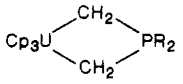
where A is the major form but where B and C also contribute significantly. As predicted by this bonding description O, N, C(1), C(2), and C(1N) are coplanar (Table V (supplementary material)). A related compound has been prepared by the reduction of Ph—N=C=O with $(MeC_5H_4)_3U$.[23] In this complex, $[(MeC_5H_4)_3U]_2(\mu\text{-}\eta^1,\eta^2\text{-}PhNCO)$, the U–N, 2.36 (2) Å, N–C, 1.31 (2) Å, and O–C, 1.36 (2) Å, distances are indistinguishable from those in **2a**.

There are not many Cp_3UXY complexes.[22,24] Some with monodentate, trans X and Y ligands have been reported,[24–28] but, with the exception of those with three-membered chelate rings,[10,11,22,23,29–31] no *cis*-Cp_3UXY complexes have been structurally characterized.[32] Since a theoretical model that considers steric effects[36] predicts that Cp_3U complexes of both *trans*-Cp_3UXY and *cis*-Cp_3UXY complexes, containing a three-membered chelate ring, will be more stable than Cp_3U complexes with larger chelate rings, the characterization of **2a** as the first *cis*-Cp_3UXY complex with a four membered chelate ring is particularly significant. In accord with the predictions that molecules of this type should be very sterically crowded,[36] the bite distance in the ligand, 2.22 (2) Å, is short, the average C(Cp)–U distance, 2.84 (2) Å, is long, and the Cp(centroid)–U–Cp(centroid) angles have been compressed from about 117°, typical for Cp_3U–X complexes, to 112°, 115°, and 110°.

We have earlier postulated[37] that



is an intermediate in the formation of $Cp_3U{=}CHP(Me)(R)_2$ from Cp_3UCl and $Li(CH_2)(CH_2)PR_2$. The existance of the four-membered chelate ring in **2** supports this hypothesis.

Acknowledgment. The support of this work by the National Science Foundation, Grants CHE 82-10244 and CHE 85-19289 (J.W.G. and R.E.C.), and by the donors of the Petroleum Research Fund, administrated by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Table I, crystal, data collection, and reduction parameters, Table II, bond distances and bond angles, Table III, positional and thermal parameters for $Cp_3U[(NPh)(O)CCHPMe_2Ph]\cdot C_7H_8$, and Table V, distances from the O, N, C(1), C(2), C(1N) least-squares plane (4 pages); Table IV, observed and calculated structure factors for $Cp_3U[(NPh)(O)CCHPMe_2Ph]\cdot C_7H_8$ (19 pages). Ordering information is given on any current masthead page.

---

(23) Brennan, J. G.; Anderson, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514.
(24) Fischer, R. D.; Klahne, E.; Kopf, J. *Z. Naturforsch., B. Anorg. Chem., Org. Chem.* **1978**, *33B*, 1393.
(25) Bagnall, K. W.; Plews, M. J.; Brown, D.; Fischer, R. D.; Klahne, E.; Landgraf, G. W.; Sienel, G. R. *J. Chem. Soc., Dalton Trans.* **1982**, 1999.
(26) Bombieri, G.; Benetollo, F.; Bagnall, K. W.; Plews, M. J.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1983**, 45.
(27) Bombieri, G.; Benetollo, F.; Klahne, E.; Fischer, R. D. *J. Chem. Soc., Dalton Trans.* **1983**, 1115.
(28) Fischer, R. D.; Klahne, E.; Sienel, G. R. *J. Organomet. Chem.* **1982**, *238*, 99.
(29) Dormond, A.; Elbouadili, A. A.; Moise, C. *J. Chem. Soc., Chem. Commun.* **1984**, 749.
(30) Zanella, P.; Paolucci, G.; Rossetto, G.; Benetollo, F.; Polo, A.; Fischer, R. D.; Bombieri, G. *J. Chem. Soc., Chem. Commun.* **1985**, 96.
(31) Paolucci, G.; Rossetto, G.; Yunlu, K.; Fischer, R. D. *J. Organomet. Chem.* **1984**, *272*, 363.
(32) While there is strong evidence that $Cp_3An(BH_4)$ (An = U or Th) contain triply bridging borohydride[33–35] and, thus, four-membered chelate rings, no diffraction studies are available to characterize this mode of ligation.
(33) Marks, T. J.; Kennelly, W. J.; Kolb, J. R.; Shimp, L. A. *Inorg. Chem.* **1972**, *11*, 2540.
(34) Marks, T. J.; Kolb, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 27.
(35) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.
(36) (a) Li, X.-F.; Feng, X.-Z.; Xu, Y.-T.; Wang, H.-T.; Shi, J.; Liu, L. *Inorg. Chim. Acta* **1986**, *116*, 85. (b) Li X.-F., personal communication.
(37) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1983**, *2*, 1336.

The Slip-Fold Distortion of π-Bound Indenyl Ligands. Dynamic NMR and X-ray Crystallographic Studies of (η-Indenyl)RhL_2 Complexes[†]

Todd B. Marder,*[‡] Joseph C. Calabrese, D. Christopher Roe, and Thomas H. Tulip[§]

Central Research & Development Department
E. I. du Pont de Nemours & Company
Experimental Station
Wilmington, Delaware 19898

Received July 11, 1986

Summary: Crystal and molecular structures of two $(\eta\text{-}C_9H_7)RhL_2$ complexes, L = $\eta\text{-}C_2H_4$ (**2a**) (R = 0.031, R_w = 0.039) and L = PMe_3 (**2b**) (R = 0.026, R_w = 0.032), are reported. Values of the indenyl ring slip parameter, Δ, are 0.161 and 0.201 Å, respectively, indicating significantly greater slip-fold distortion for **2b** than for **2a**. Comparison with the known structure of $(\eta\text{-}C_9H_7)Rh(\eta\text{-}duroquinone)$ (**2c**) for which Δ = 0.046 Å suggests a correlation between ligand σ-donor/π-acceptor capabilities and the degree of slip-fold distortion. The degree of distortion is also correlated with the ^{13}C NMR chemical shift of the ring junction carbon atoms and with the barrier to indenyl ring rotation. The latter has been studied in solution by dynamic FTNMR spectroscopy using $(\eta\text{-}1\text{-}CH_3C_9H_6)RhL_2$ complexes. Larger barriers result from increased distortions; $\Delta G^{\ddagger}_{253}$ = 11.20 ± 0.03 kcal mol^{-1} for $(\eta\text{-}1\text{-}CH_3C_9H_6)Rh(PMe_3)_2$.

There has been considerable recent interest in the enhanced reactivity of η^5-indenyl transition-metal complexes toward ligand substitution and related reactions compared with their $\eta^5\text{-}C_5R_5$ analogues.[1–4] This rate enhancement is believed to be related to the relative ease of ring slippage from η^5 to η^3.[1–4] Our interest in stoichiometric[5] and catalytic[6] reactions of η^5-indenyl rhodium complexes prompted a detailed investigation of factors effecting ground-state slip-fold distortions and related ligand dynamics in a series of (η-indenyl)RhL_2 complexes.

We recently reported[7] the first example of hindered indenyl-ring rotation in an unusual $(\eta\text{-}C_9H_7)RhLL'$ complex (1) wherein L = CO, L′ = $(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)Cr(\mu\text{-}CO)_2(CO)$, and the observed ΔG‡ was ca. 10.8 kcal mol^{-1}.

[†] Contribution No. 3939.

[‡] Present address: The Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

[§] Present address: Du Pont NEN Products, Radiopharmaceutical Research, 331 Treble Cove Road, North Billerica, Massachusetts 01862.

0276-7333/87/2306-2012$01.50/0 © 1987 American Chemical Society

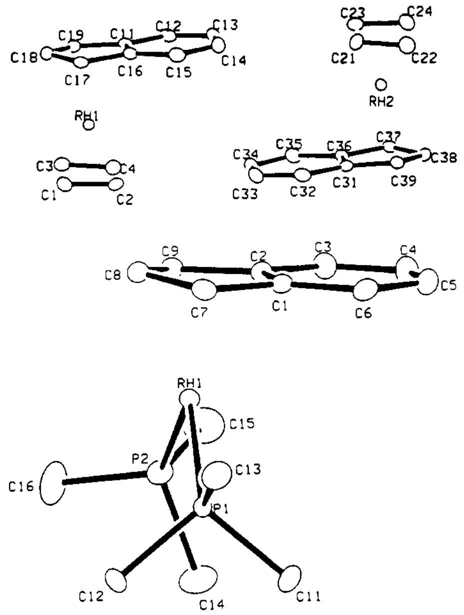


Figure 1. ORTEP views of **2a** (top) and **2b** (bottom). Important distances (Å) and angles (deg) for **2a**, molecule (1): Rh(1)–C(11), 2.359 (5); Rh(1)–C(16), 2.354 (5); Rh(1)–C(17), 2.178 (5); Rh(1)–C(19), 2.215 (5); Rh(1)–C(18), 2.203 (5); Rh(1)–C(ethylene), 2.135 (5) (average of four values). For **2a**, molecule 2: Rh(2)–C(31), 2.361 (5); Rh(2)–C(36), 2.349 (5); Rh(2)–C(37), 2.187 (5); Rh(2)–C(39), 2.201 (5); Rh(2)–C(38), 2.212 (5); Rh(2)–C(ethylene), 2.135 (5) (average of four values). For **2b**: Rh(1)–C(1), 2.449 (4); Rh(1)–C(2), 2.431 (4); Rh(1)–C(7), 2.244 (4); Rh(1)–C(9), 2.234 (4); Rh(1)–C(8), 2.229 (4); Rh(1)–P(1), 2.213 (1); Rh–P(2), 2.210 (1); P(1)–Rh(1)–P(2), 96.69 (4).

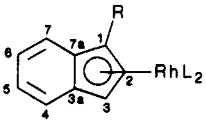
Molecular orbital arguments[8] suggest that an (η-C_9H_7)RhL_2 complex will possess a ground-state conformation in which the two ligands straddle a mirror plane incorporating Rh and C_2 of the indenyl ligand and bisecting the remainder of the indenyl ligand. To test the hypothesis that the barrier to hindered indenyl rotation is correlated with the degree of slip-fold distortion,[7] we have prepared a series of (η-1-$CH_3C_9H_6$)RhL_2 complexes[9] where L = alkene, CO, PR_3, or RNC or L_2 = $R_2PCH_2CH_2PR_2$. Incorporation of a methyl group at the 1-indenyl position breaks the molecule's ground-state C_s symmetry allowing the observation of two sets of ligand resonances at low temperature in the ^{31}P or ^{13}C NMR spectra. We report herein the preliminary results of this study, namely, the crystal and molecular structures of the parent (η-C_9H_7)RhL_2 complexes, L = C_2H_4 (**2a**) and PMe_3 (**2b**), and the dynamic $^{31}P\{^1H\}$ NMR spectra of (η-1-$CH_3C_9H_6$)Rh$(PMe_3)_2$ (**3b**).

Table I. Slip-Fold Parameters for (η-C_9H_7)RhL_2 Complexes[a]

complex	Δ, Å	HA, deg	FA, deg
2a[b]	0.160	8.34	7.30
2a[c]	0.161	7.81	7.50
2a[d]	0.161	8.08	7.40
2b[e]	0.201	8.42	7.89
2c[f]	0.046	2.35	2.55
2d[g]	0.23	10.6	8.5

[a] $\Delta = d\{(\mathrm{Rh}-C_{3a,7a}) - (\mathrm{Rh}-C_{1,3})\}$; HA (hingle angle) = angle between normals to the least-squares planes defined by C_1, C_2, C_3 and C_1, C_{7a}, C_{3a}, C_3; FA (fold angle) = angle between normals to least-squares planes defined by C_1, C_2, C_3 and C_{3a}, C_4, C_5, C_6, C_7, C_{7a}. [b] Molecule 1, this work. [c] Molecule 2, this work. [d] Average of values for two independent molecules, 1 and 2. [e] This work. [f] Reference 15. [g] Reference 11.

These results, in conjunction with those of McGlinchey et al.[10] on (η-1-$CH_3C_9H_6$)Rh(η-C_2H_4)$_2$ (**3a**), support our original hypothesis.



1, R = H, L_2 = (η-$C_6H_3Me_3$-1,3,5)Cr(μ-CO)$_2$(CO)
2a, R = H, L = η-C_2H_4
b, R = H, L = PMe_3
c, R = H, L_2 = η-duroquinone
d, R = H, L_2 = (η-C_5H_5)$_2$Zr(μ-PPh_2)$_2$
e, R = H, L_2 = (η-C_5H_5)$_2$Hf(μ-PEt_2)$_2$
3a, R = Me, L = η-C_2H_4
b, R = Me, L = PMe_3
c, R = Me, L_2 = (η-C_5H_5)$_2$Hf(μ-PEt_2)$_2$

Although several structures of indenyl rhodium complexes have been reported,[11] most contain complex ligands making an analysis of the relationship between slip-fold distortions and ligand electronic properties difficult. We therefore carried out X-ray diffraction studies[12] on **2a**,**b**, the results of which are illustrated in Figure 1. We chose three parameters[13] to define the slip-fold distortion: Δ, the slip parameter; HA, the hinge angle; and FA, the fold angle. Table I defines these parameters and lists pertinent values for **2a**–**d**. A clear trend is observed:[14] the degree of slip-fold distortion is indeed a function of the electronic parameters of the ligands; good σ-donors give rise to larger values of Δ, HA, and FA than alkene ligands, wherein each of these values diminishes as the π-acceptor capability of the alkene increases. The degree of slip-fold distortion is

---

[1] Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740. Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208.

[2] Eshtiagh-Hosseini, M.; Nixon, J. F. *J. Less-Common Met.* **1978**, *61*, 107.

[3] Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans* **1980**, 962; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648.

[4] Hart-Davis, A. J.; Mawby, R. *J. Chem. Soc. A* **1969**, 2403. White, C.; Mawby, R. *Inorg. Chim. Acta* **1970**, *4*, 261. White, C.; Mawby, R.; Hart-Davis, A. J. *Ibid.* **1970**, *4*, 441.

[5] Marder, T. B.; Williams, I. D. *J. Chem. Soc., Chem. Commun.*, in press.

[6] Marder, T. B.; Roe, D. C.; Milstein, D., in preparation.

[7] Barr, R. D.; Green, M.; Marder, T. B.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1261.

[8] See, for example: Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578. Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602. Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *Ibid.* **1978**, 1363.

[9] For the synthesis of **2a**,**b** and other bis(ligand) derivatives see ref 2, 3, and: Werner, H.; Feser, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 689. Complex **3a** has been reported: Caddy, P.; Green, M.; Smart, L. E.; White, N. *J. Chem. Soc., Chem. Commun.* **1978**, 839.

[10] Mlekuz, M.; Bougeard, P.; Sayer, B. G.; McGlinchey, M. J.; Rodger, C. A.; Churchill, M. R.; Ziller, J. W.; Kanz, S.-W.; Albright, T. A. *Organometallics* **1986**, *5*, 1656.

[11] Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839 and references therein.

[12] Crystal data collection and refinement for **2a**: $RhC_{13}H_{15}$, monoclinic, $P2_1/n$, a = 7.782 (2) Å, b = 10.838 (2) Å, c = 25.759 (4) Å, β = 98.47 (2)°, T = −102 °C, V = 2148.9 Å^3, Z = 8, μ(Mo) = 15.21 cm^{-1}; Enraf-Nonius CAD4, Mo Kα radiation, 4210 data collected by using the ω scan method, 1.6° ≤ 2θ ≤ 50.0°, 3219 unique reflections with I ≥ 3.0σ(I) used in solution and refinement; solution by automated Patterson analysis, refinement by full-matrix least squares, weights α $[\sigma^2(I) + 0.0009I^2]^{-1/2}$, 253 parameters, all non-H atoms anisotropic, H atoms fixed; R = 0.031, R_w = 0.039, largest residual density = 0.77 e/Å^3 near Rh. For **2b**: $RhP_2C_{15}H_{25}$, monoclinic, $P2_1$, a = 8.454 (2) Å, b = 12.201 (2) Å, c = 8.901 (3) Å, β = 113.54 (2)°, T = −102 °C, V = 841.7 Å^3, Z = 2, μ(Mo) = 11.70 cm^{-1}; Enraf-Nonius CAD4, Mo Kα radiation, 3015 data collected by using the ω scan method, 3.3° ≤ 2θ ≤ 62.0°, 2562 unique reflections with $I \geq 3\sigma(I)$ used in solution and refinement as for **2a**, 162 parameters, all non-H atoms anisotropic, H atoms fixed, R = 0.026, R_w = 0.032, largest residual density = 0.50 e/Å^3. Data for **2a**,**b** collected at Molecular Structure Corp.

[13] Similar parameters have been used in ref 11. See also: Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929, for a study of slip-fold distortions in (η-indenyl)ML_3 complexes.

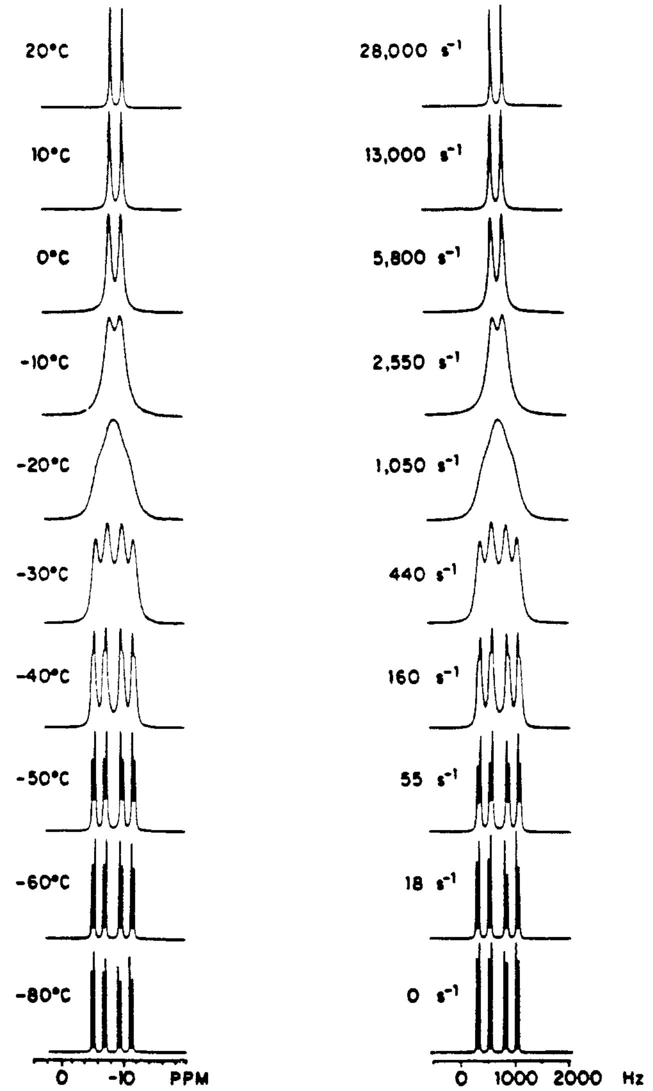


Figure 2. Observed and calculated variable-temperature $^{31}P\{^1H\}$ NMR spectra (121.69 MHz) for **3b**. Simulations were performed using a locally modified version of DNMR3. Activation parameters for indenyl rotation are ln $A = 29.81 \pm 0.55$, $E_a = 11.45 \pm 0.28$ kcal mol^{-1}, $\Delta G^{\ddagger}_{253}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

---

[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]

[15] Aleksandrov, G. G.; Struchkov, Yu. T. *Zh. Strukt. Khim.* 1971, *12*, 120.

[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(μ-H)B(3,5-$Me_2pz)_2$}Ru(η^4-C_8H_{12})H] and [(η^4-$C_8H_{12})_2Ru_2H$\{μ-N=C(Me)pz\}(μ-pz)(μ-H)]: Confirmation of the First Examples of the Ru···H–B Agostic Interaction and the Bridging Amidine Ligand

Michel O. Albers, S. Francesca A. Crosby,
David C. Liles, David J. Robinson, Alan Shaver,[†] and
Eric Singleton*

National Chemical Research Laboratory
Council for Scientific and Industrial Research, P.O. Box 395
Pretoria 0001, Republic of South Africa

Received February 3, 1987

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

---

[†] Senior Visiting Scientist from the Department of Chemistry, McGill University, Montreal, Quebec, Canada.