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Polyazolyl Chelate Chemistry. 12.[1] An Unusual Mode of Coordination for the Hydrotris(methimazolyl)borato Ligand

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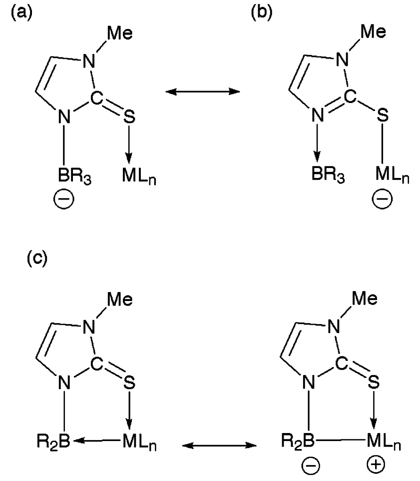
The reactions of $[RuHCl(CO)(PPh_3)_3]$ or $[RuH(NCMe)_2(CO)(PPh_3)_2]ClO_4$ with $Na[HB(mt)_3]$ (mt = methimazolyl) provide the structurally characterized complex $[RuH(CO)(PPh_3)\{\kappa^3\text{-}H,S,S''\text{-}HB(mt)_3\}]$, which hydrogenates ethynylbenzene to styrene with formation of the ruthenaboratrane $[Ru(CO)(PPh_3)\{B(mt)_3\}](Ru{\rightarrow}B)$.

Introduction

Although complexes with metal to boron dative bonds (M→B) have long been proposed,[2,3] the first structurally characterized example has only been reported recently[4] and involves a transannular Ru→B bond within a cage supported by three methimazolyl (mt) buttresses. This unusual complex, a *ruthenaboratrane*, arises from reactions of the salt $Na[HB(mt)_3]$ (mt = methimazolyl, Chart1)[5] with a range of organoruthenium precursors $[RuRCl(CO)(PPh_3)_2]$ (Scheme 1; R = CH=CH$_2$, CH=CHPh, Ph). The original targets of this reaction were organometallic complexes of the form $[RuR(CO)(PPh_3)\{HB(mt)_3\}]$ (**1**) by analogy with syntheses of the compounds $[RuR(CO)(PPh_3)\{HB(pz)_3\}]$ (**2**: pz = pyrazolyl)[6] and $[RuR(CO)(PPh_3)([9]aneS_3)]PF_6$ (**3·PF$_6$**: [9]aneS$_3$ = 1,4,7-trithiacyclononane).[7] Indeed, it was the topological similarity between **1**, **2**, and **3**$^+$ that led us to propose the intermediacy of **1** in the formation of the ruthenaboratrane $[Ru(CO)(PPh_3)\{B(mt)_3\}]$*(Ru→B)* (**4**) (Scheme 1). Intermediates of composition $[RuR(CO)(PPh_3)\{HB(mt)_3\}]$ could be isolated when the reactions were carried out in diethyl ether suspension; however their dissolution in any solvents for spectroscopic characterization resulted in spontaneous formation of **4**. Herein we wish to report further work aimed at elucidating the mechanism of formation of **4**. Our approach is guided by the principle that elimination of dihydrogen from a *cis*-dihydrido complex is generally less facile than hydrocarbon elimination from a *cis*-organylhydrido complex, possibly allowing the observation of intermediates.

Chart 1. (a) Thione and (b) Thiolate Canonical Forms for HB(mt)$_3$ Coordination and (c) B(mt)$_3$ Coordination



Results and Discussion

The synthesis of the desired hydrido complex $[RuH(CO)(PPh_3)\{HB(mt)_3\}]$ (**5**) was based on analogy with those of $[RuH(CO)(PPh_3)\{HB(pz)_3\}]$[8] and $[RuH(CS)(PPh_3)([9]aneS_3)]PF_6$.[9] Thus solutions of either $[RuH(CO)(NCMe)_2(PPh_3)_2]ClO_4$[10] or $[RuHCl(CO)(PPh_3)_3]$[11] in tetrahydrofuran react with $Na[HB(mt)_3]$ to provide a compound of composition $[RuH(CO)(PPh_3)\{HB(mt)_3\}]$ (**5**). The former salt reacts at room temperature, although isolated yields are lower than from the neutral precursor, which however requires heating under reflux for 2−3 min. Spectroscopic data for the new complex

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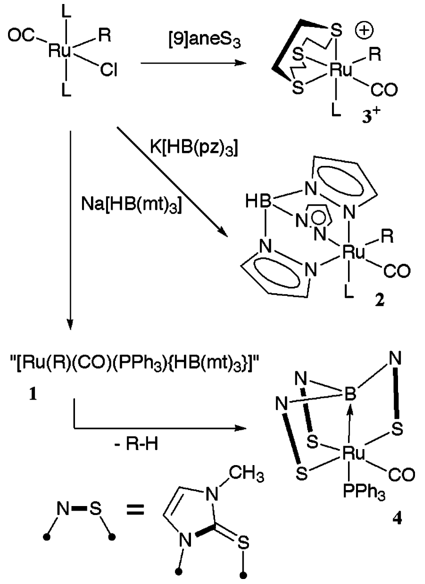
Scheme 1. Reactions of $RuRCl(CO)L_2$ with Facially Tridentate Ligands (R = vinyl, aryl; L = PPh_3)



are consistent with the gross formulation. Thus a molecular ion is observed in the FAB mass spectrum in addition to peaks attributable to the $RuB(mt)_x$ (x = 2, 3) fragments. A single resonance is observed in the ^{31}P-{^1H} NMR spectrum (58.10 ppm), suggesting a monophosphine complex, as does integration of the ^1H NMR spectrum. The ^{13}C{^1H} NMR spectrum reveals three distinct chemical environments for the mt arms, and this is also reflected in the ^1H NMR spectrum, which features six doublets for the aromatic mt protons. These data are consistent with facial coordination through three sulfur donors to the chiral *fac*-$RuH(CO)(PPh_3)$ group; however the curious high-field region of the ^1H NMR spectrum suggests that this is not the case: at room temperature this comprises a broad singlet [−14.34 ppm, half-height width 0.27 ppm] and a broad quartet centered at −3.87 ppm [$^1J(BH) = 82$ Hz]. Each of these signals integrates for one proton. At −40 °C the former is resolved into a doublet with coupling typical of a *cis*-^1H−Ru-^{31}P arrangement [26.73 Hz], while the latter is broadened beyond resolution of $^1J(BH)$ [Figure 1]. The latter resonance we assign to the borohydride group, given that no attributable resonance is observed to low field of $SiMe_4$. The resolution of the B−H−Ru quartet signal at higher temperatures is presumably a simple case of thermal decoupling of the boron quadrupole; however at present we have no explanation for the sharpening of the Ru−H resonance at low temperature, since we have no evidence for the operation of fluxional processes. The complex [RuH(cod){κ^3-*H*,*N*,*N*′-$H_2B(pz\text{-}Me_2)_2$}][12] might have provided a benchmark for interpreting these data; however the chemical shifts for the BH_2 protons were not reported. However, the resonance due to the terminal ruthenium hydride was observed as a singlet, with no reported coupling to the *trans* B−H−Ru hydrogen. This observation supports our interpretation that the coupling observed for the Ru−H resonance of **5** is due to the *cis* phosphorus and not the *trans* B−H···Ru hydrogen. Although an agostic B−H−Cd interaction is observed in the solid state for the complex [Cd{κ^3-*H*,*S*,*S*″-$HB(mt)_2(pz)$}$_2$],[13] this geometry appears not to be retained in solution, given that the broad B−H resonance appears at δ 4.90. The complex [$Re(CO)_3${κ^3-$H_2B(mt)_2$}][14] gives rise to two borohydride resonances at δ 4.50 (terminal) and −6.40 (B−H···Re), although B−H coupling is not resolved in either case. However, the resolution of B−H coupling is a feature of exopolyhedral agostic coordination of carbaboranes across metal−metal bonds,[15] e.g., the complex [WRu(μ-CMe)(μ: η^5,σ^1-$C_2B_9H_9Me_2$)$(CO)_3$(η-C_5H_5)] [B−H−Ru: δ −11.5, $^1J(BH)$ 70 Hz].[16]

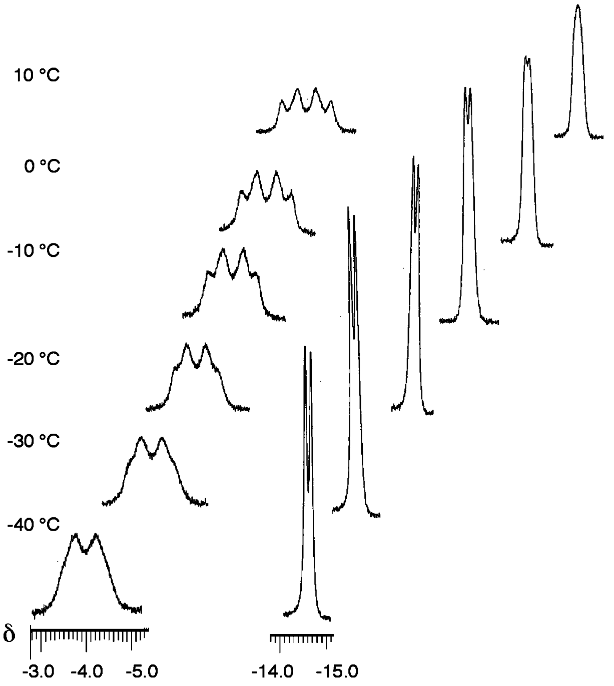


Figure 1. Variable-temperature ^1H NMR spectra for **5**.

The molecular geometry of **5** (solvate-free form; see Experimental Section) is depicted in Figure 2, which reveals an essentially octahedral arrangement of the six donor atoms with interligand *cis* angles in the range 84.2(17)−97.9(14)°, the largest of these being between the carbonyl carbon and the agostic B−H(2) hydrogen atom. The carbonyl and phosphine ligands are unremarkable, other than to note that one *ortho* hydrogen of a phenyl group points toward the terminal hydride ligand [H(1)···H(29A) 2.28 Å]. This approach indicates a possible hydrogen-bonding interaction that influences the pitch of the PPh_3 propeller. The B−H(2)···Ru and terminal Ru−H(1) hydrogen atoms were located and refined. The terminal Ru−H(1) separation of 1.50(5) Å is marginally (6σ) shorter than that between ruthenium and the agostically coordinated hydrogen [Ru−H(2): 1.75(4) Å], which has a B−H(2) bond length of 1.29(5) Å [Ru−H(2)−B 137(4)°]. The $HB(mt)_2Ru$ "boat" arrangement places the boron 2.829(5) Å from ruthenium

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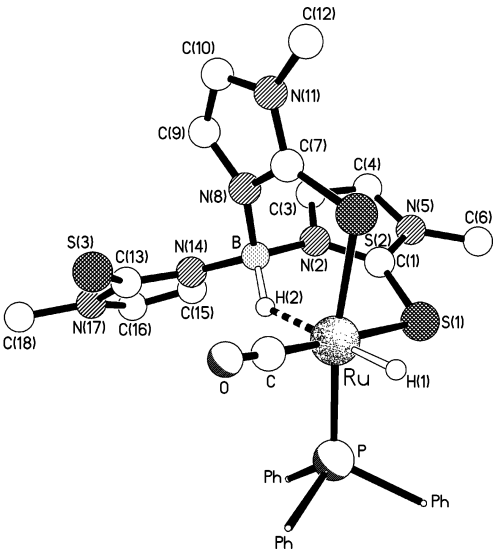

Figure 2. Molecular structure of **5** (phenyl groups omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C 1.851(5), Ru−P 2.2824(15), Ru−S(1) 2.4448(11), Ru−S(2) 2.470(2), C−Ru−P 92.7(2), C−Ru−S(2) 86.4(2), S(1)−Ru-S(2) 91.63(6), P−Ru−S(1) 88.91(6), N(8)−B−N(2) 108.9(4), N(8)−B−N(14) 111.9(4), N(14)−B−N(2) 109.1(4).

and does not appear to involve any unusual bond lengths or angles. The boron center is approximately coplanar (maximum deviation 0.16 Å) with N2, N8, and N14, with the chelate mt rings inclined to each other by ca. 83°. The metal center is noticeably displaced out of each of these planes, by 0.64 Å for the C(1) ring plane and 0.93 Å for the C(7) ring plane. A differential *trans* influence is revealed between the phosphine and carbonyl ligands, such that the Ru−S(1) bond *trans* to the π-acidic carbonyl ligand [2.4448(11) Å] is contracted relative to that *trans* to the phosphine [Ru−S(2) 2.4693(14) Å]. Although this contraction is marginal, it is probably underexpressed, given that S(1) is *cis* to the bulky phosphine ligand. The pendant mt group does not thread between the two coordinated mt groups since this would bring the sulfur into steric conflict with two of the phosphine phenyl groups. Rather, the sulfur points between the carbonyl, phosphine, and, sterically modest, hydride ligands, but lies outside any intramolecular bonding interactions.

In complexes of the dihydrobis(pyrazolyl)borate ligands, the agostic coordination of one B−H group is a recurrent feature, especially for derivatives of 3,5-dimethylpyrazole and other sterically demanding variants.[12,17] More recently, bis(methimazolyl)borates have also been observed to adopt such a coordination mode,[13,14,18] and Parkin has observed that the coordination of the hybrid ligand HB(pz)(mt)$_2$ to cobalt(II) occurs through two sulfur and one agostic B−H−Co interaction.[13] The adoption of a κ^3-*H,S,S′* coordination for the HB(mt)$_3$ ligand is however unprecedented and somewhat unexpected for a thiophilic center such as divalent ruthenium. This may, however, be traced to the less than ideal "grasp" of the HB(mt)$_3$ ligand when compared to pyrazolyl-derived ligands, which can easily accommodate a local C_{3v}-B(NN)$_3$M geometry. The inclusion of an extra atom in the buttresses of the HB(mt)$_3$ ligand by geometrical necessity inflicts a distortion to a C_3−B(NCS)$_3$M arrangement. Thus in the present case, this would appear to be less favorable than adoption of the more compact κ^3-*H,S,S′* coordination, which allows the boron and ruthenium to approach coplanarity with two of the mt rings.

Our original motivation was the elucidation of the mechanism of formation of **4**. With the establishment of the κ^3-*H,S,S′* coordination mode for **5**, we now find no evidence to suggest that the κ^3-*S,S,S″* mode of coordination is involved in the formation of **4**. Thus it appears reasonable that direct formation of [RuR(CO)(PPh$_3$){κ^3-*H,S,S′*-HB(mt)$_3$}] probably occurs prior to B−H activation. The agostic B−H−Re coordination in the complex [Re(CO)$_3${κ^3-*H,S,S′*-H$_2$B(mt)$_2$}] has been shown to be labile, allowing facile addition of ligands to provide the simple chelate complexes [Re(CO)$_3$(L){κ^2- *S,S′*-H$_2$B(mt)$_2$}] (L = CO, CNCMe$_3$, pyNMe$_2$-4, PPh$_3$).[14] The possibility that **5** could serve as a "masked" 16-electron hydrido complex was therefore investigated since such species have a rich alkyne hydrometalation chemistry.[19] Treating a dichloromethane solution of **5** [ν(CO): 1948 cm^{-1}] with ethynylbenzene resulted in a slow but clean conversion (23 h) to the ruthenaboratrane **4** [ν(CO): 1894 cm^{-1}]. A control experiment over the same time period in the absence of ethynylbenzene revealed no ruthenaboratrane formation within spectroscopically detectable limits. We thus assume that dissociation of the B−H−Ru linkage provides a vacant coordination site for alkyne coordination. This is then followed by hydroruthenation to provide the intermediate [Ru(CH═CHPh)(CO)(PPh$_3$){κ^3-*H,S,S′*-HB(mt)$_3$}], which subsequently undergoes B−H addition followed by styrene reductive elimination (Scheme 2). Given that the elimination of styrene from preformed "[Ru(CH═CHPh)(CO)(PPh$_3$){HB(mt)$_3$}]" is rapid,[4] we are inclined to suspect that it is the dissociation of the agostic B−H−Ru bond that is rate limiting.

Although no conversion of **5** to **4** was observed in dichloromethane under ambient conditions, the reaction of [RuHCl(CO)(PPh$_3$)$_3$] with Na[HB(mt)$_3$] in toluene under reflux provides, after 2 h, a separable mixture of **4** and **5**. The difference between the hydride ligand in **5** and a σ-vinyl ligand in [Ru(CH═CHPh)(CO)(PPh$_3$){HB(mt)$_3$}] would be modest with respect to its effect on the facility of B−H oxidative addition.[20,21] Thus the more forcing conditions required for the formation of **4** from **5** may be attributed, as originally presumed, to the comparative reluctance of MH$_2$ versus MHR reductive elimination.[21] The thermolysis of preisolated **5** was also investigated and found to only slowly occur in refluxing tetrahydrofuran, with approximately 65% conversion in 20 h. Notably, **4** fails to react with

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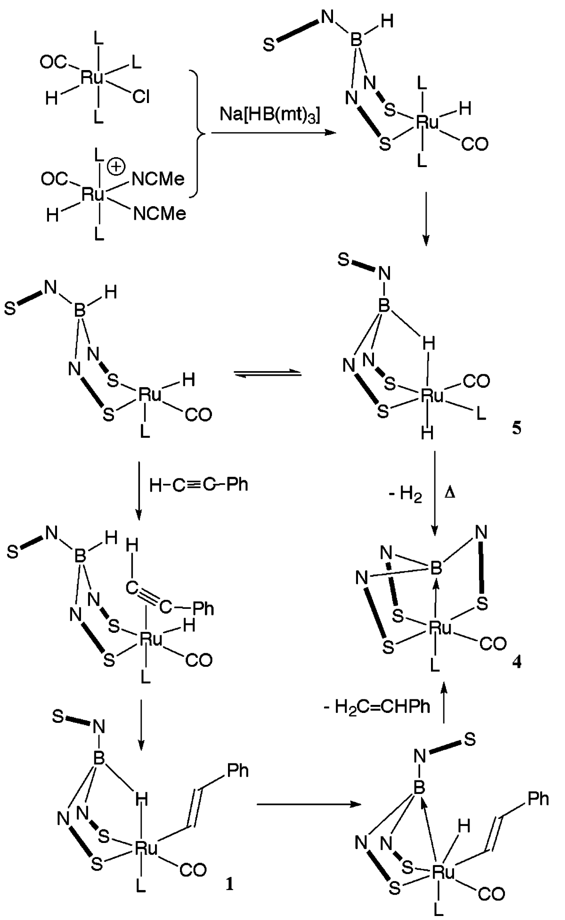
Scheme 2[a]



[a] L = PPh$_3$.

hydrogen at ambient temperatures and pressures to re-form **5**. This is a disappointing result given the attractive prospect of the B→Ru bond serving as a reservoir for heterolytic dihydrogen activation.

Conclusions

The above results suggest that, in certain circumstances, the geometrical constraints of a bicyclo[3.3.3] HB(NCS)$_3$M unit may disfavor the κ^3-*S,S′,S″* mode of HB(mt)$_3$ coordination, relative to the more compact κ^3-*H,S,S′* bicyclo[1.3.3] (mt)B(H)(mt)$_2$M arrangement involving an *agostic* B−H−M buttress (a "heteroscorpionate"). In the present case this *agostic* coordination is apparently labile, allowing access of ethynyl benzene to the metal center for a subsequent hydrometalation process. Although the HB(mt)$_3$ ligand is a somewhat exotic borane, these steps involving Ru−H and B−H transfers to ethynyl benzene provide further models for interpreting the mechanism(s) of metal-catalyzed hydroboration and hydrogenation.[20−22] The facility of formation of the ruthenaboratrane and the failure of the resulting Ru→B bond to be cleaved reversibly by hydrogen once again illustrate the tenacity of this interaction, at least in the present system. This we attribute to the electronically ideal situation that arises from the "coordination" of a five-coordinate d^8-metal center to a Lewis acid, resulting in octahedral coordination at the metal. In this respect isoelectronic analogies with Parshall's complex Na[Re(BH$_3$)(CO)$_5$]$^-$*(Re → B)*[2] and Pomeroy's demonstration of the Lewis basicity of [Os(CO)$_5$] (and related isonitrile and phosphine derivatives) in forming [(OC)$_5$OsML$_n$]*(Os → M)* adducts[23] appear germane.

Experimental Section

General Procedures. The compounds [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]ClO$_4$,[10] [RuHCl(CO)(PPh$_3$)$_3$],[11] and Na[HB(mt)$_3$][4] were prepared according to published procedures. Conventional Schlenk and vacuum line techniques were employed for the exclusion of air during reactions; however workup was generally performed under air. Tetrahydrofuran, toluene (Na, Ph$_2$C=O), and dichloromethane (CaH$_2$) were distilled under nitrogen from the indicated drying agents. Elemental microanalytical data were obtained commercially from the University of North London analytical service.

Synthesis of [RuH(CO)(PPh$_3$){HB(mt)$_3$}] (5). (a) A mixture of [RuHCl(CO)(PPh$_3$)$_3$] (0.51 g, 0.54 mmol) and Na[HB(mt)$_3$] (0.22 g, 0.58 mmol) in tetrahydrofuran (30 mL) was heated under reflux for 3 min and then allowed to cool to room temperature and freed of volatiles under reduced pressure, providing a yellow-green residual solid. The residue was extracted with dichloromethane (3 × 10 mL), and the combined extracts were filtered through diatomaceous earth. The filtrate was diluted with ethanol (30 mL) and then the solution concentrated under reduced pressure to ca. 10 mL to provide a pale yellow suspension. The supernatant was removed by cannula filtration and the precipitate washed with ethanol (2 × 5 mL) and dried in vacuo. Yield: 0.36 g (0.48 mmol, 90%). This procedure repeated on a larger scale gave 2.75 g (98%) of **5** from [RuHCl(CO)(PPh$_3$)$_3$] (3.60 g) and Na[HB(mt)$_3$] (2.75 g). (b) A mixture of [RuH(NCMe)$_2$(CO)(PPh$_3$)$_2$]ClO$_4$ (0.25 g, 0.30 mmol) and Na[HB(mt)$_3$] (0.12 g, 0.31 mmol) in tetrahydrofuran (70 mL) was stirred at room temperature for 1 h. The reaction was monitored using solution IR spectroscopy, observing the replacement of the absorption due to the starting salt [ν(CO): 1962 cm^{-1}] with that of the product. The solvent was then removed under reduced pressure and the residue purified as in (a) above. Yield: 0.13 g (56%). The reaction could also be carried out as a suspension in ethanol, in which case the product is obtained simply by filtration; however longer reaction times are required. IR CH$_2$Cl$_2$: 1948 [ν(CO)] cm^{-1}. Nujol: 2213w [ν(BHRu)], 1941vs [ν(CO)], 1566w, 1315w, 1267m, 1202s, 1091s cm^{-1}. FAB-MS: *m*/*z* (%): 743(58) [M − H]$^+$, 715(4) [M − H − CO]$^+$, 452(22) [RuB(mt)$_3$]$^+$, 339(19) [RuB-

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(mt)$_2$]$^+$, 263(92) [HPPh$_3$]$^+$. NMR (CDCl$_3$) ^{11}B (25 °C): δ −2.13 ppm. ^{31}P{^{1}H} (25 °C): δ 58.10. ^{1}H (25 °C, Figure 1) δ −14.34 [s(v br), 1 H, RuH], −3.87 [q(br), 1 H, ^1J(BH) = 82 Hz], 3.36 (s, 3 H, NCH$_3$), 3.51 (s, 6 H, NCH$_3$), 6.29, 6.50, 6.56, 6.60, 6.63, 6.77 (s × 6, 1 H × 6, NCH═CH), 7.22, 7.44 (m × 2, 15 H, C$_6$H$_5$). ^{1}H (−40 °C, Figure 1): δ −14.33 [d(br), 1 H, RuH, ^2J(PH) = 25.73], −3.92 [d(v br), 1 H, B−H−Ru], 3.27, 3.48, 3.52 (s × 3, 9 H, NCH$_3$), 6.29, 6.47, 6.55, 6.63, 6.64, 6.80 [d × 6, 1 H × 6, NCH═CH, ^3J(HH) ca. 2.9 Hz].^{13}C{^{1}H} (25 °C) δ 201.2 (RuCO), 166.3, 165.3, 163.8 (C═S), 136.7 [d, C^1(C$_6$H$_5$), ^1J(PC) = 44.2], 133.6 [s(br), C^{3,5}(C$_6$H$_5$)], 129.0 [s, C^4(C$_6$H$_5$)], 127.5 [d, C^{2,6}(C$_6$H$_5$), ^2J(PC) = 8.7 Hz], 121.4, 119.8, 119.0, 118.6, 118.3, 117.5 [NCH═CH], 34.9(1C), 34.4(2C) [NCH$_3$]. Anal. Found: C, 50.0; H, 4.1; N, 11.2. Calcd for C$_{31}$H$_{32}$BN$_6$OPRuS$_3$: C, 50.07; H, 4.34; N, 11.30. The crystal structures of **5** and of its dichloromethane solvate **5**·CH$_2$Cl$_2$ were determined. *Crystal data for* **5**: C$_{31}$H$_{32}$N$_6$OBPS$_3$Ru, M = 743.7, monoclinic, $P2_1/c$ (no. 14), a = 14.745(1) Å, b = 12.194(1) Å, c = 19.248(1) Å, β = 100.32(1)°, V = 3404.7(5) Å^3, Z = 4, D_c = 1.451 g cm^{-3}, μ(Mo Kα) = 0.73 mm^{-1}, T = 293 K, pale yellow blocks; 5990 independent measured reflections, F^2 refinement, R_1 = 0.045, wR_2 = 0.082, 3752 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 369 parameters. NB: The hydrogen atoms H1 and H2 were located and refined freely. *Crystal data for* **5**·CH$_2$Cl$_2$: C$_{31}$H$_{32}$N$_6$OBPS$_3$Ru·CH$_2$Cl$_2$, M = 828.6, monoclinic, $P2_1/n$ (no. 14), a = 9.340(1) Å, b = 26.357(2) Å, c = 15.039(2) Å, β = 94.60(1)°, V = 3690.5(7) Å^3, Z = 4, D_c = 1.491 g cm^{-3}, μ(Mo Kα) = 0.82 mm^{-1}, T = 293 K, pale yellow blocks; 6494 independent measured reflections, F^2 refinement, R_1 = 0.042, wR_2 = 0.092, 4775 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 424 parameters.

Reaction of [RuH(CO)(PPh$_3$){HB(mt)$_3$}] with Ethynyl Benzene. A solution of [RuH(CO)(PPh$_3$){HB(mt)$_3$}] (**5**, 26 mg) in dichloromethane (20 mL) was treated with ethynylbenzene (0.05 g). The reaction was monitored using solution IR spectroscopy, observing the disappearance of the ν(CO) peak due to **5** (1948 cm^{-1}) and appearance of that due to **4** (1896 cm^{-1}). The reaction was complete and spectroscopically quantitive after 23 h, at which time the solvent was removed and the residue characterized by comparison of spectroscopic data with those previously published for **4**.[4]

Supporting Information Available: X-ray crystallographic file for the structures of compounds **5** and **5**·CH$_2$Cl$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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