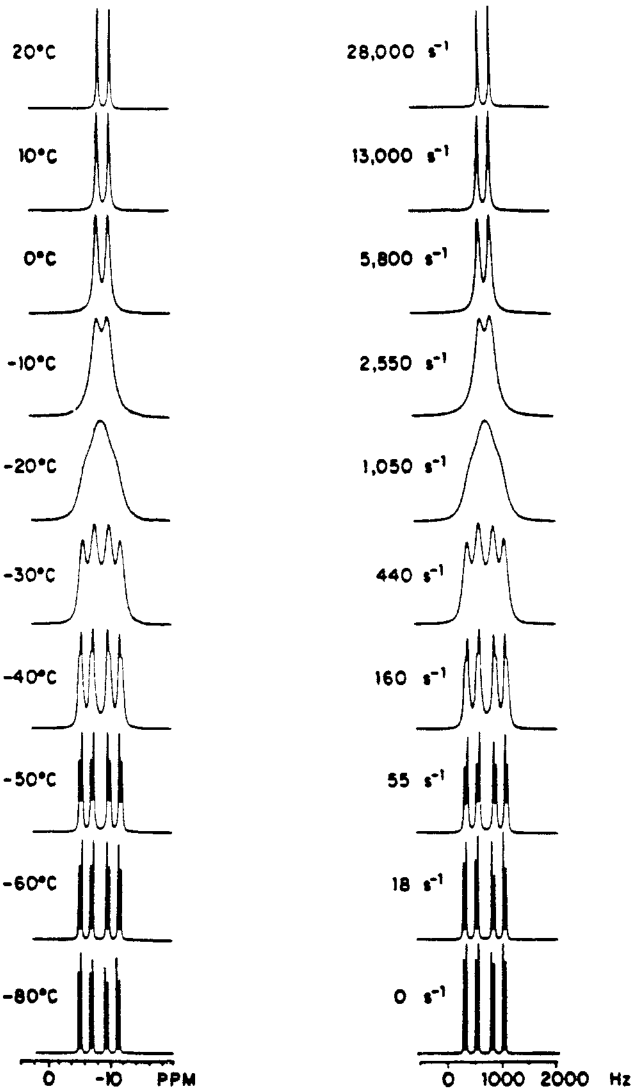

Figure 2. Observed and calculated variable-temperature $^{31}P\{^1H\}$ NMR spectra (121.69 MHz) for **3b**. Simulations were performed using a locally modified version of DNMR3. Activation parameters for indenyl rotation are $\ln A = 29.81 \pm 0.55$, $E_a = 11.45 \pm 0.28$ kcal mol^{-1}, $\Delta G^{\ddagger}_{253} = 11.20 \pm 0.03$ kcal mol^{-1}, $\Delta H^{\ddagger} = 10.95 \pm 0.28$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -0.97 \pm 1.07$ eu.

also strongly correlated with the ^{13}C chemical shift of the ring-junction carbons $C_{3a,7a}$: larger distortions resulting in larger downfield shifts.[14a,16]

We also find that the degree of distortion is paralleled by the barrier to hindered rotation of the indenyl ring.[7] In order to ascertain the effect of 1-CH_3 substitution on the observed barriers, unsubstituted and substituted complexes **2e** and **3c** were examined;[11,17] observed barriers were identical within experimental error.[17] We therefore conclude that the activation parameters obtained for **3b**[18] (Figure 2) are good estimates of those which are unavailable for **2b**. The values for **3b** are significantly larger than those for **3a** ($\Delta G^{\ddagger} = 8.5$ kcal mol^{-1})[10] in keeping with our proposal[7] that an increase in the degree of slip-fold distortion should result in a larger barrier to rotation.

We will report further analyses of (indenyl)RhL_2 (L = PR_3, CO, RNC; L_2 = $R_2PCH_2CH_2PR_2$) complexes in due course.[19]

Acknowledgment. We wish to thank B. C. West, M. P. Stepro, M. Warrington, and E. A. Conaway for skilled technical assistance, Profs. M. J. McGlinchey (McMaster) and T. A. Albright (Houston) and Drs. J. S. Merola (Exxon Research and Engineering Co.) and R. T. Baker (Du Pont Central Research) for many helpful discussions.

Registry No. **2a**, 63428-46-6; **2b**, 75094-84-7; **2e**, 100113-59-5; **3b**, 108010-58-8; **3c**, 108010-59-9.

Supplementary Material Available: A drawing of **2a** and tables of crystal data, fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, and intramolecular angles for **2a** and **2b** (8 pages); listings of structure factors for **2a** and **2b** (16 pages). Ordering information is given on any current masthead page.

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(14) (a) A similar trend has been observed for analogous iridium complexes: Merola, J. S., private communication. (b) The observed slip-fold distortions do not appear to arise from steric interactions of the ligands with the indenyl ring as there are no short intramolecular nonbonded interactions. In addition, they do not appear to be related to crystal packing constraints. Thus, real-time computer graphic analyses of the unit cell contents do not indicate any unusual intermolecular interactions, and the phenomenon has been shown to persist in solution (vide infra). (c) Preliminary results indicate significant slip-fold distortions are present in (η-indenyl)RhL_2 complexes containing certain cylindrical π-acceptor ligands, e.g. L = CO or RNC. A complete analysis of these and related complexes will appear in due course.[19]

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(16) The correlation of $\delta(^{13}C)$ of $C_{3a,7a}$ vs. indenyl hapticity was originally proposed by: Kohler, F. H. *Chem. Ber.* 1974, *107*, 570 and has recently been extended to include a large number of ML_2 species in ref 11.

(17) Baker, R. T., private communication.

(18) $^{31}P\{^1H\}$ NMR (121.69 MHz, THF-d_8, −80 °C): −3.86 (dd, J_{Rh-P} = 215, $^2J_{P-P}$ = 51 Hz), −7.93 ppm (dd, J_{Rh-P} = 215, $^2J_{P-P}$ = 51 Hz); $^{13}C\{^1H\}$ NMR (100.614 MHz, THF-d_8) 119.95 (s, C_{3a} or C_{7a}), 119.66, 119.23 (s, $C_{4,7}$), 118.27 (s, c_{3a} or C_{7a}), 114.70, 114.36 (s, $C_{5,6}$), 96.77 (d, J_{Rh-C} = 6.2 Hz, C_2), 83.73 (dt, J_{Rh-C} = 3.0, $^2J_{P-C}$ = 7.5 Hz, C_1), 69.26 (dt, J_{Rh-C} = 4.9, $^2J_{P-C}$ = 7.3 Hz, C_3), 23.42 (t, J = 12.7 Hz, $2PMe_3$), 13.52 ppm (s, CH_3); ^1H NMR (360 MHz, THF-d_8) δ 6.89–6.83 (m, 2 H, aromatic), 6.64–6.54 (m, 2 H, aromatic), 5.96 (t, $J_{H-H} = J_{Rh-H}$ = 2.5 Hz, H_2), 4.71 (m, H_3), 2.14 (t, J = 3.3 Hz, CH_3), 1.22 (m, $2PMe_3$).

(19) Full details will appear in a manuscript describing our joint efforts with the authors in ref 10.

Novel Pyrazolylborato– and Pyrazolyl–Ruthenium Complexes. The Crystal and Molecular Structures of $[\{H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2\}Ru(\eta^4\text{-}C_8H_{12})H]$ and $[(\eta^4\text{-}C_8H_{12})_2Ru_2H\{\mu\text{-}N{=}C(Me)pz\}(\mu\text{-}pz)(\mu\text{-}H)]$: Confirmation of the First Examples of the Ru···H–B Agostic Interaction and the Bridging Amidine Ligand

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Summary: The reactions of $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ and $[\{(\eta^4\text{-}C_8H_{12})RuCl(Me)(NCMe)\}_2]$ with $K[H_2B(3,5\text{-}Me_2pz)_2]$ (pz = 1-pyrazolyl) give $[\{H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2\}Ru(\eta^4\text{-}C_8H_{12})X]$ (X = H, Me), the first examples of the Ru···H–B interaction and verified in $[\{H(\mu\text{-}H)B(3,5\text{-}$

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$Me_2pz)_2\}Ru(\eta^4\text{-}C_8H_{12})H]$ by X-ray crystallography. Treatment of $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ with $K[R_2Bpz_2]$ (R = Et, Ph) in acetonitrile results in pyrazolylborate fragmentation giving the dinuclear complex $[(\eta^4\text{-}C_8H_{12})_2Ru_2H\{\mu\text{-}N{=}C(Me)pz\}(\mu\text{-}pz)(\mu\text{-}H)]$ confirmed by X-ray crystallography to contain the first example of a bridging amidine ligand.

Polypyrazolylborate anions have emerged as a uniquely unusual class of ligands in coordination chemistry.[1,2] Complexes are known for almost every transition metal, many displaying unusual structural or chemical features.[1,2] Nevertheless, there remains a noticeable paucity of second- and third-row transition metal systems, and for ruthenium in particular, only a handful of polypyrazolylborate complexes are known.[1-3] To date, all these ruthenium complexes involve tris- and tetrakis(1-pyrazolyl)borate ligands in conjunction with relatively stabilizing ancilliary ligand systems, e.g., cyclopentadienyl,[3] carbonyl,[4] and arene[5] groups. As part of our objectives in establishing new synthetic routes to cyclopentadienyl–ruthenium and –osmium complexes,[3a,6] we have come to consider the application of these procedures to the preparation of novel, reactive polypyrazolylborato–ruthenium and –osmium analogues. Herein we wish to report the first part of our studies which establishes preparative routes to novel ruthenium(II) complexes containing bis- and tris(1-pyrazolyl)borate ligands, including the first examples of the Ru···H–B agostic interaction. We also report the first example of a bridging amidine ligand, formed as the result of bis(1-pyrazolyl)borate fragmentation and pyrazolyl–acetonitrile coupling and stabilized in an unusual "agostic" 18-electron, 16-electron diruthenium dihydride complex.

The reaction of $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ (**1**; C_8H_{12} = cycloocta-1,5-diene)[7] with excess $K[H_2B(3,5\text{-}Me_2pz)_2]$ (pz = 1-pyrazolyl) in acetonitrile (40 °C, 10 min) gives, on cooling to room temperature, an orange crystalline product of stoichiometry $[\{H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2\}Ru(\eta^4\text{-}C_8H_{12})H]$ (**2**). The ^1H NMR spectrum of **2** shows the expected low-field resonance at δ 5.55 for the pyrazolyl ring protons and resonances at δ 2.16 and 2.12 for the methyl groups on the pyrazolyl ring. Multiplet resonances at δ 3.59, 3.08, 2.50, 2.23, 1.90, and 1.85 are readily assigned to the cycloocta-1,5-diene ligand while the hydride ligand resonates as a singlet at δ −7.41. Characteristic ν(B–H) and ν(Ru–H) vibrations are observed in the infrared spectrum of **2** (2480 and 2060 cm^{-1}, respectively) while an intense absorption band at 1920 cm^{-1} is strongly suggestive[8] of a Ru···H–B agostic interaction. The rarity of this unsymmetrical three-center, 2-electron bonding mode in general,[1,2] but particularly its novelity in organoruthenium chemistry, encouraged us to complete the characterization of **2** using X-ray methods.[9]

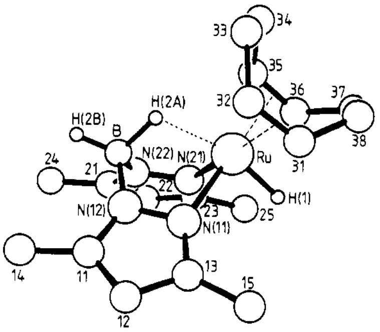

Figure 1. A perspective view of $[\{H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2\}Ru(\eta^4\text{-}C_8H_{12})H]$ (**2**) showing the atom numbering scheme. Unaccompanied numbers refer to carbon atoms. Selected bond lengths (Å) and angles (deg): Ru···B = 2.673 (2), Ru–H(1) = 1.52 (2), Ru···H(2A) = 2.06 (2), Ru–N(11) = 2.113 (2), Ru–N(21) = 2.122 (2), B–H(2A) = 1.17 (2), B–H(2B) = 1.12 (2), B–N(12) = 1.535 (2), B–N(22) = 1.537 (3), N(11)–N(12) = 1.365 (3), N(21)–N(22) = 1.371 (3), H(1)–Ru···H(2A) = 160.1 (8), N(11)–Ru-N(21) = 86.1 (1), Ru···H(2A)–B = 108.9 (11), Ru–N(11)–N(12) = 107.7 (1), Ru–N(21)–N(22) = 106.8 (1), N(11)–N(12)–B = 112.7 (2), N(21)–N(22)–B = 113.4 (2), N(12)–B–N(22) = 108.9 (2).

The structure determination (Figure 1) clearly shows the strong Ru···H–B agostic interaction in **2** with Ru···H(2A) and Ru···B distances of 2.06 (2) and 2.673 (2) Å, respectively. These internuclear distances are considerably shorter than the corresponding distances in the only other comparable systems where agostic M···H–B interactions occur and which have been structurally characterized.[12] These differences are manifested in terms of a greater puckering of the chelating RuN_4B boat conformation compared to those of the known molybdenum,[13,14] tantalum[15] and zirconium[16] systems and also to complexes

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(9) Crystal data for **2**: $C_{18}H_{29}BN_4Ru$, M_r 413.34; monoclinic, space group $P2_1/n$; a = 9.8841 (13) Å, B = 17.3053 (22) Å, c = 11.3170 (8) Å, β = 96.615 (9)°, U = 1922.9 $Å^3$, Z = 4, D_{calcd} = 1.428 Mg m^{-3}, $F(000)$ = 856; λ = 0.710 69 Å, μ(Mo Kα) = 0.730 mm^{-1}; temperature = 293 ± 1 K; Enraf-Nonius CAD4F diffractometer, 4332 reflections with $3 \leqslant \theta \leqslant 27°$ were measured and corrected for absorption.[10] Structure was solved by heavy-atom methods and refined $[\sum w|\Delta F|^2$ minimized, $w = \sigma^{-2}(F)]$ by using SHELX[11] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were located and refined. R = 0.0249 and R_w = 0.0201 for 3630 reflections with $F_o \geqslant 4\sigma(F_o)$ and 308 refined parameters.

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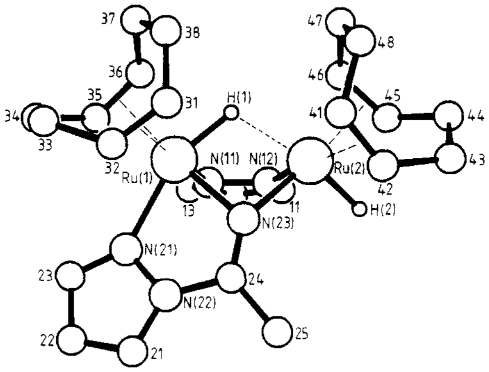

Figure 2. A perspective view of [(η^4-C$_8$H$_{12}$)$_2$Ru$_2$H{μ-N=C(Me)pz}(μ-pz)(μ-H)] (4) showing the atom numbering scheme. Unaccompanied numbers refer to carbon atoms. Selected bond lengths (Å) and angles (deg): Ru(1)···Ru(2) = 2.919 (1), Ru(1)–H(1) = 1.58 (2), Ru(2)···H(1) = 2.03 (4), Ru(2)–H(2) = 2.04 (4), Ru(1)–N(11) = 2.084 (4), Ru(2)–N(12) = 2.089 (5), Ru(1)–N(21) = 2.172 (4), Ru(1)–N(23) = 2.039 (3), Ru(2)–N(23) = 2.017 (3), N(11)-N(12) = 1.356 (5), N(21)–N(22) = 1.366 (5), N(22)–C(24) = 1.424 (6), N(23)–C(24) = 1.259 (5), H(1)–Ru(1)–N(21) = 158 (2), H(1)···Ru–H(2) = 162 (2), N(11)–Ru(1)–N(23) = 82.8 (1), N(12)–Ru(2)–N(23) = 83.3 (2), Ru(1)-H(1)···Ru(2) = 107 (2), Ru(1)–N(11)–N(12) = 112.3 (2), Ru(2)–N(12)–N(11) = 111.8 (3), Ru(1)–N(23)–Ru(2) = 92.1 (2).

bearing similar ligands but lacking the M···H–B interaction.[18]

Perhaps the most important factor in the formation of 2 from 1 is the availability of coordinative unsaturation or potential coordinative unsaturation at the ruthenium center that enables the locking of the RuN$_4$B boat conformation in the agostic mode. The reactivity patterns of 1 that support this contention are now well established,[7,21] and it is on this basis that we have been able to elaborate upon the synthesis of 2 with further examples of Ru···H–B agostic systems. Thus treatment of the methyl complex [{(η^4-C$_8$H$_{12}$)RuCl(Me)(NCMe)}$_2$][22] (3) with K[H$_2$B(3,5-Me$_2$pz)$_2$] in hot acetonitrile readily gives crystalline, air-stable [{H(μ-H)B(3,5-Me$_2$pz)$_2$}Ru(η^4-C$_8$H$_{12}$)Me] while treatment of either 1 or 3 first with a single molar equivalent of bis(diphenylphosphino)butane and then with excess K[H$_2$B(3,5-Me$_2$pz)$_2$] also in acetonitrile gives the formal substitution products [{H(μ-H)B(3,5-Me$_2$pz)$_2$}Ru(dppb)X] (X = H, Me).

In contrast to these results, however, the reactions of 1 with boron-substituted bis(1-pyrazolyl)borate anions takes a different course. Treatment of 1 with excess K[R$_2$Bpz$_2$] (R = Et, Ph) in acetonitrile at room temperature gives a bright orange solution which on standing slowly yields orange crystals of [(η^4-C$_8$H$_{12}$)$_2$Ru$_2$H{μ-N=C(Me)pz}(μ-pz)(μ-H)] (4). The infrared spectrum of 4 confirms the presence of a terminal hydrido ligand [ν(Ru–H) = 1985 cm^{-1}], but more importantly, it displays a strong band at 1653 cm^{-1} [ν(C=N)], suggestive of the amidine ligand system arising from pyrazolyl–acetonitrile coupling.[23] The ^{1}H NMR spectrum of 4 shows two coupled hydride resonances (δ -6.36, -7.44; J = 6.5 Hz) consistent with one terminal and one "semibridging" hydride ligand.[24] Thus, in order to confirm the novel amidine ligand system and also to clarify the nature of the hydride ligands in this compound, the X-ray crystal structure of 4 has been determined.[25]

The structure (Figure 2) confirms the presence in 4 of a "semibridging" hydride ligand trans to a terminal hydride ligand[26] as well as the presence of the amidine ligand, which through the nitrogen atom bridges the two ruthenium centers. A pyrazolyl anion also bridges the two metal centers, and a cycloocta-1,5-diene ligand completes the coordination sphere of each ruthenium atom. Thus, on the basis of the 18-electron formalism, 4 is to be considered as an 18-electron, 16-electron complex, only the third example thereof to date.[24] The core structure of 4 and those of [(η^4-C$_8$H$_{12}$)$_2$Ru$_2$H(L)(μ-pz)$_2$(μ-H)] [L = pzH[24] (5), PMe$_3$[27] (6)] are formally related, but most notable are the bond lengths associated with the "semibridging" hydride ligands [Ru(2)···H(1) = 2.03 (4), 2.05 (6), and 2.16 (5) Å in 4–6, respectively] compared to the agostic Ru···H(2A) distance of 2.06 (2) Å in 2. Indeed, the quantitative and qualitative resemblances between 2 and 4 (Figures 1 and 2) are remarkable. This leads us to suggest, the term "semibridging" hydride[24] notwithstanding, that the structure of 4 (and indeed this class of complexes in general) should best be considered in terms of the *agostic* interaction of a saturated 18-electron ruthenium hydride fragment (formally analogous to the pyrazolylborate ligand in 2) with an unsaturated 16-electron ruthenium fragment.

Whereas 1 reacts with bis(pyrazolyl)borate anions to give formally coordinatively unsaturated products, treatment of 1 with K[HBpz$_3$] in methanol gives, in high yield, the saturated "half-sandwich" compound [(HBpz$_3$)Ru(η^4-C$_8$H$_{12}$)H] quantitatively converted, on treatment with CCl$_4$, to the chloride complex [(HBpz$_3$)Ru(η^4-C$_8$H$_{12}$)Cl] (7). 7 is formally analogous to the cyclopentadienyl–ruthenium complexes [(η^5-C$_5$R$_5$)Ru(η^4-C$_8$H$_{12}$)Cl] (R = H,[3] Me[28], but it is notable that in its somewhat limited reactivity patterns (dominated essentially by rather sluggish cyclooctadiene displacement), 7 is apparently more closely related to [(η^5-C$_5$Me$_5$)Ru(η^4-C$_8$H$_{12}$)Cl] than to [(η^5-C$_5$H$_5$)Ru(η^4-

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(17) Hydrogen atom positions were not refined.

(18) For example M···B = 3.162 (2) Å (M = Ni)[19] and 3.22 Å (M = Cr)[20] in the square-planar complexes [{H$_2$B(3,5-Me$_2$pz)$_2$}$_2$M] and M···B = 3.48–3.52 Å in [{H$_2$B(3,5-Me$_2$pz)$_2$}$_3$V].[20]

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(25) Crystal data for 4: C$_{24}$H$_{35}$N$_5$Ru$_2$, M_r 595.72; triclinic, space group $P\bar{1}$, a = 9.803 (3) Å, b = 10.629 (3) Å, c = 12.540 (4) Å, α = 76.73 (3)°, β = 78.49 (2)°, γ = 61.81 (3)°, U = 1114.6 Å^3, Z = 2, D_{calcd} = 1.775 Mg m^{-3}, $F(000)$ = 604; μ(Mo Kα) = 1.237 mm^{-1}; temperature = 233 ± 1 K. Data collection (4875 reflections measured) and structure solution and refinement as for **2** [$w = \{\sigma^2(F) + 0.00216F^2\}^{-1}$]. R = 0.0406 and R_w = 0.0576 for 4078 reflections with $F_o \geqslant 4\sigma(F_o)$ and 390 refined parameters.

(26) The terminal Ru–H distance in **4** appears to be abnormally long [2.04 (4) Å compared to 1.52 (2), 1.65 (5),[24] and 1.59 (4) Å[27] in **2**, **5**, and **6**, respectively]. If the terminal hydride is omitted from the refinement, a peak for the hydride corresponding to the observed Ru–H distance consistently appears in the difference map. Moreover, a room-temperature structure determination using a different crystal of the same complex yielded a similarly long terminal Ru–H bond. Thus, notwithstanding the relatively high uncertainties inherent in the determination of hydrogen atom positions by X-ray methods, the long terminal Ru–H distances in **4** appears to be genuine. The reason for such a long bond is, however, not readily apparent.

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$C_8H_{12})Cl]$.[29] Since steric factors probably do not influence the reactivity of these half-sandwich compounds to any large degree, we conclude that electronic effects are largely responsible for the lack of substitutive reactivity in both $[(HBpz_3)Ru(\eta^4\text{-}C_8H_{12})Cl]$ and $[(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$. Both the steric and electronic similarities between the pentamethylcyclopentadienyl and hydrotris(1-pyrazolyl)borate ligands have already been noted.[30]

In conclusion, the reactive precursors $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ and $[\{(\eta^4\text{-}C_8H_{12})RuCl(Me)(NCMe)\}_2]$ provide a unique entry to the coordination chemistry of (dihydrobis(1-pyrazolyl)borato)- and (hydrotris(1-pyrazolyl)boratoruthenium complexes and, through the fragmentation of the pyrazolylborate ligands, also to pyrazolyl- and amidine–ruthenium systems.

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Registry No. **1**, 61042-65-7; **2**, 109744-70-9; **3**, 109744-71-0; **4**, 109744-72-1; **6**, 109744-76-5; **7**, 109744-77-6; $K[H_2B(3,5\text{-}Me_2pZ)_2]$, 18583-59-0; $[\{H(\mu\text{-}H)B(3,5\text{-}Me_2pZ)_2\}Ru(\eta^4\text{-}C_8H_{12})Me]$, 109764-46-7; $[\{(\mu\text{-}H)B(3,5\text{-}Me_2pZ)_2\}Ru(dppb)H]$, 109744-73-2; $[\{(\mu\text{-}H)B(3,5\text{-}Me_2pZ)_2\}Ru(dppb)Me]$, 109744-74-3; $K[Et_2BpZ_2]$, 109744-75-4; $K[Ph_2BpZ_2]$, 95675-62-0; $K[HBpZ_3]$, 18583-60-3; $[(HBpZ_3)Ru(\eta^4\text{-}C_8H_{12})H]$, 109744-69-6.

Supplementary Material Available: Details of the structure determinations and tables of fractional coordinates, temperature factors, and bond lengths and angles for **2** and **4** and elemental analyses and spectroscopic characterization for **2** and **4** (20 pages); listing of observed and calculated structure factors for **2** and **4** (33 pages). Ordering information is given on any current masthead page.

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[29] For example, **7** and $[(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ may be converted to the stable cations $[(HBpz_3)Ru(\eta^4\text{-}C_8H_{12})(solvent)]^+$ and $[(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}C_8H_{12})(solvent)]^{+\,28}$ respectively, whereas in the case of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$, such species have not been detected and are possibly only intermediates in certain substitution processes of this compound.

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Highly Reduced Organometallics. 21.[1] Halocarbonyls of Group 4 Elements. Synthesis, Characterization, and Molecular Structure of $(C_5Me_5)Hf(CO)_2(Me_2PCH_2CH_2PMe_2)Cl$

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Summary: The first example of a stable halocarbonyl of a group 4 element has been synthesized, isolated, and characterized. Treatment of $(C_5Me_5)HfCl_3$ with sodium naphthalenide in the presence of $Me_2PCH_2CH_2PMe_2$ at −60 °C in 1,2-dimethoxyethane followed by atmospheric pressure carbonylation provides $(C_5Me_5)Hf(CO)_2(dmpe)Cl$. The single-crystal X-ray structure of this material has been determined and is discussed in relation to spectroscopic data. Much less thermally stable zirconium and titanium analogues have also been prepared and are characterized on the basis of their spectroscopic properties.

While several classes of titanium and zirconium carbonyls are now known,[3] the carbonyl chemistry of hafnium remains poorly explored and ha been largely limited to divalent compounds of the type $(\eta^5\text{-ring})_2Hf(CO)L$, where $(\eta^5\text{-ring}) = C_5H_5$, C_5Me_5, or indenyl and L = CO, phosphines, or phosphites.[4] On the basis of the relatively high thermal stability exhibited by $(C_5H_5)Zr(CO)_4^{-\,3a}$ and $(C_5Me_5)Zr(CO)_4^-$,[5] we had hoped to extend our low-temperature sodium naphthalenide reductive carbonylation methodology to obtain an analogous hafnium species. Corresponding reductions of $(C_5Me_5)HfCl_3$ provided exceedingly unstable materials. However, we now report that addition of the excellent donor ligand 1,2-bis(dimethylphosphino)ethane, dmpe, before reduction provides the first isolable halocarbonyl of a group 4 element,[6] $(C_5Me_5)Hf(CO)_2(dmpe)Cl$ (**1**). Since this material is also the initial "half-sandwich" carbonyl of hafnium and the only known derivative of the unknown $(C_5Me_5)Hf(CO)_4X$ (X = halogen), its constitution has been verified by a single-crystal X-ray diffraction study. Equation 1 summarizes the procedure used for the synthesis of this and related zirconium and titanium complexes. Conditions: (i) 2–4 equiv of $Na\text{–}C_{10}H_8$ at −60 to −70 °C in 1,2-dimethoxyethane under argon, (ii) evacuation followed by addition of CO (1 atm) and slow warming.)

$$(C_5Me_5)HfCl_3 + dmpe \xrightarrow{(i)} \xrightarrow{(ii)} (C_5Me_5)Hf(CO)_2(dmpe)Cl \tag{1}$$

In a typical synthesis, a solution containing dmpe (0.91 mL, 5.4 mmol) and $(C_5Me_5)HfCl_3$ (2.1 g, 5.0 mmol) in 100 mL of 1,2-dimethoxyethane (dme) was cooled to −60 °C and subsequently added via cannula to a mechanically stirred slurry/solution of $Na\text{–}C_{10}H_8$ (14.9 mmol) and $C_{10}H_8$ (10.0 mmol) in 100 mL of dme at −60 °C in a 500-mL Morton flask. Within 5 min the argon atmosphere was removed under vacuum and replaced by carbon monoxide at about 1-atm pressure. The resulting yellow green reaction mixture was then slowly warmed to −25 °C over a 2-h period, filtered through Celite, and evacuated at 0 °C to remove solvent. After the residue was washed with hexane to remove naphthalene, the product was recrystallized from toluene to provide 0.51 g (18% yield, unoptimized) of a thermally stable bright green crystalline (**1**) (decomp pt 165–175 °C) which provided satisfactory analytical data.[7] Despite the presence of the good electron-donating C_5Me_5 and dmpe groups and the corre-

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[1] Part 20: Chi, K. M.; Frerichs, S. R.; Stein, B. K.; Blackburn, D. W.; Ellis, J. E., submitted for publication.

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