NMR parameters suggest that **3** has a transoid structure too. Ruiz et al. have recently reported the synthesis of the tin analogues $Cp^*Rh(H)_2(SnR_3)_2$ and the silyl trihydride $Cp^*Rh(H)_3(SiR_3)$.[20,21] The stability of the Cp analogue **3** makes it evident that the higher oxidation state can be achieved without the more strongly donating (η^5-C_5Me_5) ligands.[22] Schubert et al. have demonstrated for a series of Mn complexes that oxidative addition can be favored either by increasing the electron density available to the metal center by the use of electron-donating ligands or by incorporating electron-withdrawing groups on the silane.[17] Therefore, should the stability of the higher oxidation state be marginal, we might expect to observe three-center [M](Si–H) bonding, but this is absent. One mechanism for preserving electroneutrality in such Rh^V complexes has been proposed by Rabaa et al. in the context of oxidative addition of silanes to other d^6 and d^8 fragments. They find theoretical evidence that a negative charge on the hydridic hydrogen is partially balanced by a positive charge on the silyl group.[23] If this principle is applicable more generally, the way should be open to synthesizing a variety of $CpRh^V$(silyl) hydrides and perhaps, even, alkyl hydrides. Moreover, the presence of equilibria between Cp^*Rh^{III} and Cp^*Rh^V complexes suggests that mechanisms involving Rh^V intermediates should be considered in oxidative addition mechanisms, e.g. for C–H or Si–H activations both with CpRh and Cp*Rh complexes.

Conclusions

We have demonstrated that **1** undergoes photochemically initiated oxidative addition of both a silicon hydride producing **2** and hydrogen producing **4**. We have isolated **2**, an intermediate of the type postulated by Chalk and Harrod in hydrosilation. A Rh^V species, **3**, has also been isolated by the photochemical oxidative addition of a second molecule of Et_3SiH to **2**. The stability of Rh^V complexes[9] of the type $Cp^*Rh^V(SiR_3)_2(H)_2$ and the Ir^V complexes,[21] such as $Cp^*Ir(CH_3)_4$, has been previously attributed to the special properties of the Cp* ligand.[22] Our experiments show that this ligand is not necessary for isolation of Rh^V complexes. We have also found evidence that **2** and **4** undergo thermal rearrangement to eliminate the saturated products ethyltrialkylsilane and ethane.

Acknowledgment. We are grateful to the SERC NMR service (Edinburgh), I. Marshall (Nottingham), and Dr. B. Mann (Sheffield) for providing high-quality NMR spectra and J. M. Whalley for technical assistance. We also acknowledge the support of SERC, The Royal Society, the EEC, Nicolet Instruments Ltd, Dow Corning, ICI New Science Group, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also appreciate helpful discussions with Dr. M. A. Healy and Prof. P. Maitlis and Prof. J. J. Turner.

Registry No. **1a**, 12211-95-9; **1b**, 112680-96-3; **1c**, 112680-97-4; **2a**, 102744-67-2; **2b**, 102744-69-4; **3a**, 102744-68-3; **3b**, 102986-79-8; **4aH**, 112680-97-4; **4aD**, 113748-33-7; **4bH**, 113748-34-8; **4cH**, 113748-35-9; Et_3SiH, 617-86-7; Me_3SiH, 993-07-7.

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Syntheses and Reactions of η^5-(Dimethylboryl)cyclopentadienyl Cobalt and Rhodium Derivatives. Site-Specific Binding of Unsaturated Amines

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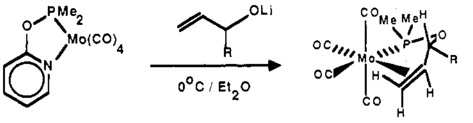
Syntheses and reactions of $(\eta^5$-$(py{\cdot}Me_2B)C_5H_4]ML_2$ complexes (M = Rh or Co; py = pyridine; C_5H_4 = η^5-cyclopentadienyl) are described. Treatment of $[(CO)_2RhCl]_2$ with $C_5H_5(BMe_2{\cdot}py)$ or $(Me_3Si)C_5H_4$-$(BMe_2{\cdot}py)$ affords $[\eta^5$-$(py{\cdot}Me_2B)C_5H_4]Rh(CO)_2$ (**2**) in 24 and 60% yields, respectively. Reaction of $(py{\cdot}BMe_2)C_5H_5$ with $Co_2(CO)_8$ provides $[\eta^5$-$(py{\cdot}Me_2B)C_5H_4]Co(CO)_2$ (**4**) in 40% yield. Substitution of **2** with triphenylphosphine affords $[\eta^5$-$(py{\cdot}Me_2B)C_5H_4]Rh(CO)(PPh_3)$. Complex **4** is converted sequentially to $[\eta^5$-$(py{\cdot}Me_2B)C_5H_4]Co(CO)I_2$ and $[\eta^5$-$(py{\cdot}Me_2B)C_5H_4]Co(PPh_3)I_2$ in high yield. Pyridine exchanges at the boron centers of both **2** and **4** are rapid on NMR time scales at ambient temperatures. The cooperative binding properties of the transition-metal and boron centers are described in the context of chelations of dimethylallylamine ($Me_2NCH_2CH{=}CH_2$) to form $[\eta^5$-$(Me_2B)C_5H_4]Co(\eta^3$-$Me_2NCH_2CH{=}CH_2)(CO)$ and $[\eta^5$-$(Me_2B)C_5H_4]Co(\eta^3$-$Me_2NCH_2CH{=}CH_2)(PPh_3)$ (**9**). The corresponding rhodium chelates cannot be prepared. Chelate **9** undergoes a photochemically mediated reaction at elevated temperatures with diphenylacetylene to afford a chelated butadiene complex, $[\eta^5$-$(Me_2B)C_5H_4]Co[\eta^5$-$R_2NCH_2CH{=}CHC$-$(Ph){=}C(Ph)H]$.

Introduction

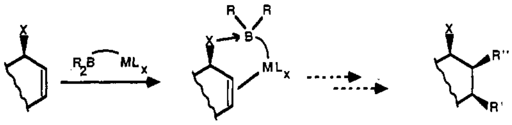
We recently began exploring new strategies for binding polyfunctional organic substrates within transition-metal coordination spheres. Our earliest efforts focussing on the use of phosphinite ester linkages to bind unsaturated alcohols under aprotic conditions met with only limited success. Despite the development of mild and highly stereoselective syntheses of phosphinite ester chelates (cf.

eq 1),[1-3] attempts to prepare chelates of more reactive metals to achieve stereocontrolled functionalizations were thwarted by facile P–O[4] and C–O bond cleavages.[4-6]



(1)

We have turned to a new strategy that uses internal Lewis acidic boranes to facilitate substrate binding (eq 2).



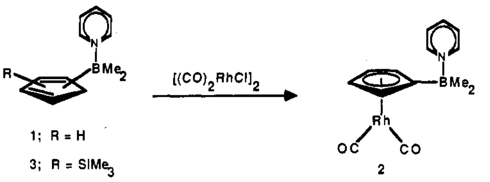
(2)

Presented herein are syntheses of [η^5-(py·Me$_2$B)C$_5$H$_4$]ML$_2$ complexes (M = Co or Rh; py = pyridine; C$_5$H$_4$ = η^5-cyclopentadienyl) and descriptions of their reactivities, including (1) reactions at the transition metal centers, (2) ligand exchanges at the boron centers, (3) the cooperative binding of allyldimethylamine involving both centers, and (4) the coupling of η^3-coordinated allyldimethylamine with diphenylacetylene.

Results

Synthesis of Cyclopentadienyldimethylborane Complexes. The numerous carbon–carbon bond-forming reactions documented for the cyclopentadienyl complexes of group 9 metals[7-9] aroused our interest in exploring the chemistry of the boron-substituted derivatives. Although a number of borylated cyclopentadienyl complexes have been reported, most are derivatives of ferrocene prepared by methods not likely to be generally applicable to other metal systems.[10,11] A number of synthesis routes to rhodium and cobalt complexes of cyclopentadienyldimethylborane were investigated, several of which are described below.[12]

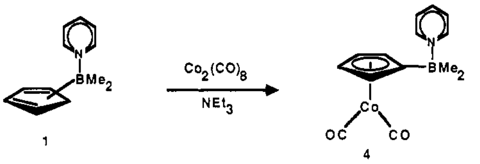
The pyridine complex of cyclopentadienyldimethylborane (C$_5$H$_5$BMe$_2$·py; 1) was prepared as a light yellow liquid in 89% distilled yield by reaction of Me$_2$BBr·py and NaCp in Et$_2$O.[13] Despite literature reports of stable alkali-metal salts of borylated cyclopentadienes,[14] we were unable to generate a stable alkali or thallium salt of 1 using a wide variety of bases or reducing agents due to facile loss of the Me$_2$B fragment.[13] Nevertheless, by stirring an ether solution of [(CO)$_2$RhCl]$_2$, pyridine, and 1 at 25 °C for 3 h, rhodium complex 2 was isolated as a red-brown solid in 24% yield after chromatography (eq 3). Alternatively, 2 was prepared in 60% yield by treatment of [(CO)$_2$RhCl]$_2$ with the trimethylsilyl-substituted reagent 3.[13] The ^{1}H NMR spectrum of 2 showed resonances characteristic of coordinated pyridine at 8.38, 6.72, and 6.37 ppm, cyclopentadienyl multiplets at 5.18 and 5.15 ppm, and a singlet for the methyl groups. The ^{13}C NMR spectrum displayed ^{103}Rh coupling of 5.5 and 81.7 Hz to the cyclopentadienyl and carbonyl carbons, respectively. The ^{11}B NMR and IR spectra and an elemental analysis were consistent with the proposed structure.



1; R = H
3; R = SiMe$_3$
2

(3)

[η^5-(py·Me$_2$B)C$_5$H$_4$]Co(CO)$_2$ (4) was most efficiently prepared as illustrated in eq 4. Heating a solution of Co$_2$(CO)$_8$ and triethylamine at 58 °C afforded analytically pure 4 as an air-sensitive red-brown solid in up to 40% yield after chromatography. The ^{1}H NMR spectrum of 4 showed resonances typical of coordinated pyridine, a pair of multiplets at 4.76 and 4.66 ppm for the cyclopentadienyl protons, and a methyl singlet at 0.58 ppm. In the ^{13}C NMR spectrum, the carbons directly attached to boron exhibited considerable broadening due to the strongly quadrupolar[15]



1
4

(4)

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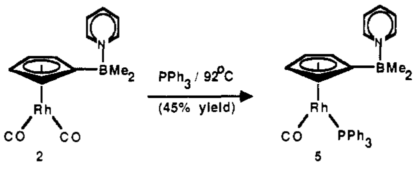
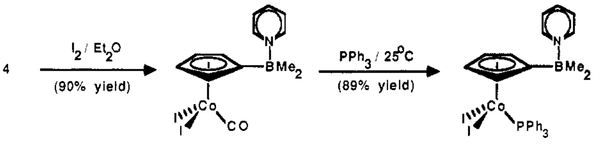
boron nucleus, appearing as a broad singlet centered at 0.58 ppm. The ^{11}B NMR spectrum consisted of a singlet at −1.6 ppm displaying a narrow peak width ($\nu_{1/2}$ = 124.4 Hz) characteristic of four-coordinate boron.[15] The IR spectrum showed CO stretching bands at 1980 and 2050 cm^{-1}.

Reactions of [η^5-(py·Me$_2$B)C$_5$H$_4$]M(CO)$_2$: Reactions at Cobalt and Rhodium. Rhodium complex 2 underwent ligand substitution characteristic of CpRh(CO)$_2$. For example, heating a benzene solution of 2 and PPh$_3$ at 92 °C for 11.5 h afforded 5 in a 45% yield as an orange solid (eq 5). The relative rates of substitution of 2 and CpRh(CO)$_2$ by triphenylphosphine were comparable, indicating only minimal electronic effects of the Me$_2$B– moiety on the rhodium center.



2 5 (5)

In contrast, thermal substitutions of cobalt complex 4 with PPh$_3$ lead to slow decomposition. Anticipating an increased reactivity of the cobalt phosphine adducts (vide infra), we explored a less direct substitution route that also provided an opportunity to further study the reactions available to 4 (eq 6).

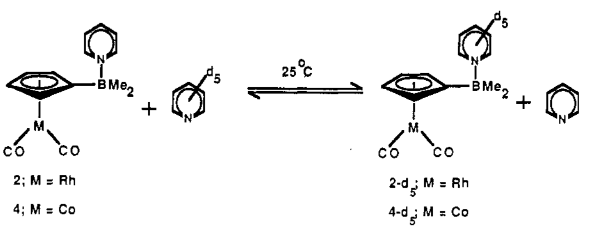


6 7 (6)

Treatment of an Et$_2$O solution of 4 with 1 equiv of iodine caused effervescence and a color change from orange to deep violet. Within minutes Co(III) diiodide 6 was isolated in >90% yield by simply evaporating the solvent in vacuo. Since 6 readily lost CO upon standing (presumably forming the halide-bridged dimer[16]), it was generally used in its crude form soon after preparation. Reaction of 6 with triphenylphosphine at 25 °C afforded 7 within 5 min as a highly insoluble blue-green crystalline solid in an 89% isolated yield. The IR spectrum showed no carbonyl stretching band.

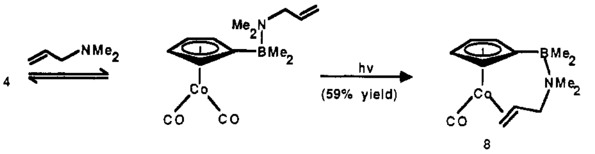
Reduction of diiodide 7 with sodium amalgam to return to the cobalt(I) oxidation state proceeds cleanly as described in a subsequent section. The general stability of the pyridine-complexed (Me$_2$B)C$_5$H$_4$ moiety to both highly oxidizing and highly reducing conditions was noted.

Reactions of [η^5-(py·Me$_2$B)C$_5$H$_4$]M(CO)$_2$: Ligand Exchange at Boron. We next explored the facility of ligand substitution at the boron centers of 2 and 4. Their thermal, photolytic, and especially chromatographic stability caused some concern that pyridine exchange rates would be very low. Nevertheless, treatment of a C$_6$D$_6$ solution of either 2 or 4 with 5.0 equiv of pyridine-d_5 at 25 °C resulted in time-averaged bound and unbound pyridine resonances (eq 7). Coalescences were observed at approximately −2 °C, below which distinct resonances for free and coordinated pyridine were readily observed.



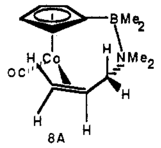
(7)

Bidentate Substrate Binding: Chelation of Allylic Amines. We next began probing the ability of 2 and 4 to selectively coordinate multifunctional organic substrates. ^{1}H NMR spectroscopic analysis on C$_6$D$_6$ solutions of 4 in the presence of 3.5 equiv of allyldimethylamine showed some evidence of reversible binding of the amino group at boron in the form of slight broadening and shifting of the pyridine and boron methyl resonances. While heating the mixture afforded intractable mixtures, photolysis at 36 °C with a 275-W sunlamp for 16 h afforded chelate 8 as an orange-brown solid in 50–60% yields after air-free chromatography (along with 15–20% unreacted 4) (eq 8).

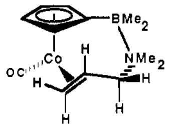


8 (8)

The chelate structure of 8 was readily apparent from the spectral asymmetry. The ^{1}H NMR spectrum of 8 exhibited four multiplets for the inequivalent cyclopentadienyl protons and four separate singlets for the diastereotopic methyl groups on nitrogen and boron. The resonances of the allyl fragment overlapped and were partially obscured by the *N*-methyl singlets in C$_6$D$_6$ solution yet could be resolved into five distinct multiplets in CDCl$_3$. The IR spectrum showed a single terminal carbonyl stretch at 1995 cm^{-1}. Analysis of molecular models indicated that there are two possible isomeric chelates, **8A** and **8B**, differing only in their olefin alignment. Despite chemical shift analogies with CpCo olefin complexes,[17] we will not attempt at this time to assign the stereochemistry of 8.

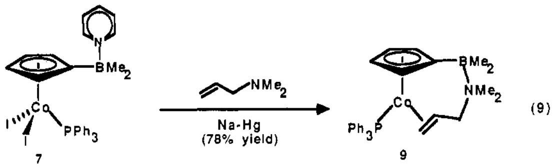


8A



8B

Attempts to synthesize phosphine- and phosphite-substituted chelates by direct thermal or photochemical substitutions produced complex mixtures. However, diiodide 7 proved to be an excellent starting material for a high yielding synthesis of chelate 9 (eq 9). Reduction of 7 (THF, 2% Na/Hg) in the presence of an excess of allyldimethylamine provided 9 as an orange solid in a 78% yield after recrystallization; no other products were visible



7 9 (9)

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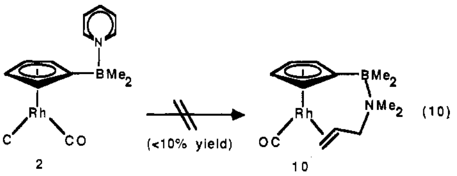
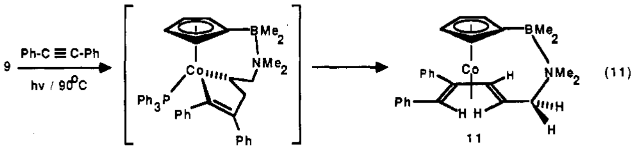
in the ^{1}H NMR spectrum of the crude reaction mixture. The spectral features of **9** were reminiscent of carbonyl containing chelate **8**. The methyl groups were diastereotopic and the cyclopentadienyl protons appeared as four separate multiplets. The olefinic protons resonated upfield between 2 and 3 ppm. In the ^{13}C NMR spectrum phosphorus coupling of 7.7 Hz to one of the cyclopentadienyl carbons and 5.5 Hz to the terminal olefinic carbon was observed. DEPT[18] (distortionless enhancement by polarization transfer) ^{13}C and J-resolved[19] ^{1}H NMR spectra and ^{1}H–^{1}H decoupling experiments allowed complete assignment of the ^{1}H and ^{13}C resonances. The ^{31}P NMR spectrum consisted of a broad singlet at 68.5 ppm. Unfortunately, the spectral data of neither chelates **8** nor **9** provided definitive stereochemical assignments, and attempts to grow crystals for molecular structure determination were not successful.[20]

We briefly explored chelations of rhodium analogue **2** with allylic amines and found them to be far less tractable. Mixing **2** and allyldimethylamine resulted in shifts in the ^{1}H NMR spectrum consistent with reversible boron–allylamine binding. However, sunlamp photolysis of the mixture afforded no further reaction, while heating the mixture at 100 °C for 40 h afforded at most traces of chelate **10** (eq 10).



[η^5-Me$_2$BC$_5$H$_4$]Co Amine Chelates: Reaction with Diphenylacetylene. Preliminary NMR scale experiments showed the amine chelates to be reactive toward a number of reagents. We will briefly describe the first to be fully characterized involving the photochemical condensation of chelate **9** with diphenylacetylene.

Sunlamp photolysis at 90 °C of a benzene solution of **9** and 1 equiv of diphenylacetylene afforded butadienyl complex **11** as an orange solid in a 47% yield after chromatography (eq 11). The ^{1}H NMR spectrum of **11** displayed four distinct cyclopentadienyl resonances, four methyl resonances, two multiplets corresponding to diastereotopic allylic protons, and three distinct vinyl resonances, all of which confirmed the chelate structure. A ^{13}C DEPT spectrum, decoupling experiments, and comparisons with known cobalt η^4-butadienyl[21] complexes completed the assignment as the E,Z isomer. A reasonable intermediate in the formation of **11** would be metallacyclopentene *i*. Although condensations to afford group 9 metallacyclopentenes are well-precedented,[8] the bimolecular versions typically require activated (electron-deficient) olefins.[22]



If more than 1 equiv of diphenylacetylene was used, small amounts of a second, unidentified organometallic product was produced. No further reaction was observed when **11** was subjected to the reaction conditions with an excess of diphenylacetylene. Not surprisingly, photolysis of **9** with allyldimethylamine and diphenylacetylene in large excess failed to provide evidence of catalytic turnover. A control experiment carried out by subjecting CpCo(PPh$_3$)$_2$,[23] allyldimethylamine, and diphenylacetylene to photolysis at 90 °C gave no evidence of butadiene products.

Discussion and Summary

Boron and aluminum Lewis acids play key roles in many important homogeneously catalyzed reactions of olefins including metatheses,[24] polymerizations,[25] hydrogenations,[26] hydroformylations,[27] and hydrocyanations.[28,29] Accordingly, there has accumulated a substantial body of literature concerned with details of transition-metal complex–Lewis acid interactions.[30–34] The borylated cyclopentadienyl derivatives[9,10] are members of a large class of compounds containing boron nuclei within the transition-metal complex.[31] However, they represent a relatively small subset in which the boron centers *retain the capacity to function as Lewis acids*.[34] The group 9 and 13 centers of the complexes described herein display their distinctly different reactivities. Despite the characteristically low ligand substitution rates of group 9 cyclopentadienyl complexes, a number of substitution and redox reactions

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could be effected at the cobalt and rhodium centers in the presence of the Me_2B moieties. Substitutions of N-donor ligands at the boron centers were fast even on NMR time scales. Indeed, it is curious that we did not observe direct evidence of transition-metal–boron interactions in light of the many group 9 $CpML_2$–Lewis acid adducts reported to date.[32]

The binding of unsaturated amines illustrated cooperativities and selectivities rivaling even the most selective transition-metal heterodinuclear complexes.[35] In the context of our long term goals to effect stereocontrolled, catalytic substrate functionalizations, the observed rapid ligand exchange at boron provided encouraging evidence that such binding would be sufficiently reversible to support a catalytic cycle. We have only briefly explored the potential of the boron–transition-metal complexes for effecting substrate functionalizations. The stoichiometric reaction of chelate **9** with diphenylacetylene to form chelated butadiene complex **11** under strenuous reaction conditions was interesting, although not very useful in its present form; the slow substitution and reaction rates at the transition-metal centers posed the most serious problems. Thus, ongoing efforts to develop highly reactive boron-containing difunctional catalysts now can be focussed upon the historically well-defined problem of enhancing the reactivity of the transition-metal center.

Experimental Section

General Data. ^{13}C NMR spectra were recorded on Varian XL-400 (100.57 MHz) or JEOL FX90Q (22.49 MHz) spectrometers; chemical shifts are reported in parts per million downfield of tetramethylsilane using the solvent resonances as secondary references. ^{1}H NMR spectra were recorded on Varian XL-200 (200 MHz), Varian XL-400 (400 MHz), and Bruker WM-300 (300 MHz) spectrometers with chemical shifts in parts per million downfield of tetramethylsilane. ^{31}P and ^{11}B NMR spectra were recorded on a JEOL FX90Q spectrometer operating at 36.23 and 28.69 MHz, respectively. Chemical shifts are reported in parts per million downfield of 85% H_3PO_4 with PCl_3 as a secondary reference for ^{31}P NMR spectra and in parts per million downfield of $BF_3{\cdot}OEt_2$ for ^{11}B NMR spectra. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer and were calibrated to the 1601 cm^{-1} absorbance of polystyrene.

Microanalyses were performed by Alfred Bernhardt Analytisches Laboratorien, Elbach, West Germany, or Schwarzkopf Microanalytical Laboratory, Woodside, NY. All manipulations of air- or moisture-sensitive compounds were performed by using standard vacuum and inert-atmosphere techniques. Photolyses were effected under argon or vacuum with a 275-W sunlamp with forced air cooling. Flash chromatography was carried out by the method of Still in a nitrogen-filled glovebox using deoxygenated solvents and silica gel.[36]

All solvents were dried and deoxygenated prior to use. Benzene, benzene-d_6, toluene, toluene-d_8, hexane, diethyl ether, and tetrahydrofuran were distilled in vacuo from solutions of sodium benzophenone ketyl. Methylene chloride and chloroform were distilled in vacuo from P_2O_5. The $Co_2(CO)_8$ was obtained from Strem and used as received. Allyldimethylamine was obtained from PCR/SCM Specialty Chemicals and distilled from CaH_2 under nitrogen before use. Dimethylbromoborane,[37] $Me_2BBr{\cdot}py$,[13] $C_5H_4(SiMe_3)BMe_2{\cdot}py$,[13] and $[(CO)_2RhCl]_2$[38] were prepared by literature methods. Other reagents were obtained from Aldrich.

Experimental Procedures. $C_5H_5BMe_2{\cdot}py$ (1). A glass bomb reactor was charged with NaCp·THF (7.3 g, 45.6 mmol), $BrBMe_2{\cdot}py$ (8.3 g, 41.5 mmol), and Et_2O (60 mL). The vessel was wrapped in aluminum foil and the mixture heated to 70 °C for 20 h. After cooling, the reaction mixture was transferred (in the glovebox) to a 100-mL flask; the solids were filtered off and washed with Et_2O until white. The solvent was removed from the filtrate in vacuo, and the residue was distilled through a 15-cm Vigreaux column under vacuum (10^{-2} mm). Collection of the fraction distilling at 60–62 °C gave 6.8 g of **1** (88.7% yield) as a viscous yellow liquid: ^{1}H NMR (200 MHz, C_6D_6) δ 8.25 (br, 2 H), 6.85 (m, 1 H), 6.64 (m, 5 H), 6.33 (m, 2 H), 3.02 (s, 1 H), 0.61 (s, 6 H); $^{13}C\{^1H\}$ NMR (22.49 MHz, C_6D_6) δ 145.0 (s), 138.4 (s), 133.7 (s), 132.9 (s), 131.7 (s), 124.4 (br), 44.8 (s), 11.7 (br), $^{11}B\{^1H\}$ NMR (C_6D_6) δ −0.34 ($\nu_{1/2}$ = 122.8 Hz); IR (C_6D_6) 3300 (m), 3090 (s), 1270 (m), 1120 (m), 1055 (s), 1015 (s), 930 (m), 750 (s) cm^{-1}.

$[\eta^5$-(py·$Me_2B)C_5H_4]Rh(CO)_2$ (2). Method 1. A solution of $[(CO)_2RhCl]_2$ (0.450 g, 1.15 mmol) in benzene (20 mL) was cooled to 0 °C, and **3** (0.743 g, 2.89 mmol) was added. The mixture was warmed to ambient temperature and stirred under Ar for 3 h, and the volatiles were removed in vacuo to leave a dark red oil. Flash chromatography in the glovebox (60% Et_2O/hex) gave 480 mg of **2** (60% yield) as a red-brown solid: ^{1}H NMR (200 MHz, C_6D_6) δ 8.38 (m, 2 H), 6.72 (m, 1 H), 6.37 (m, 2 H), 5.18 (dd, J_{HH} = 1.3, 1.3 Hz, 2 H), 5.15 (dd, J_{HH} = 1.7, 1.8 Hz, 2 H), 0.59 (s, 6 H); $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6) δ 195.0 (d, J_{RhC} = 81.7 Hz), 145.3 (s), 138.9 (s), 124.6 (s), 90.8 (d, J_{RhC} = 5.5 Hz), 87.3 (d, J_{RhC} = 5.4 Hz), 7.4 (br); $^{11}B\{^1H\}$ NMR (C_6D_6) δ −1.90 ($\nu_{1/2}$ = 127.7 Hz); IR (C_6D_6) ν(CO) 1990 (s), 2065 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{15}BNO_2Rh$: C, 49.02; H, 4.41; N, 4.08. Found: C, 48.84; H, 4.40; N, 4.20.

Method 2. A solution of $[(CO)_2RhCl]_2$ (0.806 g, 2.07 mmol) in Et_2O (25 mL) at 0 °C was treated with **1** (0.767 g, 4.15 mmol) and pyridine (0.328 g, 4.15 mmol). The mixture was warmed to ambient temperature and stirred under Ar for 45 min. Workup as above gave 347 mg of **2** (24% yield).

$[\eta^5$-(py·$Me_2B)C_5H_4]Co(CO)_2$ (4). A glass bomb reactor was charged with a solution of $Co_2(CO)_8$ (12.8 g, 37.4 mmol) in CH_2Cl_2 (100 mL), triethylamine (4.8 g, 47.4 mmol), and **1** (8.75 g, 47.4 mmol). The reaction vessel was wrapped in aluminum foil and the mixture heated at 70 °C for 14 h under partial vacuum. The reaction mixture was then transferred to a 250-mL round-bottom flask, the volatiles were removed in vacuo, and the residue was extracted well with Et_2O. Chromatography as above gave 4.5 g of **4** (40% yield): ^{1}H NMR (200 MHz, C_6D_6) δ 8.39 (m, 2 H), 6.62 (m, 1 H), 6.30 (m, 2 H), 4.76 (dd, J_{HH} = 1.9, 1.9 Hz, 2 H), 4.66 (dd, J_{HH} = 1.9, 1.9 Hz, 2 H), 0.58 (s, 6 H); $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6) δ 208.5 (s), 145.6 (s), 139.5 (s), 125.3 (s), 119.8 (br), 88.6 (s), 85.2 (s), 12.8 (br); $^{11}B\{^1H\}$ NMR (C_6D_6) δ −1.63 ($\nu_{1/2}$ = 124.1 Hz); IR (C_6D_6) ν(CO) 1980 (s), 2050 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{15}BCoNO_2$: C, 56.23; H, 5.06; N, 4.71. Found: C, 56.18; H, 4.98; N, 4.53.

$[\eta^5$-(py·$Me_2B)C_5H_4]Rh(CO)PPh_3$ (5). A glass bomb reactor charged with **2** (0.200 g, 0.58 mmol), PPh_3 (0.372 g, 1.41 mmol), and benzene (40 mL) was partially evacuated and heated to 92 °C for 11.5 h. After cooling, the homogeneous orange solution was transferred to a 50-mL flask and the volatiles were removed in vacuo to leave a red oil. Dissolution in Et_2O and addition of hexane caused an orange solid to precipitate. Reduction of the volume of solvent, cooling to 0 °C, filtration, and drying in vacuo gave 150 mg of **5** (45% yield) as an orange solid: ^{1}H NMR (200 MHz, C_6D_6) δ 8.68 (m, 2 H), 7.82 (m, 6 H), 7.17 (m, 9 H), 6.71 (m, 1 H), 6.39 (m, 2 H), 5.23 (m, 2 H), 5.10 (m, 2 H), 0.80 (s, 6 H); $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6) δ 184.6 (dd, J_{RhC} = 68.9 Hz, J_{PC} = 19.0 Hz), 142.4 (s), 136.9 (s), 136.6 (s), 136.2 (s), 133.0 (d, J_{PC} = 11.6 Hz), 129.3 (s), 125.0 (s), 122.6 (br), 97.6 (d, J_{RhC} = 4.5 Hz), 96.9 (d, J_{RhC} = 4.9 Hz), 36.2 (br); $^{11}B\{^1H\}$ NMR (C_6D_6) δ 5.1 ($\nu_{1/2}$ = 1061.4 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 52.8 (d, J_{RhP} = 200.2 Hz); IR (C_6D_6) ν(CO) 1960 (s) cm^{-1}. Anal. Calcd for $C_{31}H_{30}BNORh$: C, 64.50; H, 5.24; N, 2.43. Found: C, 64.37; H, 5.08; N, 2.60.

$[\eta^5$-(py·$Me_2B)C_5H_4]Co(CO)I_2$ (6). To a solution of **4** (1.53 g, 5.12 mmol) in Et_2O (25 mL) at 25 °C was added iodine (1.62 g, 6.4 mmol). The solution immediately turned purple and vigorously evolved gas. After being stirred under Ar at 25 °C for 2 h, the dark purple mixture was filtered and the volatiles were removed in vacuo to leave 2.42 g of **6** (90% yield) as a sticky dark purple solid which was sufficiently pure for synthetic purposes: ^{1}H NMR (300 MHz, C_6D_6) δ 8.21 (m, 2 H), 6.79 (m, 1 H), 6.52 (m, 2 H),

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5.20 (dd, J_{HH} = 1.8, 1.9 Hz, 2 H), 4.57 (dd, J_{HH} = 2.0, 1.9 Hz, 2 H), 0.39 (s, 6 H); $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6) δ 145.6 (s), 140.4 (s), 125.7 (s), 93.0 (s), 91.6 (s), 12.1 (br); $^{11}B\{^1H\}$ NMR (C_6D_6) δ -3.4 ($\nu_{1/2}$ = 279 Hz); IR (C_6D_6) ν(CO) 2110 cm^{-1}.

[η^5-(py·Me_2B)C_5H_4]$CoI_2(PPh_3)$ (7). Triphenylphosphine (0.420 g, 1.60 mmol) was dissolved in Et_2O (25 mL) at 25 °C, and **6** (0.815 g, 1.47 mmol) was added. Gas evolution was seen immediately, and after about 5 min a blue-green solid began to precipitate. After being stirred for 5 h, the solids were filtered off and dried in vacuo. Recrystallization of the solid from CH_2Cl_2/hexane gave 1.31 g of **7** (89% yield) as a blue-green solid: ^1H NMR (200 MHz, $CDCl_3$) δ 9.38 (br, 2 H), 8.10–7.30 (m, 18 H), 5.40 (m, 2 H), 3.75 (m, 2 H), 0.45 (s, 6 H); IR (C_6D_6) 2900 (w), 1450 (w), 1100 (w), 920 (vs), 710 (vs) cm^{-1}. Anal. Calcd for $C_{30}H_{30}BCoI_2NP$: C, 47.47; H, 3.98; N, 1.85. Found: C, 47.27; H, 3.85; N, 1.74.

[η^5-(Me_2B)C_5H_4]Co(η^3-$Me_2NCH_2CH{=}CH_2$)(CO) (8). A Pyrex Schlenk tube was charged with **4** (0.200 g, 0.67 mmol), allyldimethylamine (0.202 g, 2.37 mmol), and benzene (5 mL). The mixture was photolyzed (275 W sunlamp) at 36 °C under 1 atm of Ar for 16 h. After 2 h liberated CO was removed by means of two freeze–pump–thaw cycles. When photolysis was complete, the volatiles were removed in vacuo and the residue chromatographed (40% Et_2O/hex) in a glovebox to give 110 mg of **8** (59% yield) as an orange-brown solid: ^1H NMR (300 MHz, C_6D_6) δ 5.30 (m, 1 H), 5.20 (m, 1 H), 4.95 (m, 1 H), 3.47 (m, 1 H), 2.20 (s, 3 H), 2.13 (m, 3 H), 1.73 (s, 3 H), 1.68 (m, 2 H), 0.11 (s, 3 H), –0.21 (s, 3 H); ^1H NMR (400 MHz, $CDCl_3$) δ 5.46 (m, 1 H), 5.34 (m, 1 H), 5.21 (m, 1 H), 3.65 (m, 1 H), 3.01 (dd, J_{HH} = 11.0, 4.5 Hz, 1 H), 2.89 (s, 3 H), 2.52 (s, 3 H), 2.47 (dddd, J_{HH} = 10.5, 10.4, 7.8, 4.5 Hz, 1 H), 2.28 (d, J_{HH} = 10.5 Hz, 1 H), 2.21 (dd, J_{HH} = 11.0, 10.4 Hz, 1 H), 2.09 (d, J_{HH} = 7.8 Hz, 1 H), –0.04 (s, 3 H), –0.32 (s, 3 H); $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6) δ 204.4 (br), 110.9 (br), 92.1, 88.2, 85.6, 84.2, 64.1, 48.1, 43.2, 41.1, 32.4, 6.5 (br); $^{11}B\{^1H\}$ NMR (C_6D_6) δ –5.4 ($\nu_{1/2}$ = 63.9 Hz); IR (C_6D_6) ν(CO) 1995 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{21}BCoNO$: C, 56.35; H, 7.64; N, 5.06. Found: C, 56.22; H, 7.47; N, 4.92.

[η^5-(Me_2B)C_5H_4]Co(η^3-$Me_2NCH_2CH{=}CH_2$)(PPh_3) (9). To a solution of **7** (0.325 g, 0.410 mmol) in THF (15 mL) at –78 °C was added 2% Na/Hg (1.43 g, 1.24 mmol Na) and allyldimethylamine (0.351 g, 4.1 mmol). The heterogeneous mixture was allowed to warm to 25 °C and stirred under Ar for 2 h. The volatiles were then removed in vacuo, the residue was extracted with benzene, and the insoluble materials were filtered off. Evaporating the benzene in vacuo left an orange foam which was recrystallized from hexane to provide 320 mg of **9** (78% yield) as an orange solid: ^1H NMR (400 MHz, C_6D_6) δ 7.69 (m, 6 H), 7.06 (m, 12 H), 5.58 (m, 1 H), 5.21 (m, 1 H), 4.14 (m, J_{PH} = 3.1 Hz, 1 H), 3.59 (m, 1 H), 2.78 (s, 3 H), 2.23 (dd, J_{HH} = 12.2, 5.4 Hz, 1 H), 2.15 (dd, J_{HH} = 9.8 Hz, J_{PH} = 1.0 Hz, 1 H), 2.04 (dd, J_{HH} = 12.2, 10.2 Hz, 1 H), 1.92 (s, 3 H), 1.22 (dd, J_{HH} = 7.3 Hz, J_{PH} = 8.5 Hz, 1 H), 0.90 (dddd, J_{HH} = 10.2, 9.8, 7.3, 5.4 Hz, 1 H), 0.41 (s, 3 H), 0.07 (s, 3 H); $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6) δ 136.3 (d, J_{PC} = 35.5 Hz), 134.0 (d, J_{PC} = 11.1 Hz), 132.0 (d, J_{PC} = 90.5 Hz), 129.2 (s), 107.4 (br), 87.7 (s), 86.3 (s), 85.8 (d, J_{PC} = 7.7 Hz), 83.0 (s), 65.7 (s), 48.2 (s), 43.6 (s), 37.0 (s), 27.3 (d, J_{PC} = 5.3 Hz), 8.7 (br), 7.0 (br); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 68.5 (s); $^{11}B\{^1H\}$ NMR (C_6D_6) δ –4.4 ($\nu_{1/2}$ = 502.2 Hz); IR (C_6D_6) 3100 (s), 1960 (m), 1475 (m), 1425 (s), 1280 (m), 1085 (s), 1055 (m), 1050 (m), 742 (s), 690 (s) cm^{-1}. Repeated attempts at analysis provided highly variable results registering low percentages of C, H, and N in each instance.

[η^5-(Me_2B)C_5H_4]Co(η^5-$Me_2NCH_2CH{=}CHC(Ph){=}C(Ph)H$) (11). A Pyrex tube charged with **9** (0.15 g, 0.29 mmol), diphenylacetylene (0.052 g, 0.29 mmol), and benzene (3 mL) was irradiated with a 275-W sunlamp at 90 °C for 21.5 h. The solvent was removed in vacuo and the residue chromatographed in a glovebox (10% Et_2O/hex) to give 59 mg (47% yield) of **11** as an orange solid: ^1H NMR (400 MHz, C_6D_6) δ 7.77 (m, 2 H), 7.20–7.00 (m, 8 H), 5.60 (m, 1 H), 4.60 (d, J_{HH} = 6.8 Hz, 1 H), 4.40 (m, 1 H), 4.19 (m, 1 H), 4.11 (m, 1 H), 2.19 (s, 3 H), 2.02 (dd, J_{HH} = 12.5, 10.8 Hz, 1 H), 1.88 (dd, J_{HH} = 12.5, 4.9 Hz, 1 H), 1.84 (s, 3 H), 0.98 (s, 1 H), 0.22 (s, 3 H), 0.00 (s, 3 H), –0.06 (ddd, J_{HH} = 10.8, 6.8, 4.9 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6) δ 146.4 (s), 142.0 (s), 131.8 (s), 130.4 (s), 129.7 (s), 129.4 (s), 125.0 (s), 98.9 (s), 96.0 (s), 85.5 (s), 83.3 (s), 82.7 (s), 82.2 (s), 63.7 (s), 53.0 (s), 49.8 (s), 45.3 (s), 41.7 (s), 7.4 (br s); $^{11}B\{^1H\}$ NMR (C_6D_6) δ –4.7 ($\nu_{1/2}$ = 279.0 Hz); IR (C_6D_6) 2800 (m), 2180 (m), 1020 (m), 800 (s), 700 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{31}BCoN$: C, 73.07; H, 7.31. Found: C, 72.39; H, 7.10.

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