Organometallics **2000,** *19,* 2853−2857 2853

Neutral Ru(η^5-pyrrole) Complexes. Synthesis and Structure of Diazaruthenocenes and Ru(1-3:5,6-η^5-C_8H_{11})(η^5-pyrrole) Complexes

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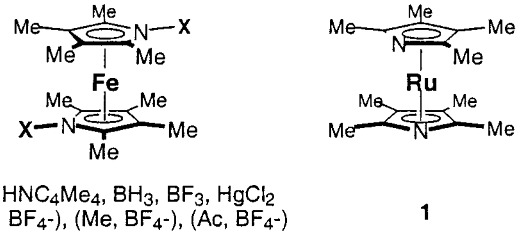
The synthesis of metal complexes with anionic η^5-pyrrole ligands is generally complicated by the free nitrogen lone pair. Methods are reported for the synthesis of two types of neutral η^5-tetramethylpyrrolyl (NC_4Me_4) ruthenium complexes. Ru(η^5-NC_4Me_4)$_2$ is prepared from $(Ph_3P)_3RuCl_2$ and lithium tetramethylpyrrolide in refluxing THF. A chiral diazaruthenocene with C_2 symmetry is prepared from 2,3-dimethyl-4,5,6,7-tetrahydroindole. Attempts to prepare diazaruthenocenes from $[Ru(\eta^4\text{-}C_8H_{12})Cl_2]_x$ led to deprotonation of the COD ligand to form a complex Ru(1-3:5,6-η^5-C_8H_{11})(η^5-NC_4Me_4) isoelectronic with Ru(η^5-NC_4Me_4)$_2$.

Introduction

In contrast to η^5-cyclopentadienyl metal complexes, the corresponding η^5-pyrrolyl metal complexes are a sparsely populated class.[1,2] From a synthetic perspective, the nitrogen lone pair of the η^5-pyrrolyl ligand is a liability. Unlike Cp and Cp* ligands, pyrrolyl and tetramethylpyrrolyl ligands can form stable η^1 complexes. Although Fe(NC_4H_4)$_2$ and Fe(NC_4Me_4)$_2$ have resisted isolation, Kuhn and co-workers have shown that masking of the nitrogen lone pairs with Lewis acids leads to stable, isolable complexes.[3−5] In diazametallocene complexes, addition of alkyl groups to the pyrrolyl ligand has the expected effect of increasing stability.[6]

η^5-Pyrrolyl metal complexes are important for catalytic applications and in organic synthesis. Rakowski-Dubois has shown that η^5-coordination of the pyrrolyl anion to ruthenium makes it susceptible to nucleophilic addition.[7,8] In addition, the reactions associated with the η^5-pyrrole offer insight into the potential reaction pathways catalyzed by hydrodenitrogenation catalysts.[9] Recently, Fu and co-workers have shown that the lone pair of η^5-pyrrolyl ligands can participate in acyl transfer catalysis.[10] The stable complex Cp*Fe[η^5-NC_4H_4] was shown to catalyze a nucleophilic acyl transfer reaction, providing an opportunity to exploit asymmetric environments around metal centers.



1

Figure 1. Some diazametallocenes with η^5-NC_4Me_4 ligands.

Kelly and Parthun have reported the synthesis of the first diazaruthenocene with free lone nitrogen lone pairs.[11] Addition of $[Ru(\eta^4\text{-}C_7H_8)Cl_2]_x$ to lithium tetramethylpyrrolide in THF afforded Ru[η^5-NC_4Me_4]$_2$, **1** (Figure 1). Unfortunately, the insolubility of the reagents diminishes the reliability of this chemistry. In this article, we present a reliable alternative method for the synthesis of diazaruthenocene and analogues by the modification of the procedure of Rakowski-Dubois for preparing half-sandwich η^5-pyrrole complexes. In addition, we demonstrate an important side reaction in the synthesis of η^5-pyrrolylruthenium complexes from $[Ru(\eta^4\text{-}C_8H_{12})Cl_2]_x$ that leads to the formation of neutral Ru(1-3:5,6-η^5-C_8H_{11})(η^5-pyrrolyl) complexes, isoelectronic with metallocene **1**.

Results and Discussion

Preparation of η^5-Pyrrolyl Ru(1-3:5,6-η^5-C_8H_{11}) Complexes. At the outset of these investigations we intended to synthesize several new diazaruthenocene complexes using the procedure of Kelly and Parthun.[11] We first sought to optimize the original procedure involving the addition of the norbornadienyl complex $[Ru(\eta^4\text{-}C_7H_8)Cl_2]_x$ to a slurry of lithium tetramethylpyrrolide **2** in THF at room temperature. Unfortunately the insolubility of both reagents prevented reaction,

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(1) Kuhn, N. *Bull. Soc. Chim. Belg.* **1990**, *99*, 707.

(2) Janiak, C.; Kuhn, N. In *Advances in Nitrogen Heterocycles*; Moody, C. J., Ed.; JAI Press Inc.: Greenwich, CT, 1996; Vol. 2, p 179.

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(9) Kvietok, F.; Allured, V.; Carperos, V.; Rakowski DuBois, M. *Organometallics* **1994**, *13*, 60.

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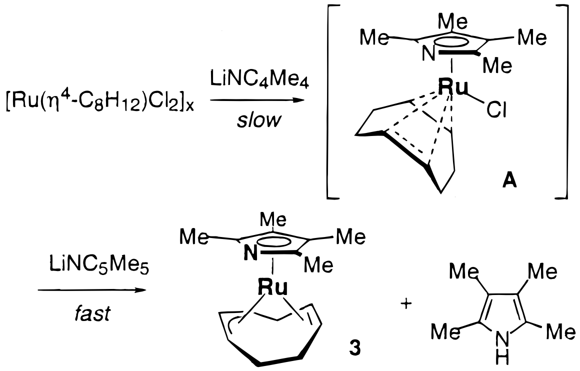
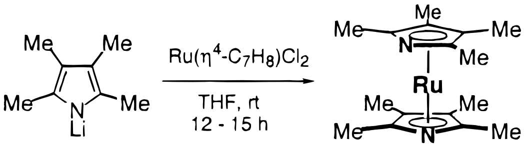
(11) Kelly, W. J.; Parthun, W. E. *Organometallics* **1992**, *11*, 4348.

10.1021/om000189n CCC: $19.00

Scheme 1

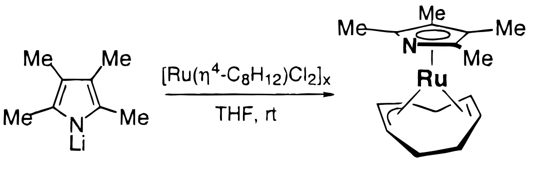


even at reflux temperature. When the reaction was filtered through alumina, unreacted tetramethylpyrrole was recovered quantitatively.



2 1 (1)

$[Ru(\eta^4\text{-}C_7H_8)Cl_2]_x$ exists in a bridged, polymeric structure that is insoluble in all organic solvents.[12] Surface area is an important parameter for dissolution rates, and it was hoped that the reaction might be dependent on the source of $[Ru(\eta^4\text{-}C_7H_8)Cl_2]_x$. The viability of the $[Ru(\eta^4\text{-}C_7H_8)Cl_2]_x$, obtained commercially (Aldrich) or prepared according to the procedure of Wilkinson, was confirmed by conversion to $Ru(pyridine)_4Cl_2$.[12] Regardless of source, $[Ru(\eta^4\text{-}C_7H_8)Cl_2]_x$ failed to react with lithium tetramethylpyrrolide, as did $Ru(pyridine)_4Cl_2$. Extensive efforts to increase the solubility of the reagents by changing solvents and temperature proved ineffective.While the related complex $[Ru(\eta^4\text{-}C_8H_{12})Cl_2]_x$ is also insoluble in THF, it slowly reacts with lithium tetramethylpyrrolide at room temperature to give a single isolable complex in 78% yield. However, the product obtained from this reaction was not the expected metallocene but an unexpected complex $Ru(1\text{-}3{:}5,6\text{-}\eta^5\text{-}C_8H_{11})(\eta^5\text{-}NC_4Me_4)$, **3**.



3 (2)

Presumably, the formation of complex **3** proceeds via the coordinatively saturated intermediate $RuCl(\eta^4\text{-}C_8H_{12})(\eta^5\text{-}NC_4Me_4)$, **A** (Scheme 1), but the basic pyrrole anion deprotonates the COD ligand faster than it displaces the chloride. In an attempt to isolate the putative intermediate $RuCl(\eta^4\text{-}C_8H_{12})(\eta^5\text{-}NC_4Me_4)$, $[Ru(\eta^4\text{-}C_8H_{12})Cl_2]_x$ was reacted with only 1 equiv of lithium tetramethylpyrrolide. Unfortunately the lithium pyrrolide appears to deprotonate the intermediate **4** faster than it reacts with $[Ru(\eta^4\text{-}C_8H_{12})Cl_2]_x$, and complex **3** was isolated in 35% yield along with tetramethylpyrrole.

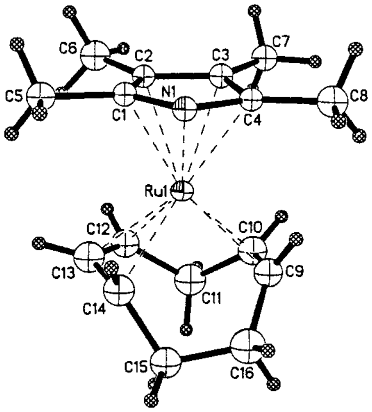
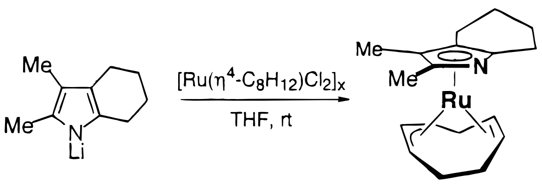


Figure 2. Structure of $Ru(1\text{-}3{:}5,6\text{-}\eta^5\text{-}C_8H_{11})(\eta^5\text{-}NC_4Me_4)$ complex **3**. Data were refined isotropically (50% level). Selected bond distances (Å) and torsion angles (deg) are as follows: Ru(1)−Cnt 1.888, Ru(1)−C(12) 2.209(6), Ru(1)−C(13) 2.147(6), Ru(1)−C(14) 2.196(6), Ru(1)−C(9) 2.172(5), Ru(1)−C(10) 2.178(6), C(11)−C(12)−C(13)−C(14) 22.6(9), C(12)−C(13)−C(14)−C(15) 48.4(9), C(16)−C(9)−C(10)−C(11) 23.9(9).

The facility of this reaction led us to explore an alternative pyrrole ligand. 2,3-Dimethyl-4,5,6,7-tetrahydroindole was deprotonated with butyllithium in THF. As with lithium tetramethylpyrrolide, no reaction was observed when heated at reflux with $[Ru(\eta^4\text{-}C_7H_8)Cl_2]_x$. However, anion **4** reacted at room temperature with $[Ru(\eta^4\text{-}C_8H_{12})Cl_2]_x$ to afford the corresponding neutral $(1\text{-}3{:}5,6\text{-}\eta^5\text{-}C_8H_{11})$ complexes **5a** and **5b** in 58% yield as a mixture of diastereomers. These diastereomers were inseparable by chromatography and resisted attempts at crystallization.



4 **5a**, **5b** (3)

X-ray Structure of Complex 3. Initially, the structure of complex **3** (Figure 2) was tentatively assigned using a combination of mass spectrometry, ^{1}H NMR, and ^{13}C NMR. In particular, the $1\text{-}3{:}5,6\text{-}\eta^5$-bonding mode was assigned on the basis of the analogy with spectral data reported for the cationic complex $[Ru(\eta^6\text{-}C_6H_6)(1\text{-}3{:}5,6\text{-}\eta^5\text{-}C_8H_{11})]^+BF_4^-$.[13] Complex **B** was subsequently crystallized from hexane, and the structure was determined unambiguously by X-ray diffraction. The symmetry plane of the pyrrolyl ligand bisects the codyl ligand between the η^2 and η^3 fragments. Unfortunately, the crystals were not of sufficient quality to allow further refinement.

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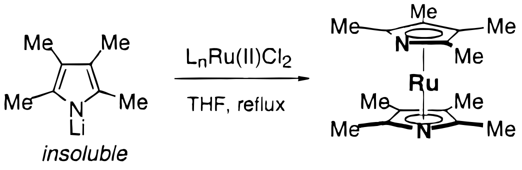
Table 1. Spectroscopic and Physical Data for Ru(η^5-NC$_4$Me$_4$)$_2$

	found	reported[11]
^{1}H NMR (ppm)[a]	2.03	2.18
	1.77	1.94
^{13}C NMR (ppm)[a]	102.9	103.7
	88.8	89.0
	13.2	13.9
	9.2	8.3
mp	119−122 °C	63−66 °C
	(ether)	(pentane)
	yellow-orange	brown

[a] CDCl$_3$.

There are fewer than 20 examples of [Ru(1-3:5,6-η^5-C$_8$H$_{11}$)] complexes. Of these, there are three examples of cationic [Ru(η^6-arene)(1-3:5,6-η^5-C$_8$H$_{11}$)]$^+$ complexes,[13−15] but no reported examples of the corresponding neutral [Ru(η^5-arene)(1-3:5,6-η^5-C$_8$H$_{11}$)]. Pyrrolyl complexes **3**, **5a**, and **5b** are the first examples of neutral ruthenium (1-3:5,6-η^5-C$_8$H$_{11}$) complexes with a Cp-type ligand.

Synthesis of Diazaruthenocenes. Since lithium tetramethylpyrrolide was insoluble, solubility of the ruthenium(II) precursor became a focal point for our investigation. In the hopes that discrete complexes might exhibit greater kinetic solubility than the oligomeric ruthenium complexes, several other alternatives were examined. While [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ gave no reaction, the corresponding η^6-benzene dimer afforded low but variable yield (eq 4).



1 (4)

L$_n$Ru(II)Cl$_2$	yield
[Ru(η^6-*p*-cymene)Cl$_2$]$_2$	no rxn
[Ru(η^6-C$_6$H$_6$)Cl$_2$]$_2$	5-20%
Ru(Ph$_3$P)$_3$Cl$_2$	24%

Rakowski-Dubois and co-workers have shown that Ru(η^5-NC$_4$H$_4$)(Ph$_3$P)$_2$Cl can be prepared by addition of 1 equiv of lithium pyrrolide to Ru(Ph$_3$P)$_3$Cl$_2$ in refluxing toluene, but this procedure was not applicable to lithium tetramethylpyrrolide.[7] The success achieved using [Ru(η^6-C$_6$H$_6$)Cl$_2$]$_2$ led us to substitute Ru(Ph$_3$P)$_3$Cl$_2$, which is soluble in THF. This modification led to reproducible formation of diazaruthenocene **1** in about 24% yield.

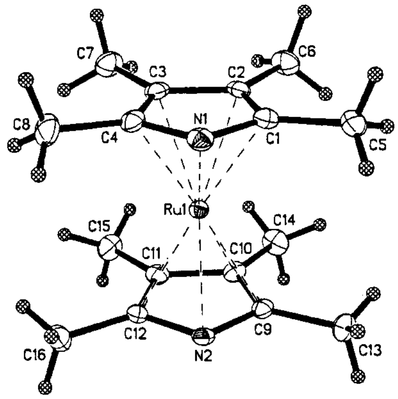


Figure 3. Molecular structure of diazaruthenocene **1**. Thermal ellipsoids are at the 50% probability level.

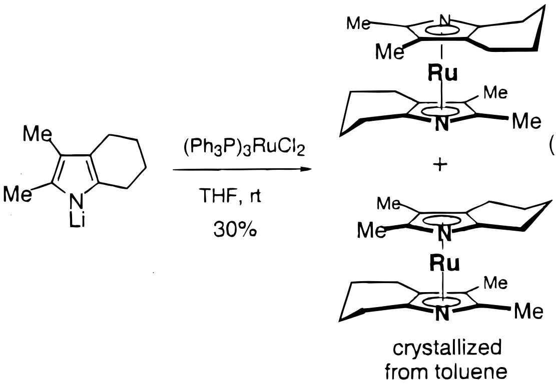
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Complex 1

Ru(1)−N(1)	2.1820(13)	Ru(1)−N(2)	2.1818(12)
Ru(1)−C(1)	2.1652(15)	Ru(1)−C(4)	2.1605(15)
Ru(1)−C(2)	2.1907(15)	Ru(1)−C(3)	2.1919(15)
Ru(1)−Cnt(1)	1.814	Ru(1)−Cnt(2)	1.812

N(2)−Ru(1)−N(1)	113.32(5)
Cnt(1)−Ru(1)−Cnt(2)	178.6
C(1)−N(1)−C(4)	106.05(12)
C(1)−C(2)−C(3)	106.24(13)
N(1)−C(1)−C(2)	110.91(13)

With an entry into the diazaruthenocene series, the preparation of chiral complexes incorporating 4,5,6,7-tetrahydroindoles[16,17] was next explored. While η^5-tetrahydroindenyl complexes are often prepared by hydrogenation of the corresponding η^5-indenyl complexes, it was expected that η^5-indolylruthenium precursors would be either too unstable or too difficult to prepare.

2,3,-Dimethyl-4,5,6,7-tetrahydroindole was deprotonated with butyllithium in THF at room temperature to produce a homogeneous solution. After addition of Ru(Ph$_3$P)$_3$Cl$_2$ the solution was heated at reflux for 12 h. As expected, the diazaruthenocenes **6** and **7** were obtained as a 1:1 mixture of diastereomers. Unlike the corresponding η^5-tetrahydroindenyl ligand, the η^5-tetrahydroindolyl ligand possesses enantiotopic faces. The combined yield for these diazaruthenocene complexes (30%) was similar to the yield for the symmetric diazaruthenocene **1**.



6 (meso)

7 (C_2)

(5)

X-ray Structures of Diazaruthenocenes. Diazaruthenocene **1** crystallized from ether differs in physical properties from material crystallized from pentane (Table 1).[11] To confirm the sandwich structure of **1** (Figure 3), a single crystal was subjected to X-ray diffraction. The results show unequivocally that Ru(η^5-NC$_4$Me$_4$)$_2$ prepared from Ru(Ph$_3$P)$_3$Cl$_2$ possesses two η^5-pyrrole ligands. In this structure both nitrogen atoms

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(14) Ashworth, T. V.; Nolte, M. J.; Reimann, R. H.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1977**, 9377.

(15) Bouachir, F.; Chaudret, B.; Neibecker, D.; Tkatchenko, I. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 347.

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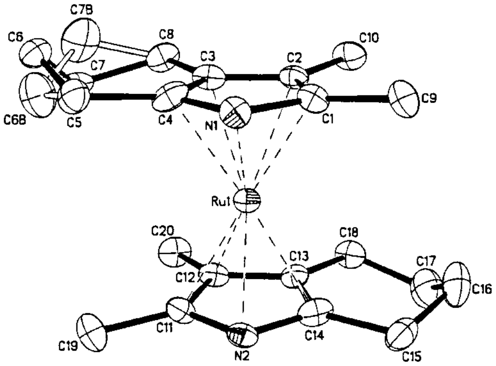

Figure 4. X-ray structure of C_2 diazaruthenocene **7**. Thermal ellipsoids are at the 50% probability level. One of the six-membered rings shows disorder at C6 and C7 due to the presence of two half-chair conformations.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 7

Ru(1)−N(1)	2.195(5)	Ru(1)−N(2)	2.184(5)
Ru(1)−C(1)	2.159(6)	Ru(1)−C(4)	2.194(6)
Ru(1)−C(2)	2.185(6)	Ru(1)−C(3)	2.185(6)
Ru(1)−Cnt(1)	1.821	Ru(1)−Cnt(2)	1.815

N(2)−Ru(1)−N(1)	114.4(2)
Cnt(1)−Ru(1)−Cnt(2)	177.7
C(18)−C(13)−C(14)−C(15)	−3.5(10)
C(20)−C(12)−C(13)−C(18)	1.0(10)

are oriented in the same direction. No conformational preference is predicted for Fe(η^5-NC_4H_4)$_2$, so it is not surprising that the orientation of pyrrole nitrogens in diazaferrocene complexes depends on the bulk of the substituents or the type of electrophile that is coordinated to the nitrogen lone pairs.[18] In the crystal structure of Fe(η^5-NC_4Me_4)$_2$·2(HNC_4Me_4) the pyrrole nitrogens are pointed in opposite directions to avoid steric interactions with the free pyrrole rings.[3] In contrast, the dimeric [Fe(η^5-NC_4Me_4)$_2$·$AgBF_4$·CH_3OH]$_2$ complex crystallizes such that the two silver atoms can bridge two diazaferrocenes with linear N−Ag−N geometries.[4] Unlike the diazaferrocenes, the corresponding diazaruthenocenes seem to be stable even in the absence of electrophiles that can coordinate to the nitrogen.

It was not possible to separate diastereomers **6** and **7** using chromatography. However, it was possible to selectively crystallize one of the diastereomers, **7**, from ether/toluene. From the spectroscopic data, it was not possible to assign either the meso or C_2 stereochemistry to diastereomer **7**, but X-ray structure determination (Figure 4) showed that diastereomer **7** possessed C_2 symmetry. Diazaruthenocene complex **7** crystallizes with nitrogen atoms oriented in the same direction, like the Ru(η^5-NC_4Me_4)$_2$ complex **1**. However, there was disorder in one of the two six-membered rings caused by the presence of two half-chair forms.

Conclusions

Despite recent interest in η^5-pyrrolyl metal complexes, pyrroles are sensitive and make reluctant η^5 ligands for sandwich complexes. This work shows that substituted diazaruthenocenes are available from the corresponding lithium pyrrolide and either of the monomeric ruthenium complexes [Ru(η^6-C_6H_6)Cl_2]$_2$ and Ru(Ph_3P)$_3Cl_2$. In contrast, oligomeric [Ru(diene)Cl_2]$_x$ complexes suffer from poor reactivity and alternative reaction pathways. Structural details of three new η^5-pyrrolyl ruthenium complexes are now available. The structures of diazaruthenocenes are similar to those of diazaferrocenes except the nitrogen lone pairs of diazaruthenocenes do not show the same demand for coordination.

Experimental Section

All commercially available starting materials and reagents were used without further purification unless otherwise indicated. Tetramethylpyrrole was obtained from Lancaster and distilled prior to use. Reactions were carried out according to established procedures from these laboratories.[19] All reactions were run under an argon atmosphere unless otherwise indicated. For all new compounds, the appropriate molecular ion cluster was observed in the mass spectrum using LSIMS.

Ru(1-3:5,6-η^5-C_8H_{11})(η^5-NC_4Me_4), 3. In a dry three-neck flask, 2,3,4,5-tetramethylpyrrole (0.12 g, 1.0 mmol) was dissolved in 10 mL of THF. A solution of *n*-butyllithium in hexanes (0.73 mL, 1.1 mmol) was added dropwise, and the resulting solution was stirred for 30 min. [Ru(η^4-C_8H_{12})Cl_2]$_x$ (0.14 g, 0.50 mmol) was added, and the reaction mixture was stirred for 12 h at room temperature. After this time the reaction mixture was filtered through Celite and washed through with ether. Concentration of the filtrate in vacuo and purification of the crude product by silica gel chromatography (10% acetone/ether) afforded **3** (0.117 g, 71%) as yellow crystals.

3: mp 91−93 °C (ether); $R_f = 0.56$ (10% acetone/ether); IR (KBr) 2901, 1436, 1377 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (dt, $J = 8.8$, 6.8 Hz,1H, C*H*), 3.20−3.27 (m, 1H, C*H*), 3.01−3.10 (m, 1H, C*H*), 2.96 (dt, $J = 13.6$, 8.0 Hz, 1H, C*H*), 2.76 (t, $J = 6.8$ Hz, 1H, C*H*), 2.34−2.46 (m, 1H, CH_2), 2.27 (dd, $J = 5.2$, 2.4 Hz, 1H, CHH_4), 2.24 (dt, $J = 4.4$,1.6 Hz, 1H, $CHH_{4'}$), 2.02 (s, 3H, *Me*), 2.00−1.92 (m, 1H, $CHH_{8'}$), 1.85 (s, 3H, *Me*), 1.79 (s, 3H, *Me*), 1.70 (s, 3H, *Me*), 1.34−1.24 (m, 1H, CHH_8); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.0, 110.2, 97.7, 95.2, 78.5, 75.0, 65.8, 35.9, 30.3, 25.8, 22.7, 16.7, 12.4, 12.1, 10.0, 8.7. HRMS (LSIMS): Calcd for $C_{16}H_{23}N^{104}Ru$ 333.0886, found 333.0883. Anal. Calcd for $C_{16}H_{23}NRu$: C, 58.16; H, 7.02; N, 4.24. Found: C, 58.22; H, 7.10; N, 4.23.

Ru(1-3:5,6-η^5-C_8H_{11})(η^5-2,3-dimethyl-4,5,6,7-tetrahydroindole), 5a and 5b. In a dry three-neck flask, 2,3-dimethyl-4,5,6,7-tetrahydroindole (0.13 g, 0.89 mmol) was dissolved in 5 mL of THF. A solution of *n*-butyllithium in hexanes (0.66 mL, 0.98 mmol) was added dropwise, and the mixture was stirred for 30 min. [Ru(η^4-C_8H_{12})Cl_2]$_x$ (0.13 g, 0.45 mmol) was added, and the reaction mixture was stirred for 12 h at room temperature. After this time the reaction mixture was filtered through Celite and washed through with ether. Concentration of the filtrate in vacuo and purification of the crude product by silica gel chromatography (5% acetone/ether) afforded **5a** and **5b** (0.086 g, 54%) as a yellow oil (45:55 mixture of two diastereomers).

5a and **5b** (45:55 mixture): $R_f = 0.68$ (5% acetone/ether); IR (KBr) 2936, 1437, 1373 cm^{-1}; distinctive peaks from the mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (s, *Me*), 1.90 (s, *Me*), 1.87 (s, *Me*), 1.64 (s, *Me*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 113.7, 113.1, 111.4, 110.8, 99.3, 93.4, 92.9, 79.6, 78.6, 76.6, 74.5, 66.3, 65.3, 35.9, 35.8, 30.3, 30.2, 25.9, 25.6, 24.1, 23.9, 23.2, 23.1, 22.9, 22.8, 22.6, 22.5, 22.0, 21.3, 17.3, 16.7, 12.8, 12.2, 9.4, 8.3. HRMS (LSIMS): Calcd for $C_{18}H_{25}N^{102}Ru$ 357.1036, found 357.1032. Anal. Calcd for $C_{18}H_{25}NRu$: C, 60.65; H, 7.07; N, 3.93. Found: C, 60.59; H, 7.12; N, 3.83.

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Table 4. Crystallographic Data for Ruthenium Complexes 1, 3, and 7

	1	**3**	**7**
empirical formula	$C_{16}H_{24}N_2Ru$	$C_{16}H_{23}NRu$	$C_{20}H_{28}N_2Ru$
fw	345.44	330.42	397.51
temperature	158 K	168(2) K	163(2) K
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1$	$P\bar{1}$
a, Å	6.7396(3)	6.4571(3)	6.6626(7)
b, Å	7.6114(4)	13.3962(6)	8.2033(9)
c, Å	15.7190(8)	8.2209(3)	17.0014(19)
α, deg	76.9920(10)	90	76.723(2)
β, deg	88.1170(10)	100.6910(10)	88.340(2)
γ, deg	75.8370(10)	90	71.782(2)
volume, Å^3	761.57(7)	698.77(5)	858.12(16)
Z	2	2	2
density (calcd), g cm^{-3}	1.506	1.570	1.538
μ, mm^{-1}	1.018	1.104	0.915
cryst size, mm	0.28 × 0.27 × 0.07	0.26 × 0.26 × 0.17	0.45 × 0.25 × 0.25
θ range for data collection, deg	1.33−28.30	2.52−28.27	1.23−28.31
no. of reflns collected	8121	7508	8910
no. of ind reflns	3580	3306	3958
	[R(int) = 0.0178]	[R(int) = 0.0173]	[R(int) = 0.0529]
completeness to θ = 28.27°	95.0%	98.0%	92.9%
abs corr	semiempirical via SADABS	none	numerical
max. and min. transmission		0.8345 and 0.7622	0.8035 and 0.6835
no. of data/restraints/params	3580/0/269	3306/1/79	3958/0/226
goodness-of-fit on F^2	1.042	1.062	1.219
R1, wR2 [$I > 2\sigma(I)$]	0.0179, 0.0438	0.0353, 0.0882	0.0600, 0.1782
R1, wR2 (all data)	0.0204, 0.0446	0.0381, 0.0917	0.0611, 0.1787
largest diff peak and hole, e Å^{-3}	0.389 and −0.408	1.373 and −0.566	3.079 and −1.937

Ru(η^5-NC_4Me_4)$_2$, 1. In a dry round-bottom flask under an argon atmosphere, 2,3,4,5-tetramethylpyrrole (0.25 g, 2.0 mmol) was dissolved in 20 mL of THF. A solution of *n*-butyllithium in hexanes (1.4 mL, 2.1 mmol) was added dropwise, and the resulting suspension was stirred for 30 min. $Ru(PPh_3)_3Cl_2$ (0.48 g, 0.50 mmol) was added, and the reaction mixture was heated to reflux for 12 h. After this time the reaction mixture was diluted with ether, filtered through Celite, and concentrated in vacuo. Residue was purified by preparative thin-layer chromatography on neutral alumina (50% acetone/ether). Removal of the product from the alumina by washing with ethyl acetate afforded **1** (0.04 g, 22%) as yellow crystals.

1: mp 119−122 (ether); R_f = 0.51 (25% acetone/ether on neutral alumina); IR (KBr) 2908, 1475, 1364, 1032 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.03 (s, 12H, *Me*), 1.77 (s, 12H, *Me*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.9, 88.8, 13.2, 9.2. HRMS (LSIMS): Calcd for $C_{16}H_{24}N_2{}^{96}Ru$ 340.1002, found 340.1015. Anal. Calcd for $C_{16}H_{24}N_2Ru$: C, 55.63; H, 7.00; N, 8.11. Found: C, 55.69; H, 6.98; N, 8.02.

Ru(η^5-2,3-dimethyl-4,5,6,7-tetrahydroindole)$_2$, 6 and 7. In a dry round-bottom flask under an argon atmosphere 2,3-dimethyl-4,5,6,7-tetrahydroindole (0.17 g, 1.1 mmol) was dissolved in 5 mL of THF. A solution of *n*-butyllithium in hexanes (0.7 mL, 1.2 mmol) was added dropwise, and the resulting suspension was stirred for 30 min. $Ru(PPh_3)_3Cl_2$ (0.52 g, 0.55 mmol) was added, and the reaction mixture was heated at reflux under nitrogen for 12 h. After this time the reaction mixture was diluted with ether, filtered through Celite, and concentrated in vacuo. Residue was purified by preparative thin-layer chromatography on neutral alumina (20% acetone/ether). Removal of the product from the alumina by washing with ethyl acetate afforded a mixture of **6** and **7** (0.07 g, 30%) as a yellow solid.

6 and **7:** mp 98−100 (ether); R_f = 0.65 (20% acetone/ether on neutral alumina); IR (KBr) 2928, 1436, 1377 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40−2.54 (m, 8H, benzylic C*H*$_2$), 2.18−2.25 (m, 8H, benzylic C*H*$_2$), 2.03 (s, 6H, *Me*), 2.00 (s, 6H, *Me*), 1.70−1.90 (m, 12H, ring C*H*$_2$), 1.74 (s, 6H, *Me*), 1.72 (s, 6H, ring C*H*$_2$), 1.55−168 (m, 4H, ring C*H*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.6, 105.9, 102.7, 102.0, 91.5, 86.3, 86.2, 24.5, 24.4, 23.4, 23.3, 22.9, 22.9, 20.8, 13.2, 12.9, 8.7, 8.6. HRMS (CI$^+$): Calcd for $C_{20}H_{28}N_2{}^{102}Ru$ 398.1302, found 398.1310. Anal. Calcd for $C_{20}H_{28}N_2Ru$: C, 60.43; H, 7.10; N, 7.05. Found: C, 60.71; H, 6.97; N, 6.84.

A crystal of diastereomer **7** was prepared by slow evaporation from ether/toluene.

X-ray Structure Determinations. The SMART program package was used to determine the unit-cell parameters and for data collection (20 or 30 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT and SADABS[20] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[21] program. All structures were refined by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. For diazaruthenocene **1**, hydrogen atoms were located from a difference Fourier map and refined (x,y,z and U_{iso}). For complexes **3** and **7**, hydrogen atoms were included using a riding model. Carbon atoms C(6) and C(7) in diazaruthenocene **7** were disordered and included with two components and assigned partial site-occupancy factors. Crystallallographic data for complexes **1**, **3**, and **7** are given in Tables 2−4.

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Supporting Information Available: Tables of bond distances and angles and positional and thermal parameters for compounds **1**, **3**, and **7**. ^{1}H NMR spectra for compound **3** and the mixture of **5a** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Sheldrick, G. M. *SADABS*; Bruker Analytical X-ray Systems: Madison, WI, 1999.

[21] Sheldrick, G. M. *SHELXTL* Version 5.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.