polymer, which was separated from the mother liquor by filtration. The mother liquor which remained after the last cycle was colorless.

Analysis of the sty–mah–12 Copolymer. IR (THF): ν_{CO} 2002 (vs), 1925 cm^{-1} (vs); ν_{NO} 1649 cm^{-1} (vs); $\nu_{polystyrene}$ 1602 cm^{-1} (m). The metal loading of the polymer was determined by a Beer's law analysis using the carbonyl stretches of the polymer-supported organometallic compound and the 1602-cm^{-1} peak of poly(sty–mah) (ϵ = 0.111 L g^{-1} cm^{-1}).

Incorporation of 16·hex into a Preformed Styrene–Maleic Anhydride (sty–mah) Copolymer. A flask was charged with 30 mL, THF, 0.8711 g of poly(sty–mah), 40.1 mg (0.040 mmol) of **16**·hex, and 6.0 mg (0.049 mmol) of 4-(dimethylamino)pyridine. The solution was stirred for 24 h and then concentrated to ca. 10 mL by removal of solvent in vacuo. Addition of hexane resulted in precipitation of the desired polymer, which was separated from the mother liquor by filtration. The polymer was purified by three cycles consisting of dissolution in THF, followed by addition of hexane and precipitation of the polymer, which was separated from the mother liquor by filtration. The mother liquor which remained after the last cycle was colorless.

Analysis of the sty–mah–16 Copolymer. UV/vis (THF): λ_{max} = 628 nm. Beer's law analysis of the polymer utilizing the 628-nm absorbance of the cluster indicated that the polymer contained 0.64 mol % **16**.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society for partial support of this research. Further funding of this project was provided by the West Virginia University Coal and Water Research Center.

Notes

Regioselective Reduction Reactions of the Cationic Benzene Complex $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$

Frederick L. Joslin and D. Max Roundhill*

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Received September 23, 1991

Summary: The new cationic ruthenium(II) complex $[(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ has been prepared by treating $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with $Cy_2PCH_2CH_2PCy_2$ and $AgCF_3SO_3$. This cationic complex reacts with sodium/potassium alloy to give the ruthenium(0) complex $(\eta^6\text{-}C_6H_6)Ru(Cy_2PCH_2CH_2PCy_2)$ and with $NaBH_4$ or $LiAlH_4$ to give $[(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ and $(\eta^5\text{-}C_6H_7)RuH(Cy_2PCH_2CH_2PCy_2)$, respectively.

η^6-Arene complexes of ruthenium(II) have been studied by several different groups of researchers.[1] These complexes have attracted interest because they represent one of the few examples of a series of stable η^6-arene complexes of a transition metal which are amenable to isolation in high yield. The particular group of complexes which are relevant to this work are those of type $(\eta^6\text{-arene})RuXL_2^+$ (X = anionic ligand; L = tertiary phosphine), which have a piano-stool structure.[2] These complexes have been shown to undergo two-electron reduction to the ruthenium(0) complex $(\eta^6\text{-arene})RuL_2$.[3] Alternately, these cationic complexes, like those of other transition metals, can undergo nucleophilic attack at the η^6-arene ligand to give a η^5-cyclohexadienyl complex.[4] When the nucleophile is hydride, an alternate possibility is that attack can occur at the metal center rather than at the benzene ring to give a ruthenium hydride product.[5] In this paper we report the synthesis of the new cationic complex $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$, and report the selectivity of its reduction chemistry. We find that it is possible to choose reagents either to effect selectively its reduction to a ruthenium(0) complex, to achieve hydride ion coordination to the ruthenium(II) center by chloride ion substitution, or to effect hydride ion transfer to *both* the ruthenium(II) center and the complexed η^6-arene. Results are presented that show a parallel with those found for $(\eta^6\text{-}C_6H_6)Mn(CO)_3^+$.[6]

Experimental Section

The complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ was prepared by standard procedures. The compound 1,2-bis(dicyclohexylphosphino)ethane was purchased from Strem Chemicals. Hydrated ruthenium trichloride was supplied by Matthey Bishop Corp., Malvern, PA. Silver trifluoromethanesulfonate was purchased from Aldrich Corp. Sodium borohydride and lithium aluminum hydride were commercial samples, and sodium/potassium alloy was prepared by standard procedures. Solvents were dried by standard techniques, and NMR spectra were measured in C_6D_6. All reactions were carried out either in a Vacuum Atmospheres drybox or by using cannula techniques. The NMR spectra were run on a Bruker AC200 or on a GE Omega 400 spectrometer. Microanalyses were carried out by Galbraith Inc., Knoxville, TN.

---

(1) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Eds.; Pergamon; Oxford, U.K., 1982; Vol 4, Chapter 32.3. Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47–137. Le Bozec, H.; Touchard, D.; Dixneuf, P. *Adv. Organomet. Chem.* **1989**, *29*, 163–247.

(2) Robertson, D. R.; Stephenson, T. A.; Arthur, T. *J. Organomet. Chem.* **1978**, *162*, 121–36.

(3) Werner, H.; Werner, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 683–4.

(4) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458–63. Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638–49. Werner, H.; Werner, R.; Burschka, C. *Chem. Ber.* **1984**, *117*, 152–60. Robertson, D. R.; Robertson, I. W.; Stephenson, T. A. *J. Organomet. Chem.* **1980**, *202*, 309–18.

(5) Bennett, M. A.; Huang, T. N.; Smith, A. K.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1978**, 582–3. Werner, H.; Kletzin, H. *J. Organomet. Chem.* **1982**, *228*, 289–300. Werner, H.; Kletzin, H. *J. Organomet. Chem.* **1983**, *243*, C59–C62. Bennett, M. A.; Latten J. *Aust. J. Chem.* **1987**, *40*, 841–9. Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003–8.

(6) Bladon, P.; Munro, G. A. M.; Pauson, P. L.; Mahaffy, C. A. L. *J. Organomet. Chem.* **1981**, *221*, 79–84. Brookhart, M.; Lamana, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638–49. Elschenbroich, Ch.; Salzer, A. *Organometallics, A Concise Introduction*; VCH: New York, 1989; p 290.

0276-7333/92/2311-1749$03.00/0

Chloro(benzene)[bis(dicyclohexylphosphino)ethane]ruthenium(II) Trifluoromethanesulfonate, $[(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$. Solid $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.485 g, 1.94 mmol) was placed in a Schlenk tube along with $Cy_2PCH_2CH_2PCy_2$ (0.819 g, 1.94 mmol) and a magnetic stir bar. The Schlenk tube was then sequentially evacuated and purged with argon. Using cannula techniques, THF (20 mL) was added to give a brown suspension. The suspension was stirred for 10 min, when a solution of silver trifluoromethanesulfonate (0.5 g, 1.94 mmol) in THF was added. The mixture was heated at reflux temperature for 1 h, during which time the color changed to dark green. The solid AgCl was filtered through fritted glass, and the dark green filtrate was collected. The THF solvent was removed in vacuo, and the residue was extracted with diethyl ether to give the product as green solid. Yield: 1.51 g (99%). Anal. Calcd for $C_{33}H_{54}ClF_3O_3P_2RuS$: C, 50.5; H, 6.93. Found: C, 49.5; H, 7.08. NMR (measured in C_6D_6): ^1H δ 5.52 (s, C_6H_6), 1.0–2.5 (m, CH and CH_2 of PCH_2 and Cy); $^{31}P\{^1H\}$ δ 74.6 (s); $^{13}C\{^1H\}$ δ 91.5 (s, C_6H_6), 41.5 ("vt", PCH (Cy), $|^1J(PC) + {}^3J(PC)| = 10.5$ Hz), 36.3 ("vt", PCH (Cy), $|(^1J(PC) + {}^3J(PC)| = 13.2$ Hz), 19.7 (PCH_2, $|^1J(PC) + {}^2J(PC)| = 21$ Hz), 10 unassigned cyclohexyl carbons in the range δ 25–34.

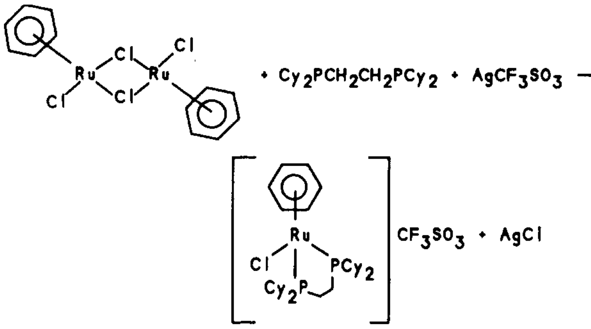
(Benzene)[bis(dicyclohexylphosphino)ethane]ruthenium(0), $(\eta^6\text{-}C_6H_6)Ru(Cy_2PCH_2CH_2PCy_2)$. A solution of $[(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (0.2 g, 0.255 mmol) in THF (10 mL) was added to sodium/potassium alloy (ca. 1 cm^3). The green solution was stirred for 12 h, during which time the color of the solution changed to a very dark red. The supernatant was removed by syringe, and removal of the solvent in vacuo gave the product as a dark red sticky solid. Yield: 0.115 g (75%). Attempted purification resulted in decomposition. NMR (measured in C_6D_6): ^1H δ 5.14 (s, C_6H_6), 0.9–2.3 (m, CH and CH_2 of PCH_2 and Cy); $^{31}P\{^1H\}$ δ 95.8 (s); $^{13}C\{^1H\}$ δ 76.4 (t, C_6H_6), $^2J(PC)$ 2.0 Hz), 40.3 ("vt", PC(1), $|^1J(PC) + {}^3J(PC)| = 9.0$ Hz), 28.0 ("vt", C(2), $|^2J(PC) + {}^4J(PC)| = 5.9$ Hz), 29.7 ("vt", C(3), $|^3J(PC) + {}^5J(PC)|$ unresolved), 27.3 (s, C(4)), 29.6 (s, C(5)), 27.8 ("vt", C(6), $|^2J(PC) + {}^4J(PC)| = 4.7$ Hz), 23.8 ("vt", PCH_2, $|^1J(PC) + {}^2J(PC)|$ = 22.7 Hz). The numbering C(1) through C(6) designates the cyclohexyl carbons.

Hydrido(benzene)[bis(dicyclohexylphosphino)ethane]ruthenium(II) Trifluoromethanesulfonate, $[(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$. Solid $[(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (0.1 g, 0.127 mmol) was dissolved in THF (10 mL) and excess sodium borohydride (20 mg) added. The mixture was stirred for 2 h, during which time the color changed from dark green to red brown. The supernatant liquid was filtered through glass wool to remove any solids, and then the THF solvent was removed in vacuo. The complex was obtained as a red brown solid. Yield: 0.083 g (87%). Anal. Calcd for $C_{33}H_{55}F_3O_3P_2RuS$: C, 52.7; H, 7.37. Found: 52.1; H, 7.27. NMR (measured in C_6D_6): ^1H δ 5.80 (s, C_6H_6), −12.4 (t, RuH, $^2J(PH) = 36.3$ Hz), 0.8–2.2 (m, CH and CH_2 of PCH_2 and Cy); $^{31}P\{^1H\}$ δ 97.8 (s); $^{13}C\{^1H\}$ (CD_3CN) δ 91.6 (s, C_6H_6), 39.1 (m, PCH (Cy)), 37.4 (m, PCH (Cy)), 22.2 ("vt", PCH_2, $|^1J(PC) + {}^2J(PC)|$ = 25.2 Hz), 10 unassigned cyclohexyl carbons in the range δ 26–31.

Hydridocyclohexadienyl[bis(dicyclohexylphosphino)ethane]ruthenium(II), $(\eta^5\text{-}C_6H_7)RuH(Cy_2PCH_2CH_2PCy_2)$. Solid $[(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (0.095 g, 0.121 mmol) was dissolved in THF (10 mL) and excess lithium aluminum hydride (0.02 g) added. The mixture was stirred for 2 h, and then the solids were allowed to settle. The dark red solution was filtered through alumina. Removal of the THF solvent from the filtrate gave the complex as a dark red sticky solid. Yield: 0.063 g (91%). Attempted purification resulted in decomposition. NMR (measured in C_6D_6): ^1H δ 3.04 (m, H(1) exo/endo), 3.41 (m, H(1) exo/endo), 2.95 (t, H(2,6), $^3J(HH) = 6.0$ Hz), 4.82 (t, H(3,5), $^3J(HH) = 5.74$ Hz), 5.83 (t, H(4), $^3J(HH) = 4.70$ Hz), −11.3 (broad, RuH); $^{13}C\{^1H\}$ δ 31.8 (s, C(1)), 37.5 (s, C(2,6)), 91.7 (s, C(3,5)), 73.7 (s, C(4)), 38.8 (d, PCH, $^1J(PC) = 16.3$ Hz), 38.3 (d, PCH, $^1J(PC) = 28.9$ Hz), 23.3 (dd, PCH_2, $|^1J(PC) + {}^2J(PC)|$ unresolved), 10 unassigned cyclohexyl carbons in the range δ 26–33. The numbering C(1) through C(6) designates the cyclohexadienyl ring carbons.

Results and Discussion

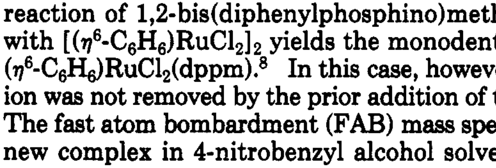
When the complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$[7] is treated with 1,2-bis(dicyclohexylphosphino)ethane and silver triflate in THF solvent, the dark green cationic 18-electron ruthenium(II) complex $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$ is obtained in quantitative yield (eq 1). The ^1H and $^{13}C\{^1H\}$ NMR spectra each show single resonances for the complexed benzene ring at δ 5.52 and 91.5, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a single resonance at δ 74.6, which confirms chelation of the diphosphine. The reaction of 1,2-bis(diphenylphosphino)methane (dppm) with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ yields the monodentate complex $(\eta^6\text{-}C_6H_6)RuCl_2(dppm)$.[8] In this case, however, a chloride ion was not removed by the prior addition of the silver ion. The fast atom bombardment (FAB) mass spectrum of this new complex in 4-nitrobenzyl alcohol solvent shows an envelope of peaks for the molecular ion of $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$ at m/z 637. This mass peak envelope results from the isotopomer distribution of the elements present in the cation, and the close correspondence between the experimental and calculated mass distribution confirms the stoichiometry of the cation. Mass peaks are also observed at m/z 544, 461, 378, and 295 for the sequential loss of the four cyclohexyl groups from the cation.



(1)

These spectral data support the piano-stool structure for the cation. The singlets in the ^1H and $^{13}C\{^1H\}$ NMR spectra for the complexed benzene confirm that this molecule is undergoing free rotation.[9]

With sodium/potassium alloy, a solution of $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$ in THF is quantitatively reduced to the zerovalent ruthenium complex, $(\eta^6\text{-}C_6H_6)Ru(Cy_2PCH_2CH_2PCy_2)$ (eq 2). This dark red complex is very air sensitive. The ^1H NMR spectrum of this Ru(0) complex shows a singlet resonance due to the benzene hydrogens at δ 5.14. This shift position is 0.38 ppm upfield of the benzene hydrogens in $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$, which correlates with the expected increase in shielding on going from a cationic Ru(II) to a neutral Ru(0) complex.[3] The $^{13}C\{^1H\}$ NMR spectrum shows a triplet resonance at δ 76.4 ($^2J(PC) = 2$ Hz) due to the benzene carbons; this shift is 15.1 ppm upfield of that in $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2PCy_2)^+$. The $^{13}C\{^1H\}$ NMR spectrum of this complex in the cyclohexyl region has the characteristically simple pattern for the C_{2v} symmetry of



(2)

---

[7] Arthur, T.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *208*, 369–87. Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233–41.

[8] Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063–72.

[9] Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* **1978**, *50*, 1–9.

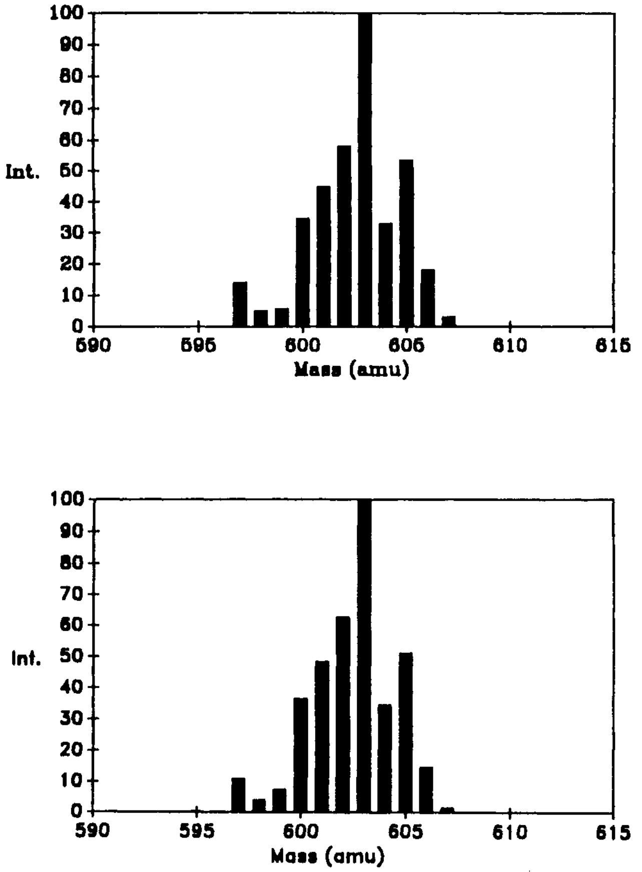
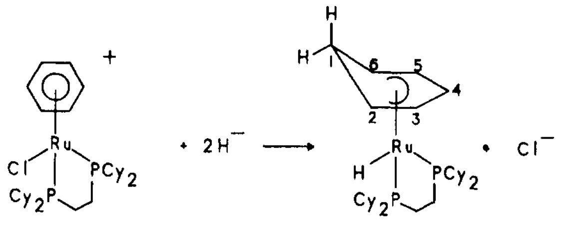


Figure 1. Calculated and observed FAB mass spectra of $[(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$.

the "two-legged" stool. In this symmetry all four cyclohexyl groups are chemically equivalent, and therefore only six cyclohexyl carbon signals are observed. For the complex $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$, only pairs of cyclohexyl groups are equivalent, and 12 cyclohexyl carbon signals are observed.[10] The FAB mass spectrum of $(\eta^6\text{-}C_6H_6)Ru(Cy_2PCH_2CH_2PCy_2)$ shows an envelope of peaks at m/z 603. The mass and intensity isotopomer distribution matches that for the molecular formula $(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)^+$. The Ru(0) complex has therefore been protonated by the 4-nitrobenzyl alcohol solvent matrix used in the FAB experiment.

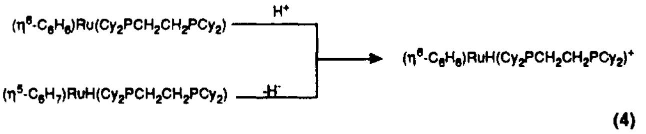
With sodium borohydride as reductant, a THF solution of $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$ undergoes selective metathetical replacement of the chloride ligand by a hydride ion. The hydride complex formed, $(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)^+$, shows a characteristic triplet in the ^{1}H NMR spectrum for RuH at δ -12.4 (^2J(PH) = 36 Hz). The protons of the benzene ring are observed at δ 5.80, which is 0.28 ppm downfield from the comparable resonance in $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$.[11] By contrast, the ^{13}C NMR shifts of the benzene carbons in the two complexes are identical. It is possible, therefore, that the difference in ^{1}H chemical shifts is due to steric rather than electronic reasons. The FAB mass spectrum of this complex is shown in Figure 1, along with the calculated isotope distribution. The close correspondence between these intensity plots confirms the stoichiometry of the cation as $(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)^+$. The isolation of this compound shows that the Ru–H bond is stable and that hydride migration to the ring does not spontaneously occur. Such migrations of a methyl group have, however, been observed for the complex $(\eta^6\text{-}C_6H_6)MnCH_3(CO)_2$.[12]

With lithium aluminum hydride, a stronger reducing agent than sodium borohydride, a THF solution of $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$ gives the η^5-cyclohexadienyl complex $(\eta^5\text{-}C_6H_7)RuH(Cy_2PCH_2CH_2PCy_2)$ as the sole identifiable product (eq 3). This product results from a reaction where *both* the metathetical replacemnt of chloride by hydride and the nucleophilic attack by hydride at the benzene ring have occurred. A likely pathway involves formation of $(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)^+$ as an intermediate, which then undergoes hydride ion attack at the complexed benzene ring. This proposal is supported by the observation that the first product of the reaction between $(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)^+$ and lithium aluminum deuteride is the monodeuteride complex $(\eta^6\text{-}C_6H_6)RuD(Cy_2PCH_2CH_2PCy_2)^+$. Longer reaction times give the doubly deuterated complex $(\eta^5\text{-}C_6H_6D)RuD(Cy_2PCH_2CH_2PCy_2)$.[13] The ^{1}H NMR spectrum of $(\eta^5\text{-}C_6H_7)RuH(Cy_2PCH_2CH_2PCy_2)$ shows a broad resonance for Ru–H at δ −11.3, which has no observable fine structure when the spectrum is measured at either 200 or 500 MHz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 95.6. The $^{13}C\{^1H\}$ NMR spectrum for the cyclohexyl carbons directly bonded to phosphorus now show doublets rather than virtual triplets ("vt"). The ^{1}H and $^{13}C\{^1H\}$ resonances for the η^5-cyclohexadienyl ring have been observed and assigned. The assignments have been made from an analysis of these COSY spectra. The ^{1}H NMR spectrum shows two resolved resonances at δ 3.04 and 3.41 due to the exo and endo hydrogens on C(1). This observation of two separate resonances for the exo and endo hydrogens on C(1) shows that fast exchange in solution between these hydrogens does not occur. The FAB mass spectrum of this complex gives the same envelope of peaks as $(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)^+$, presumably by loss of hydride from $(\eta^5\text{-}C_6H_7)^-$ in the matrix.



(3)

Under the conditions of the mass spectroscopic experiment, it appears that the ion $(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)^+$ is particularly stable. The conversions of $(\eta^6\text{-}C_6H_6)Ru(Cy_2PCH_2CH_2PCy_2)$ by proton capture and $(\eta^5\text{-}C_6H_7)RuH(Cy_2PCH_2CH_2PCy_2)$ by hydride loss into the ion $(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH(Cy_2PCH_2CH_2PCy_2)^+$, are shown in eq 4.



(4)

Acknowledgment. We thank the Louisiana Educa-

---

[10] Joslin, F. L.; Pontier Johnson, M.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781–94.

[11] Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047–77. Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1–48. Warren, K. D. *Struct. Bonding* **1976**, *27*, 45–159.

[12] Rush, P. K.; Noh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745–7.

[13] In the reaction with $LiAlD_4$ the NMR signals due to the exo and endo hydrogen atoms could not be fully resolved from those due to the THF solvent occluded in the compound. If diethyl ether was used as solvent instead of THF, no reaction was observed.

tional Support Fund, administered by the Louisiana Board of Regents, for financial support. We thank Dr. B. Tobias for assistance with the 2D NMR spectra. We thank Matthey Bishop Inc. for a loan of ruthenium trichloride.

Registry No. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, 37366-09-9; $Cy_2PCH_2CH_2PCy_2$, 23743-26-2; $[(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$, 139378-00-0; $(\eta^6\text{-}C_6H_6)Ru(Cy_2PCH_2CH_2PCy_2)$, 139378-01-1; $[(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$, 139378-03-3; $[(\eta^5\text{-}C_6H_7)RuH(Cy_2PCH_2CH_2PCy_2)]$, 139378-04-4; silver trifluoromethanesulfonate, 2923-28-6.

Molecular Structures of Germacyclohexane and 1,1-Dimethylgermacyclohexane As Determined by Gas-Phase Electron Diffraction

Quang Shen,*[†] Shannon Rhodes,[†] Yoshito Takeuchi,[‡] and Katsumi Tanaka[‡]

Department of Chemistry, Colgate University, 13 Oak Drive, Hamilton, New York 11346,
and Department of Chemistry, The College of Arts and Sciences,
The University of Tokyo, Kamaba, Meguro-ku, Tokyo, 153 Japan

Received October 24, 1991

Summary: The molecular structures of germacyclohexane and 1,1-dimethylgermacyclohexane have been studied by gas-phase electron diffraction. Both molecules exist in the chair conformation with similar structures. The important geometrical parameter values (r_g and $\angle_\alpha$) obtained from least-squares analysis for germacyclohexane are r(C–H) = 1.108 (6) Å, r(Ge–H) = 1.530 (32) Å, r(C–C)$_{av}$ = 1.535 (3) Å, r(Ge–C) = 1.956 (4) Å, $\angle C_2C_3C_4$ = 114.4 (29)°, $\angle GeC_2C_3$ = 110.9 (20)°, FlapG [Flap angle at the germanium end of the ring] = 140 (9)°, Flap = 122 (3)°. Error limits are given as 2σ.

The molecular structures of germacyclohexane and several methyl-substituted germacyclohexanes have been studied by NMR spectroscopy and molecular mechanics calculations.[1] The calculations showed that the six-membered ring has a chair conformation flattened around the germanium atom. In 1-methylgermacyclohexane the axial form is slightly favored over the equatorial form. The ^{13}C and ^{73}Ge chemical shifts were consistent with the calculations.

We have been interested in the structure of five- and six-membered rings[2] and have reported the structure of silacyclohexane[3] which is found to exist in the gas phase in a chair conformation. The six-membered ring is slightly flattened at the silicon atom. The CSiC valence angle is smaller than the tetrahedral value. The Si–C bond length is comparable to the ones found in strained cyclic silanes. We felt that the structures of germacyclohexane and 1,1-dimethylgermacyclohexane would provide an interesting comparison with the structures of cyclohexane and silacyclohexane. Experimental structural information for germacyclohexane (GCH) and 1,1-dimethylgermacyclohexane (DMGCH) will help to improve the force field used in molecular mechanics calculations. In this note we are reporting the gas-phase structures of GCH and DMGCH obtained from electron diffraction experiments.

Table I. Structural Parameters Obtained from Least-Squares Analysis for Germacyclohexane and 1,1-Dimethylgermacyclohexane[a]

molecule	germacyclohexane	1,1-dimethylgermacyclohexane
r(C–H)	1.108 (6)	1.107 (4)
r(Ge–H)	1.530 (32)	
R(C–C)$_{av}$	1.535 (3)	1.539 (3)
r(Ge–C)	1.956 (4)	1.957 (2)[b]
$\angle C_2C_3C_4$	114.4 (38)	114.4 (15)
$\angle GeC_2C_3$	110.9 (30)	111.1 (15)
$\angle C_mGeC_m$[c]		114.0 (53)
FlapG[d]	140.7 (96)	140.6 (42)
Flap[e]	121.8 (30)	123.8 (31)
	Dependent Parameters	
$\angle C_2GeC_6$	102.5 (35)	103.1 (18)
$\angle C_3C_4C_5$	114.1 (28)	116.9 (32)
tGe234[f]	55.6 (47)	53.5 (25)
t2345	67.4 (37)	64.5 (37)
t2Ge65	42.0 (98)	42.3 (48)

[a] Distances (r_g) in angstroms, angles ($\angle_\alpha$) in degrees. Values in parentheses are 2θ which include estimates of systemic errors. [b] Average value, Ge–C$_2$ = Ge–C$_7$ assumed. [c] C$_m$ (methyl carbon atoms, C$_7$ and C$_8$). [d] Flap value at the gemanium end of the molecule; angle between planes formed by atoms Ge, C$_2$, and C$_6$ and C$_2$, C$_6$, C$_3$, and C$_5$ (with planar = 180°). [e] Flap angle at the carbon end of the molecule; angle between planes formed by atoms C$_4$, C$_3$, and C$_5$ and C$_3$, C$_5$, C$_2$, and C$_6$ (with planar = 180°). [f] Torsion angle Ge–C$_2$–C$_3$–C$_4$.

Experimental Section

Germacyclohexane (GCH) and 1,1-dimethylgermacyclohexane (DMGCH) were prepared and purified according to the procedures described in the literature.[1] The electron diffraction patterns were recorded using the Colgate apparatus with an r^3 sector at nozzle-tip temperatures of 23 °C (GCH) and 65 °C (DMGCH), an accelerating voltage of 40 keV, exposure times of 1 (long camera) to 3 min (short camera) and a background pressure of 1.2×10^{-5} Torr with the help of a liquid nitrogen trap. Benzene calibration plates taken under conditions identical with those of the experiment were used for the wavelength calibration standard.[4] For each molecule, four plates from the 100-mm and four plates from the 245-mm camera distances were used for the analysis.

The photographic plates were traced on the densitometer at intervals of 0.20 mm for the long and 0.15 mm for the short camera plates. These data were corrected for emulsion saturation, plate flatness, and sector imperfections and interpolated to integral $q[(40/\pi)\sin(\theta/2)]$ units. Least-squares analysis of the data was

---

[†] Colgate University.

[‡] University of Tokyo.

(1) Takeuchi, Y.; Shimoda, M.; Tanaka, K.; Tomoda, S.; Ogawa, K.; Suzuki, H. *J. Chem. Soc. Perkin Trans.* **1988**, 7.

(2) Hilderbrandt, R. L.; Shen, Q. *J. Phys. Chem.* **1982**, *86*, 587. Shen, Q. *J. Mol. Struct.* **1982**, *96*, 133.

(3) Shen, Q.; Hilderbrandt, R. L.; Mastryukov, V. *J. Mol. Struct.* **1979**, *54*, 121.

(4) Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243.