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Synthesis and Characterization of a 1,2-Dibenzoylruthenocene and a Derived Pyridazine

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Summary: The reaction of 1-benzoyl-6-hydroxy-6-phenylfulvene with thallous ethoxide results in the formation of [Tl{1,2-$C_5H_3(COPh)_2$}]. Subsequent reaction with [Ru(μ_3-Cl)(Cp)]$_4$ gives [Ru{η^5-1,2-$C_5H_3(COPh)_2$}(Cp*)] (**3**, 79%). Treatment of **3** with hydrazine monohydrate results in the formation of the pyridazine [Ru{η^5-1,2-$\overline{C_5H_3(CPh)_2N_2}$}(Cp*)] (**6**, 73%). The structures of **3** and **6** have been determined by X-ray crystallography.*

Introduction

Since the discovery that polyacetylene could undergo an increase in its conductivity by 12 orders of magnitude upon charge-transfer oxidative doping,[1] scientists have striven to synthesize better conductive polymers for use as electronic materials. The current research has focused primarily on developing materials with small semiconducting band gaps, high processibility, and high stability.[2]

Polyheterocycles such as polythiophene and polypyrrole have been studied extensively due to their increased environmental stability compared to polyacetylene. The nitrogen and sulfur atoms tend to stabilize the positive charges of the p-doped polymers.[3] Furthermore, substituents on the polymers allow solubility and increased processibility, as shown by poly(3-alkylthiophenes).[4]

The chemistry of fusing the cyclopentadienyl ring of a metallocene to the heterocycles of these polymers is largely unexplored.[5,6] The benefits of such materials could be the ability to induce a reversible "doping" of the polymers by the redox chemistry of the fused metallocene. To this end, we first approached the task of synthesizing monomeric thiophenes and pyrroles with metallocenes fused to their [3,4-*c*] positions.

1,2-Dibenzoyl-1′,2′,3′,4′,5′-pentamethylruthenocene (**3**) was chosen as a precursor to heterocycle-fused ruthenocenes based on the variety of methods for the transformation of organic γ-diketones to heterocycles.[7−9]

Results and Discussion

Synthesis of [Ru{η^5-1,2-$C_5H_3(COPh)_2$}(Cp*)] (3). Linn and Sharkey[10] devised a general method for the preparation of 1,2-diacylcyclopentadienides via the reaction of lithium cyclopentadienide with acid chlorides. In their protonated forms, these exist as fulvenes with acidic hydroxy protons resonating at δ_H 18.2−19.3 ppm. Deprotonation of 1-benzoyl-6-hydroxy-6-phenylfulvene (**1**) with thallous ethoxide resulted in [Tl{1,2-C_5H_3-$(COPh)_2$}] (**2**) in nearly quantitative yield (Scheme 1), as evidenced by loss of the hydroxy proton (δ_H 18.5 ppm) in the ^{1}H NMR spectrum. The thallium salt was reacted with [Ru(μ_3-Cl)(Cp*)]$_4$[11] to give 1,2-dibenzoyl-1′,2′,3′,4′,5′-pentamethylruthenocene (**3**) in 79% yield. The similar 1,2-dibenzoylruthenocene was prepared as a minor product of the benzoylation of ruthenocene,[12,13] and its structure was elucidated by NMR.[14] 1,1′,2,2′-tetrabenzoylferrocene is *not* formed by the reaction of the lithium or sodium salt of the fulvene (**1**) with ferrous chloride.[15] Apparently, the electron-withdrawing effect of the acyl groups on the dibenzoylcyclopentadienide ion causes sufficient loss of electron density from the ring to hinder formation of a stable ferrocene. For [Ru(Cp*)] compared to [Fe(Cp)], the greater ruthenium−carbon bond strengths and the increased electron density resulting from a pentamethylcyclopentadienyl co-ligand allows for effective bonding of the dibenzoylcyclopentadienide ligand.

The three protons of the cyclopentadienyl fragment of these compounds give distinctive patterns in the ^{1}H NMR spectra. A doublet of two protons is slightly downfield of a triplet of one proton. The pattern shifts upfield approximately 0.5 ppm upon conversion of the fulvene **1** to its thallium complex **2**. Formation of 1,2-dibenzoyl-1′,2′,3′,4′,5′-pentamethylruthenocene (**3**) shifts the resonances an additional 1 ppm upfield.

Syntheses of [Ru{η^5-1,2-$\overline{C_5H_3(CPh)_2N_2}$}(Cp*)] (6). The pyridazine [Ru{η^5-1,2-$\overline{C_5H_3(CPh)_2N_2}$}(Cp*)] (**6**) was synthesized by two different methods. First, [Ru{η^5-1,2-$C_5H_3(COPh)_2$}(Cp*)] (**3**) reacts with hydrazine monohydrate to form **6** in 73% yield. The formation of pyridazines by the reaction of γ-diketones with hydrazine monohydrate has long been established.[10,16] Alternatively, the free pyridazine (**4**), synthesized by the procedure developed by Linn and Sharkey,[10] was depro-

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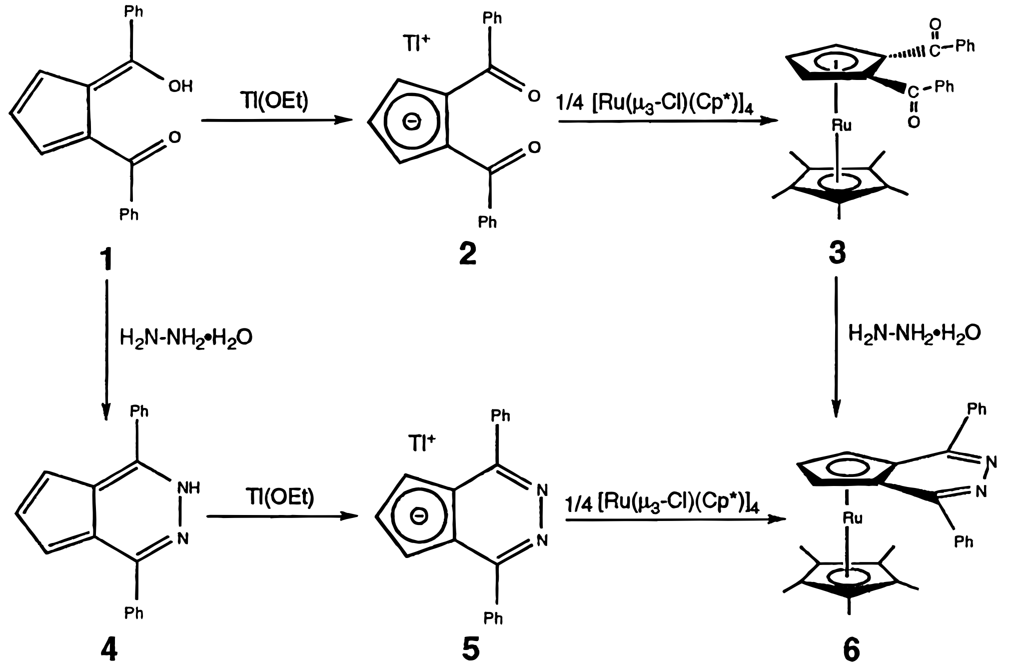
Scheme 1



tonated with thallous ethoxide (74% yield). Reaction of $[\mathrm{Tl}\{1,2\text{-}\overline{\mathrm{C_5H_3(CPh)_2N_2}}\}]$ (**5**) with $[\mathrm{Ru}(\mu_3\text{-Cl})(\mathrm{Cp^*})]_4$ gives **6** (51%), which is the first example of a metallocene fused to the *d*-edge of a pyridazine.

$[\mathrm{Tl}\{1,2\text{-C_5H_3(COPh)_2}\}]$ (**2**) and $[\mathrm{Tl}\{1,2\text{-}\overline{\mathrm{C_5H_3(CPh)_2N_2}}\}]$ (**5**) have similar shifts for the doublet–triplet pattern for the cyclopentadienyl protons in the ^{1}H NMR. An interesting characteristic of the thallium pyridazine salt is that the doublet–triplet pattern is reversed with the triplet appearing downfield of the doublet, due either to the ring current of the pyridazine or to the more rigid orientation of the phenyl groups adjacent to the cyclopentadienyl ring. $[\mathrm{Ru}\{\eta^5\text{-1,2-C_5H_3(COPh)_2}\}(\mathrm{Cp^*})]$ (**3**) and $[\mathrm{Ru}\{\eta^5\text{-1,2-}\overline{\mathrm{C_5H_3(CPh)_2N_2}}\}(\mathrm{Cp^*})]$ (**6**) have a similar ordering of their doublet–triplet patterns, with the pattern for **6** appearing slightly further downfield.

X-ray Crystal Structures of $[\mathrm{Ru}\{\eta^5\text{-1,2-C_5H_3(COPh)_2}\}(\mathrm{Cp^*})]$ (3) and $[\mathrm{Ru}\{\eta^5\text{-1,2-}\overline{\mathrm{C_5H_3(CPh)_2N_2}}\}(\mathrm{Cp^*})]$ (6). Plots of the molecular structures of **3** and **6** are shown in Figures 1 and 2 together with the atom-numbering schemes; selected bond distances and angles are given in Table 2. The structures show typical ruthenocene geometries with nearly linear centroid–Ru–centroid bonds for both **3** and **6**. For both **3** and **6**, the average carbon–ruthenium bond distance is shorter by about 0.02 Å to the Cp* ligand compared to the Cp ligand, probably because the Cp* ring is more electron rich. The same structural effect was observed for 1,2,3,4,5-pentamethylruthenocene.[17]

In **3**, the Ru–C bonds to the benzoyl-substituted carbons C1 and C2 are about 0.03 Å shorter than those to C3–C5 because of the electron-withdrawing character of the benzoyls. The benzoyl groups of **3** are oriented such that the phenyl groups point away from the bulky Cp* ligand. The oxygen atoms of the benzoyl groups are positioned 1.045(3) Å from the Cp plane on the same side as the ruthenium atom, whereas the phenyl ipso carbons C7 and C14 are positioned 1.313(3) Å on the opposite side of the Cp plane.

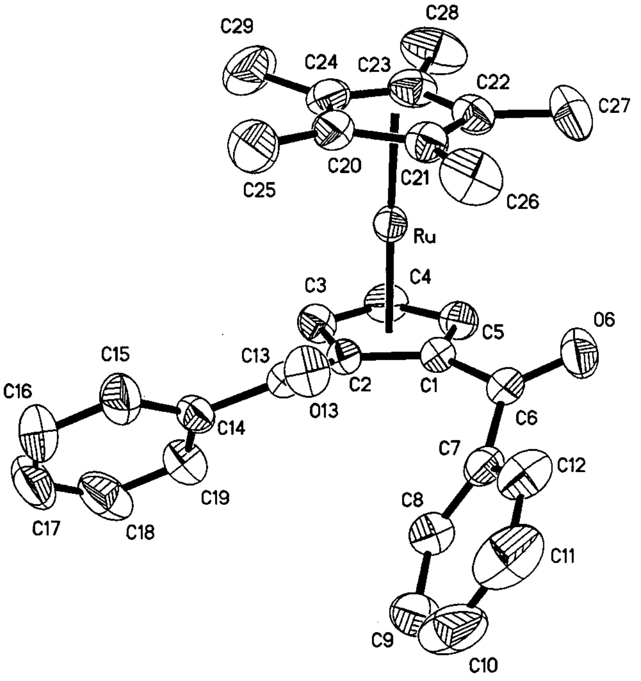


Figure 1. SHELXL-93 perspective drawing of $[\mathrm{Ru}\{\eta^5\text{-1,2-C_5H_3(COPh)_2}\}(\mathrm{Cp^*})]$ (**3**). The ellipsoids correspond to 50% probability contours of atomic displacement. Hydrogen atoms have been omitted for clarity.

The structure of **6** shows the metallocene fused to a six-membered ring containing the two nitrogens. All atoms of the fused pyridazine and cyclopentadienyl rings are nearly coplanar, with a very slight fold angle of 2.3(3)° between the Cp (C1–C5) and pyridazine (N1, C6, C1, C2, C13, N2) planes. The phenyl groups are

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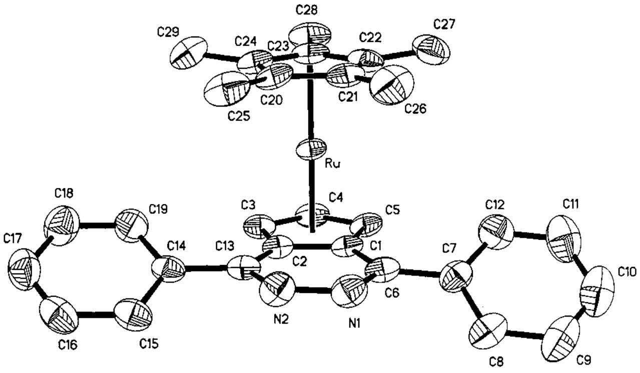

Figure 2. SHELXL-93 perspective drawing of $[Ru\{\eta^5\text{-}1,2\text{-}C_5H_3(CPh)_2N_2\}(Cp^*)]$ (**6**). The ellipsoids correspond to 50% probability contours of atomic displacement. Hydrogen atoms have been omitted for clarity.

Table 1. Crystal Data and Structure Refinements for Compounds 3 and 6

	3	**6**
empirical formula	$C_{29}H_{28}O_2Ru$	$C_{29}H_{28}N_2Ru$
fw (amu)	509.61	505.63
temp (K)	295(1)	296(2)
space group	$P2_1/n$	$P\bar{1}$
unit cell dimens (Å, deg)	$a = 12.496(5)$ $b = 14.583(3)$ $c = 13.571(5)$ $\alpha = 90.00(0)$ $\beta = 106.138(17)$ $\gamma = 90.00(0)$	$a = 8.0746(18)$ $b = 12.316(2)$ $c = 12.538(2)$ $\alpha = 107.258(16)$ $\beta = 99.216(16)$ $\gamma = 99.172(16)$
V (Å^3)	2375.6(3)	1146.7(4)
Z	4	2
D(calcd) (g/cm^{-3})	1.425	1.464
F(000)	1048 (1042.3)[a]	520 (517.2)[a]
cryst size (mm^3)	0.5 × 0.4 × 0.4	0.2 × 0.45 × 0.55
radiation	Mo Kα ($\lambda = 0.7107$ Å)	Mo Kα ($\lambda = 0.7107$ Å)
monochromator	graphite	graphite
abs coef μ (mm^{-1})	0.668	0.688
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
2θ range (deg)	4−50	4−50
limiting indices	$-14 < h < 14$ $0 < k < 17$ $0 < l < 16$	$-9 < h < 9$ $0 < k < 14$ $-14 < l < 14$
no. of reflns collcd	4361	4229
no. of indep reflns	4173 ($R_{int} = 0.032$)	4022 ($R_{int} = 0.022$)
abs corr	none needed	none needed
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
data/restraints/ params	4173/0/289	4022/0/289
goodness-of-fit on F^2	1.32	1.17
R [on F; $I > 2\sigma(I)$]	0.031	0.051
wR [on F^2; all data]	0.097	0.133
$(\Delta/\sigma)_{max}$	0.017	0.12
$\Delta(\rho)_{max}$ (e Å^{-3})	+0.33	+1.97
$\Delta(\rho)_{min}$ (e Å^{-3})	−0.61	−1.62

[a] Including anomalous dispersion contributions.

twisted like oars, with interplanar angles of 34.0(3)° (C7−C12) and 26.2(3)° (C14−C19) with respect to the pyridazine plane. This twist is similar to the phenyl ring orientations in 3,4:10,11-bis[3′,6′-diphenyl-4′,5′-pyridazino]tricyclo[6.3.0.0]undecane.[18]

Conclusion

1,2-Dibenzoyl-1′,2′,3′,4′,5′-pentamethylruthenocene (**3**) has been synthesized by reaction of the thallium salt of 1,2-dibenzoylcyclopentadienide (**2**) with $[Ru(\mu_3\text{-}Cl)(Cp^*)]_4$. Compound **3** is an appropriate precursor for the pyridazine-fused metallocene, **6**. Current work in our laboratory focuses on the synthesis of similar *c*-metallocene-fused thiophenes and pyrroles.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), Torsion Angles (deg), and Interplanar Angles (deg) for 3 and 6

	3	**6**
Length		
C1−C2	1.451(5)	1.439(6)
C1−C6	1.477(4)	1.449(5)
C2−C13	1.481(4)	1.428(5)
C6−C7	1.496(5)	1.469(6)
C6−O6	1.213(4)	
C6−N1		1.311(6)
C13−C14	1.506(4)	1.478(6)
C13−O13	1.215(4)	
C13−N2		1.324(5)
N1−N2		1.375(5)
Ru-X1A[a]	1.823(5)	1.843(4)
Ru-X1B[a]	1.805(5)	1.802(4)
Angle		
C1−C6−C7	118.6(3)	123.2(4)
C2−C13−C14	117.3(3)	124.1(3)
O6−C6−C1	120.7(3)	
O6−C6−C7	120.7(3)	
N1−C6−C1		120.8(4)
N1−C6−C7		115.9(4)
O13−C13−C2	122.6(3)	
O13−C13−C14	120.0(3)	
N2−C13−C2		121.4(4)
N2−C13−C14		114.5(3)
C6−N1−N2		122.0(4)
C13−N2−N1		121.2(4)
X1A-Ru-X1B[a]	178.0(3)	179.4(2)
Torsion Angle		
C1−C6−C7−C12	36.42(4)	34.95(6)
C1−C6−C7−C8	−147.47(3)	−144.61(4)
C2−C13−C14−C15	−149.75(3)	155.13(4)
C2−C13−C14−C19	34.72(4)	−28.20(6)
C5−C1−C6−C7	−145.81(4)	−2.01(6)
C3−C2−C13−C14	34.33(4)	−2.12(5)
C2−C1−C6−C7	30.53(5)	175.31(4)
C1−C2−C13−C14	−154.21(5)	177.62(6)
C3−C2−C13−O13	−145.55(4)	
C5−C1−C6−O6	30.72(4)	
C2−C1−C6−O6	−153.03(5)	
C1−C2−C13−O13	26.02(4)	
N1−N2−C13−C2		−0.61(5)
N2−N1−C6−C1		−1.42(5)
C5−C1−C6−N1		−178.72(5)
C3−C2−C13−N2		178.13(5)
C2−C1−C6−N1		−1.43(6)
C1−C2−C13−N2		−2.11(5)
Interplanar Angle		
A−B	4.8(3)	0.9(3)
B−C	122.9(3)	144.6(3)
B−D	122.0(3)	151.9(3)
B−G		2.3(3)
C−D	66.7(3)	11.4(3)
C−E	143.2(3)	
D−F	32.8(3)	

[a] X1A = Centroid of Cp, X1B = Centroid of Cp*. A = C20, C21, C22, C23, C24, B = C1, C2, C3, C4, C5. C = C7, C8, C9, C10, C11, C12, D = C14, C15, C16, C17, C18, C19. E = C1, C6, O6, F = C2, C13, O13, G = N1, C6, C1, C2, C13, N2.

Experimental Section

General Considerations. All reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere unless otherwise noted. Solvents were dried and distilled under nitrogen before use, including tetrahydrofuran

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over sodium benzophenone ketyl and methanol over magnesium turnings. Compounds **1** and **4** were synthesized according to Linn and Sharkey.[10] [Ru(μ_3-Cl)(Cp*)]$_4$ was synthesized according to Fagan.[11] TlOEt (Aldrich) and hydrazine monohydrate (J. T. Baker) were used as received. Proton and carbon NMR spectra were obtained on a Varian Gemini 200 system. Infrared spectra were obtained on a Mattson Galaxy Series FTIR 5000. Melting points were uncorrected. Elemental analyses were performed at the University of Illinois, Urbana. Mass spectra were obtained at the University of Kentucky Mass Spectrometry Facility.

Synthesis of [Tl{1,2-$C_5H_3(COPh)_2$}] (2). Thallium(I) ethoxide (570 mg, 2.29 mmol), weighed out in a tared syringe, was added to a solution of **1** (481 mg, 2.06 mmol) in THF (about 30 mL). A bright yellow solid precipitated immediately. The solution was stirred for 3 h. The precipitate was filtered and washed with 5 mL of cold ethyl ether, affording 958 mg (98%) of **2** as an air-stable bright yellow powder. ^{1}H NMR (200 MHz, DMSO-d_6, ppm): δ 5.66 (t, 1H, $J = 2.2$ Hz, CHC*H*CH), 6.21 (d, 2H, $J = 2.2$ Hz, C*H*CHC*H*), 7.2−7.4 (m, 6H, Ph *m*, *p*), 7.58−7.68 (dd, 4H, $J = 7.2$ Hz, 1.2 Hz, Ph *o*). MS (EI): M$^+$ calcd for $^{12}C_{19}{}^1H_{13}{}^{16}O_2{}^{205}Tl$, 478.07; found 478.0. IR (KBr, cm^{-1}): 3148 (CH), 1538 (CO).

Synthesis of [Ru{η^5-1,2-$C_5H_3(COPh)_2$}(Cp*)] (3). THF (30 mL) was added to a Schlenk flask charged with [Tl{1,2-$C_5H_3(COPh)_2$}] (**2**, 1.013 g, 2.12 mmol) and [Ru(μ_3-Cl)(Cp*)]$_4$ (576 mg, 0.53 mmol). The reaction mixture was stirred overnight at room temperature. A pale green solution formed, and TlCl precipitated out as a white solid. The solution was filtered through Celite to remove TlCl. The Celite was then washed with approximately 20 mL of ethyl ether. The solvent was removed under reduced pressure to give a green solid. The solid was dissolved in ethyl ether and chromatographed in air on alumina (neutral, activity III) with ethyl ether as the eluent. Removal of the solvent under reduced pressure gave **3** as a yellow oil, which yielded 857 mg (79%) of air-stable solid upon scraping. Mp: 103−105 °C. ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ 1.77 (s, 15H, Cp*), 4.57 (t, 1H, $J = 2.5$ Hz, CHC*H*CH), 4.83 (d, 2H, $J = 2.5$ Hz, C*H*CHC*H*), 7.23−7.45 (m, 6H, Ph *m*, *p*), 7.7−7.8 (m, 4H, Ph *o*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, ppm): δ 10.72 ($C_5(CH_3)_5$), 76.37 (CH*C*HCH), 78.94 (*C*HCH*C*H), 87.10 ((CO)*CC*(CO)), 87.91 ($C_5(CH_3)_5$), 127.91 (Ph *o*, *m*), 128.37 (Ph *o*, *m*), 131.67 (Ph *p*), 139.39 (Ph *ipso*), 194.14 (C=O). IR (KBr, cm^{-1}): 1642 (CO). MS (EI): M$^+$ calcd for $^{102}Ru^{12}C_{29}{}^1H_{28}{}^{16}O_2$, 510.11; found 509. Anal. Calcd for $RuC_{29}H_{28}O_2$: C, 68.35; H, 5.54. Found: C, 68.52; H, 5.59.

Synthesis of [Tl{1,2-$\overline{C_5H_3(CPh)_2N_2}$}] (5). Thallium(I) ethoxide (185 mg, 0.74 mmol), weighed in a tared syringe, was added to a solution of **4** (200 mg, 0.74 mmol) in THF (about 30 mL). A yellow solid immediately precipitated. The solution was stirred for 3 h. The precipitate was filtered and washed with about 5 mL of cold ethyl ether, affording 258 mg (74%) of **5** as an air-stable yellow powder. ^{1}H NMR (200 MHz, DMSO-d_6, ppm): δ 5.60 (d, 2H, $J = 3.7$ Hz), 6.03 (t, 1H, $J = 3.7$ Hz), 6.5−6.7 (m, 6H), 7.20−7.26 (dd, 4H, $J = 7.3$, 1.5 Hz). IR (KBr, cm^{-1}): 3056 (C−H), 1387. MS (EI): M$^+$ calcd for $^{12}C_{19}{}^1H_{13}{}^{16}N_2{}^{205}Tl$, 474.08; found, 474.1.

Synthesis of [Ru{η^5-1,2-$\overline{C_5H_3(CPh)_2N_2}$}(Cp*)] (6). Method A. Hydrazine hydrate ($N_2H_4 \cdot H_2O$, 10 drops, ca. 20.6 mmol) was added to a methanolic solution (approximately 20 mL) of [Ru{η^5-1,2-$C_5H_3(COPh)_2$}(Cp*)] (100 mg, 0.20 mmol), **3**. The yellow solution was refluxed overnight and cooled to room temperature, and the solvent was removed under reduced pressure. The remaining solid was dissolved in ethyl ether and chromatographed in air on neutral alumina (activity III) with ethyl ether. The product eluted as a yellow band. Removal of the solvent under reduced pressure gave 72 mg (73%) of orange solid. Slow recrystallization from methanol at room temperature in air gave single crystals. Mp: 100 °C (dec). ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ 1.53 (s, 15H, Cp*), 4.77 (t, 1H, $J = 2.7$ Hz, CHC*H*CH), 5.25 (d, 2H, $J = 2.7$ Hz, C*H*CHC*H*), 7.4−7.55 (m, 6H, Ph *m*, *p*), 8.0−8.2 (m, 4H, Ph *o*). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6, ppm): δ 10.80 ($C_5(CH_3)_5$), 71.19 (*C*HCH*C*H), 81.87 (CH*C*HCH), 86.11 ((CO)*CC*(CO)), 100 ($C_5(CH_3)_5$), 129.21 (Ph *o*, *m*), 129.42 (Ph *o*, *m*), 130.38 (Ph *p*), 139 (Ph *ipso*), 200.11 (C=N). IR (KBr, cm^{-1}) 3122 (br, s, C−H). MS (FAB): M$^+$ calcd for $^{102}Ru^{12}C_{29}{}^1H_{29}{}^{16}N_2$, 507.13; found, 507.1. Anal. Calcd for $RuC_{29}H_{28}N_2$: C, 68.89; H, 5.58; N, 5.54. Found: C, 68.96; H, 5.63; N, 5.63

Method B. THF (30 mL) was added to a Schlenk flask charged with **5** (258 mg, 0.545 mmol) and [Ru(μ_3-Cl)(Cp*)]$_4$ (148 mg, 0.136 mmol). The reaction mixture was stirred overnight at room temperature. A brown solution formed, and TlCl precipitated as a white solid. The solution was filtered through Celite to remove TlCl. The Celite was then washed with approximately 20 mL of THF. Approximately one-half of the solvent was removed under reduced pressure. The remaining solution was chromatographed on alumina (neutral, activity III) with ethyl ether/hexane as the eluent. Removal of the solvent under reduced pressure gave **6** as 140 mg (51%) of red-brown solid. Spectra were identical to that reported for **6** using method A.

X-ray Structural Analysis of [Ru{η^5-1,2-$C_5H_3(COPh)_2$}(Cp*)] (3) and [Ru{η^5-1,2-$\overline{C_5H_3(CPh)_2N_2}$}(Cp*)] (6). The crystals for which data were collected were typical of the others in the batch, which had been grown by slow evaporation from methanol. The crystals were mounted on glass fibers using quick-dry epoxy. The long axes of the crystals were nearly aligned with the glass fibers. The structures were solved with the program package SHELXL PC[19] and refined with the program SHELXL93.[20] H atoms were included in the refinements in calculated positions ($U_H = 1.2U_{iso}$ for the attached C atom). For additional crystal data and experimental details see Table 1.

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Supporting Information Available: Tables of coordinates and *U* values for the refined atoms, all bond lengths and angles, and hydrogen atom parameters for the crystal structures of **3** and **6** (11 pages). Ordering information is given on any current masthead page.

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