 mmol) were combined in 20 mL of CH_2Cl_2 to form an orange-yellow solution with some orange solid (undissolved palladium complex). The solution was stirred under nitrogen for 5 h at room temperature. The ^{1}H NMR spectrum (CD_3CN) of an aliquot showed only resonances for the starting materials. The solution was then refluxed under N_2 for 24 h, but still no reaction was observed spectroscopically. A similar procedure was followed for the attempted reaction of **1a** with $Cl_2Pd(NCCH_3)(PPh_3)$. No reaction was observed by NMR spectroscopy.

Synthesis of Cl$_2$Pd(PPh$_3$)(η^1-indoline), 2. Indoline (0.080 mL, 0.71 mmol) was added to a solution of $Cl_2Pd(PPh_3)(NCCH_3)$ (0.107 g, 0.222 mmol) in 30 mL of CH_2Cl_2. The dark yellow solution, which contained some undissolved yellow solid, was refluxed for 3 h. Solvent was evaporated to give a yellow solid, which was partly soluble in Et_2O and insoluble in EtOH. The product was recrystallized from Et_2O/EtOH or from Et_2O/CH_2Cl_2. Yield: 0.123 g (98.9%). ^{1}H NMR chemical shift assignments were based on COSY NMR data. ^{1}H NMR (CD_2Cl_2): δ 7.62−7.73 (m, 7H, H7 and H6 of PPh_3), 7.48−7.51 (m, 3H, PPh_3), 7.36−7.45 (m, H4 and 6H of PPh_3), 7.25 (m, 1H, H5), 7.16 (m, 1H, H6), 6.61 (br s, NH), 5.77 (m, NCH), 4.14 (m, NCH), 3.55 (m, NCH_2CH), 3.02 (m, NCH_2CH). ^{13}C NMR (CD_2Cl_2): δ 147.0, 135.1, 130.0, 129.2, 127.7, 118.7 (indoline quat C and CH), 135.2 (d, J = 10.4 Hz, *m*-C of PPh_3), 128.5 (d, J = 10.9 Hz, *o*-C of PPh_3), 131.5 (s, *p*-C of PPh_3), 125.8 (d, J = 26.9 Hz, *i*-C of PPh_3), 50.3 (NCH_2), 31.7 (NCH_2CH_2). ^{31}P NMR ($CDCl_3$): δ 30.7 (s, PPh_3 of *trans*−isomer, 75%), 23.9 (s, PPh_3 of *cis*-isomer, 25%). MS (FAB$^-$): *m*/*e* 628 (627 calcd for M + 2Cl), 592 (M + Cl), 578 (579 calcd for $Pd_2(PPh_3)Cl_3$). IR (KBr, cm^{-1}): 3448 (m, br, ν_{N-H}). Anal. Calcd for $C_{26}H_{24}NPCl_2Pd\cdot{}^1/_4CH_2Cl_2$: C, 54.60; H, 4.24; N, 2.40. Found: C, 54.22; H, 4.53; N, 2.23. (A trace amount of dichloromethane was observed in the ^{1}H NMR spectrum of this sample).

X-ray Diffraction Study of $Cl_2Pd(PPh_3)(\eta^1$-indoline)·$^1/_2Et_2O$. Complex **2** was crystallized by slow diffusion of Et_2O into a CH_2Cl_2 solution of the compound. X-ray structural studies were performed on a Siemens P4 diffractometer using automated search and refinement routines in XSCANS. Solution of the Patterson function revealed the Pd position, and a difference Fourier map showed most of the non-hydrogen structure. Subsequent cycles of least-squares refinement followed by difference Fourier synthesis located the remaining atoms.

A disordered region of electron density was found near an inversion center. Analysis by SQUEEZE[31] located a solvent-accessible volume of 173.2 Å^3 and residual electron density of 42.4 e$^-$. This area was modeled as disordered diethyl ether, which has predicted values of 121.6 Å^3 and 42 e$^-$. The most reasonable model relates two half-molecules of diethyl ether through the inversion center. A linear C−O−C bond is created in this model; this is likely the result of the short contact distance between the half-oxygens across the inversion center. Because SQUEEZE handled this solvent region so well, no *ad hoc* model for the solvent was included in the final refinement. Values for molecular weight and formula have been adjusted to include one molecule of diethyl ether per unit cell or half a molecule of diethyl ether per molecule of **2**. Details on the crystal data, experimental conditions, and solution and refinement are provided in Table 4.

$[Cl_2Pd(PPh_3)(\eta^1$-indolinyl)]Li, 3. Indoline (0.070 mL, 0.62 mmol) was dissolved in 30 mL of THF to form a pale yellow solution, which was cooled to −78 °C. To this solution was added to 0.60 mL of 1.4 M *n*-BuLi (solution in hexanes), causing it to become bright yellow. After 1 h, $Cl_2Pd(NCCH_3)(PPh_3)$ (0.30 g, 0.62 mmol) was added and the solution was warmed to 0 °C. The solution was stirred for 80 min at 0 °C, after which it was red-orange with an orange-brown solid. This solid was collected by filtration and extracted with acetone. Solvent was evaporated from the acetone solution to give a brown solid, which was washed with Et_2O. The ^{1}H NMR spectrum of the brown solid ($CDCl_3$) showed peaks for two isomers of complex **3** in a 2:1 ratio. Yield: 0.184 g (53%). ^{1}H NMR chemical shift assigments were based on COSY. ^{1}H NMR of major isomer: δ 8.82 (d, H7, J = 8 Hz), 7.45 (t, 6H, PPh_3), 7.32 (m, 3H, PPh_3), 7.19 (dt, 7H, PPh_3 and H6), 6.68 (t, H5, J = 7 Hz), 6.46 (d, H4, J = 7 Hz), 4.70 (m, 1H, NCH), 3.25 (m, 1H, NCH), 2.83 (m, 1H, NCH_2CH), 1.32 (m, 1H, NCH_2CH). ^{1}H NMR of minor isomer: δ 8.50 (d, H7), 7.1−7.5 (m, PPh_3), 7.05 (t, H6), 6.60 (t, H5), 6.39 (d, H4), 4.82 (br, NCH), 3.58 (br, NCH), 2.91 (m, NCH_2CH), 1.48 (m, NCH_2CH). ^{31}P NMR ($CDCl_3$): δ 26.8 (s). MS (FAB$^+$): m/e 631 (630 calcd for $Pd(PPh_3)_2$), 369 (368 calcd for $Pd(PPh_3)$).

Reaction of $Cl_2Pd(PPh_3)(\eta^1$-indoline) with *n*-BuLi. Complex **2** (0.0324 g, 0.0580 mmol) was dissolved in a mixture of 20 mL of THF and 20 mL of Et_2O to form a yellow solution. To it was added 0.10 mL of 0.78 M *n*-BuLi in hexanes. The solution turned from yellow to orange-red. After 10 min, the solvent was evaporated to give a brownish-red sticky solid, which was soluble in Et_2O. The solid was recrystallized from Et_2O/EtOH and dried under vacuum. The ^{1}H NMR ($CDCl_3$) displayed peaks for the starting complex **2** (44%) and both isomers of the deprotonated complex **3** (56%).

Reaction of $Cl_2Pd(PPh_3)(NCCH_3)$ with 1-Methylindoline. To a solution of $Cl_2Pd(PPh_3)(NCCH_3)$ (0.0416 g, 0.0865 mmol) in 35 mL of CH_2Cl_2 was added 0.030 mL of 1-methylindoline. The orange solution was stirred at room temperature for 1 h and then refluxed at 45 °C for 3 h before the solvent was evaporated. The resulting brown-yellow solid was extracted with 2 mL of Et_2O and 20 mL of EtOH, leaving a dark yellow precipitate, which was washed with EtOH. The ^{1}H NMR spectrum ($CDCl_3$) of this crude product showed resonances for unidentified $Pd(PPh_3)$ derivatives, but significant resonances for a product with coordinated 1-Me-indoline were not observed.

Reaction of $[Cl_2Pd(PPh_3)(\text{indolinyl})]^-Li^+$ with Methyl Iodide. Complex **3** (0.010 g, 0.018 mmol) was dissolved in 30 mL of CH_3CN to form a brown yellow solution. To it was added excess methyl iodide (0.020 mL, 0.32 mmol). The solution was heated to 60 °C for 40 h. The solvent was then evaporated, leaving an orange-brown solid. The ^{1}H NMR spectrum (CD_3CN) indicated a complex mixture of products, which was not successfully separated.

Acknowledgment. Support for this work by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, is gratefully acknowledged. The structure determinations were performed using equipment acquired under National Science Foundation Grant No. CHE-9505926. This equipment includes a Siemens P4 diffractometer system and a Silicon Graphics Indigo2 XL workstation.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond distances, bond angles, anisotropic displacement parameters, and hydrogen coordinates and additional diagrams for **1a** and **2** (26 pages). Ordering information is given on any current masthead page.

OM960744E

(31) BYPASS, van der Sluis, P.; Spek, A. L. *Acta Cryst.* **1990**, *A46*, 1194. SQUEEZE is a routine included in PLATON, Spek, A. L. *Acta Cryst.* **1990**, *A46*, C34.