Azaruthenocenes: Preparation of $[(\eta^5\text{-}C_4Me_4N)Ru(\eta^5\text{-}C_5Me_5)]$ and $[(\eta^5\text{-}C_4Me_4N)_2Ru]$, the First Ruthenium Metallocenes Incorporating η^5-Pyrrolyl Ligands

William J. Kelly* and William E. Parthun

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008

Received August 12, 1992

Summary: Treatment of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_x$ with (2,3,4,5-tetramethylpyrrolyl)lithium affords the novel azaruthenocene $[(\eta^5\text{-}C_4Me_4N)Ru(\eta^5\text{-}C_5Me_5)]$ (**1**) in 81% yield. The novel diazaruthenocene $[(\eta^5\text{-}C_4Me_4N)_2Ru]$ (**2**) is obtained as a minor byproduct in this reaction. The reaction of (2,3,4,5-tetramethylpyrrolyl)lithium and $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$ gives **2** in 78% yield. These new complexes have been characterized by a combination of elemental analysis and NMR spectroscopic methods and exhibit notable stability.

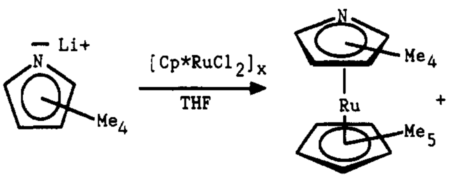
Since the synthesis of azaferrocene, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_4H_4N)$,[1] in 1964 there has been considerable interest in the synthesis of metallocenes incorporating one or more heterocyclopentadienyl ligands.[2] Five-membered heterocycle ligands such as C_4H_4N (pyrrolyl), C_4H_4P (phosphoryl), and C_4H_4As (arsolyl), which are iso-π-electronic with the cyclopentadienyl ring, have been employed in the preparation of various metallocenes.[3-6] The nitrogen analogues have a chemistry which is far different from that of the phospha- and arsaferrocenes. Most striking is that, for the elements of phosphorus and arsenic, multiple incorporation of the heteroatom can be easily achieved; 1,1′-diphosphaferrocenes and 1,1′-diarsaferrocenes have been synthesized and structurally characterized.[4] Earlier attempts to synthesize derivatives of ferrocene in which more than one methine group was substituted by a nitrogen atom were unproductive.[5] The failure had been ascribed to both the marked tendency of nitrogen to function as a monodentate ligand and to the fact that, compared to C_5H_5, the pyrrolyl group is a weaker π-donor and/or stronger π-acceptor. Recently, Kuhn reported the preparation and X-ray structure of bis(2,3,4,5-tetramethylpyrrolyl)iron(II), $(\eta^5\text{-}C_4Me_4N)_2Fe$, the first group VIII metallocene incorporating two η^5-pyrrolyl ligands.[6b,c] In this compound both σ-rearrangement of the coordinated pyrrolyl ligand and nucleophilic attack by the basic nitrogen atoms are prevented by the steric demand of the flanking methyl groups at the C_2 and C_5 ring positions.

Ruthenocene, first prepared in 1952,[7] was the second member of the group VIII metallocenes to be prepared and characterized. In contrast to the extensive chemistry of the ferrocenes, ruthenium metallocenes have not received similar study, due to the lack of convenient methods for their preparation. Heterocyclopentadienyl complexes of ruthenium have not been reported. Recent accounts of convenient, high-yield synthetic routes to ruthenocenes make azaruthenocenes more accessible.[8,9] In this note we wish to report the preparation and characterization of $(\eta^5\text{-}C_4Me_4N)Ru(\eta^5\text{-}C_5Me_5)$ (1) and $(\eta^5\text{-}C_4Me_4N)_2Ru$ (2), the first ruthenium metallocenes to incorporate one or two η^5-pyrrolyl ligands.

Results and Discussion

Singleton[8] and Gassman[9a] pioneered the use of ruthenium half-sandwich complexes in the preparation of ruthenocenes. In particular, the ruthenium(III) complex $[(\eta^5\text{-}C_5Me_5)RuCl_2]_x$ has been used for the efficient preparation of mixed-ligand ruthenocenes incorporating a pentamethylcyclopentadienyl (Cp*) ligand.[9a] Accordingly, we set out to explore the propensity of the pyrrole anion to form a stable metallocene wherein the other ligand is the π-basic, electron donating Cp*.

Treatment of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_x$[10] with 2 molar equiv of the lithium salt of 2,3,4,5-tetramethylpyrrole in tetrahydrofuran for 12 h, followed by workup and purification by column chromatography on alumina, afforded the azaruthenocene 1 in 81% yield (eq 1). However, also isolated from this reaction was diazaruthenocene **2**. Complexes 1 and 2 were readily characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by elemental analysis, and the data bear no remarkable features. Complex 1 has a ^1H NMR spectrum consisting of the expected singlet at 1.73 ppm (15 H), for the protons of the five equivalent Cp* methyl groups, and two singlets at 1.95 and 1.69 ppm (6 H each), corresponding to the C_2–C_5 and C_3–C_4 pyrrole methyl groups, respectively. Characteristic $^{13}C\{^1H\}$ NMR signals are observed at 84.02 and 10.12 ppm for the Cp* ring and methyl carbons. The ring carbons of the tetramethylpyrrolyl ligand resonate at 102.08 and 88.94 ppm, while the methyl carbons appear at 12.78 and 9.10 ppm for the C_2–C_5 and C_3–C_4 positions. The ^1H NMR spectrum of complex 2 reveals two singlets of equal intensity at 2.18 and 1.94 ppm, as expected for two sets of equivalent



1 2

(1)

---

(1) (a) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 796. (b) Joshi, K. K.; Pauson, P. L.; Qazi, A. R.; Stubbs, W. H. *J. Organomet. Chem.* **1964**, *1*, 471.

(2) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1982; Vol. 4, pp 486–487.

(3) (a) Mathey, F.; Mitschler, A.; Weiss, A. *J. Am. Chem. Soc.* **1977**, *99*, 3537. (b) Fischer, J.; Mitschler, A.; Ricard, L.; Mathey, F. *J. Chem. Soc., Dalton Trans.* **1980**, 2522.

(4) de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994.

(5) Seel, F.; Sperber, V. *J. Organomet. Chem.* **1968**, *14*, 405.

(6) (a) Kuhn, N.; Horn, E.-M.; Boese, R.; Augart, N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1368. (b) Kuhn, N.; Horn, E.-M.; Boese, K.; Augart, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 342. (c) Kuhn, N.; Kuhn, A.; Lampe, E.-M. *Chem. Ber.* **1991**, *124*, 997.

(7) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6146.

(8) (a) Albers, M. O.; Liles, D. C.; Robinson, D.; Shaver, A.; Singleton, E.; Wiege, M. B.; Boegens, J. C. A.; Levendis, D. C. *Organometallics* **1986**, *5*, 2321. (b) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199.

(9) (a) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130. (b) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274. (c) Oshima, N.; Suzuki, H.; Moro-Oka, Y. *Chem. Lett.* **1984**, 1161.

(10) Brown, G. M.; Hedberg, F. L.; Rosenberg, J. *J. Chem. Soc., Chem. Commun.* **1972**, 5.

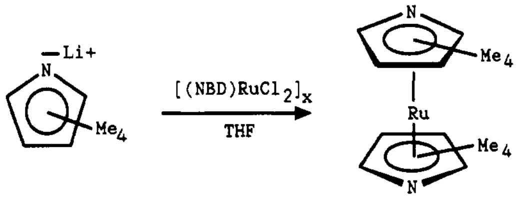
0276-7333/92/2311-4348$03.00/0

methyl protons. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows signals at 103.70 and 98.04 ppm for the ring carbons and 13.91 and 8.26 ppm for the methyl carbons.

Presumably complex **2** is formed in this case by the reaction of the pyrrolide anion and $RuCl_2$, which is present in small amounts as a contaminant in $[(\eta^5\text{-}C_5Me_5)RuCl_2]_x$. Elemental analysis of the Ru(III) polymer showed values for C and H somewhat lower than expected, while the value for Cl was slightly higher.[11] Some parts of the polymer chain of $[\eta^5\text{-}C_5Me_5)RuCl_2]_x$ are lacking in a pentamethylcyclopentadienyl ligand. Similar mixtures have been observed in polymeric bis(μ-chloro)(π-benzene)ruthenium(II) complexes.[12]

Although our initial synthesis of the novel dipyrrolyl complex **2** was by a fortuitous accident, we were encouraged by the results obtained and by the apparent stability of the complex to explore an alternate route to **2**. However, the direct reaction between lithium 2,3,4,5-tetramethylpyrrolide and anhydrous $RuCl_3$ produced low and variable yields of complex **2**, ranging from 8 to 27%. Three equivalents of the pyrrole anion is required for optimum yield, since 1 equiv is involved in the reduction of Ru(III) to Ru(II).

The problems associated with the use of ruthenium trichloride in the formation of ruthenium metallocenes can be avoided by the use of ruthenium(II) diolefin complexes such as $[(\eta^4\text{-}C_8H_{12})RuCl_2]_x$. Complexes of this type bear labile diolefin and chloro ligands which are easily displaced.[8a] The polymeric ruthenium(II) complex $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$,[13] obtainable in high yield from norbornadiene and ruthenium trichloride in refluxing ethanol, was employed in the preparation of **2**. Treatment of $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$ with 2 molar equiv of (2,3,4,5-tetramethylpyrrolyl)lithium in tetrahydrofuran for 12 h, followed by workup and purification, afforded **2** in 78% yield (eq 2). Complex **2** obtained by this route was identical in all respects with **2** isolated previously. It is notable that this route gives reproducible, high yields of **2** as the only metallocene product, and the preparation can be successfully scaled up to produce large quantities of the product.



2 (2)

Complexes **1** and **2** are reasonably air-stable as solids but are best kept in the solid phase under an inert atmosphere. However, both are unstable in solution. Complex **2** slowly decomposes in pentane solution over a period of 14 days to give decamethylruthenocene and metallic ruthenium. Both complexes exhibit remarkable thermal stability; **2** survives intact for over 2 h in refluxing, degassed toluene. Complex **1** slowly decomposes over a period of 24 h in refluxing xylenes to give ruthenium metal and a black solid of undetermined composition.

In contrast to the ease with which carbon monoxide displaces the pyrrolyl ligand in azaferrocene to form $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_4H_4N)$,[14] preliminary results indicate that the ruthenium-complexes C_4Me_4N ligand is quite resistant to η^5-η^1 (π–σ) rearrangements in the azaruthenocenes. Carbon monoxide was bubbled through a solution of **1** (0.10 mmol) in 25 mL of dry, oxygen-free benzene, and then the saturated solution was heated to 80 °C in a sealed tube for 8 h. The benzene was evaporated under vacuum, and analysis of the crude reaction mixture by IR spectroscopy failed to show the presence of complexed CO ligands in the carbonyl stretching region (1900–2100 cm^{-1}). Upon purification of column chromatography, 92% of the starting material was recovered unaffected. This is confirmation of Kuhn's observation of the stabilization of nitrogen-containing metallocenes by methylation of the heterocyclic ring.[6a]

The procedures reported here are the first syntheses of ruthenium metallocenes incorporating one or two π-complexed pyrrolyl ligands. Complexes of this type can now be prepared in high yield and in large quantities for further studies of their physical and chemical properties.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran and pentane were distilled from Na, and benzophenone was distilled under an atmosphere of dry nitrogen. The ruthenium complexes used here, $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$,[13] and $[(\eta^5\text{-}C_5Me_5)RuCl_2]_x$,[10] were prepared by literature methods. Anhydrous $RuCl_3$ was purchased from Aldrich Chemical Co. and used as obtained. The organic reagents used to prepare ligands were purchased from Aldrich Chemical Co. and used as received; 2,3,4,5-tetramethylpyrrole was prepared by the literature method.[15] ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were obtained in chloroform-*d* using tetramethylsilane as an internal standard on an IBM AFT 200 nuclear magnetic resonance spectrometer. Mass spectra were obtained with a Hewlett-Packard 5890 gas chromatograph with a 5970 mass selective detector. Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Preparation of (η^5-2,3,4,5-Tetramethylpyrrolyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (1) and Bis(η^5-2,3,4,5-tetramethylpyrrolyl)ruthenium(II) (2). In a 100-mL three-necked round-bottom flask, equipped with a bar stirrer, nitrogen inlet, and septum, was placed 2,3,4,5-tetramethylpyrrole (1.22 g, 10.0 mmol) and dry tetrahydrofuran (70 mL). To the stirred solution under nitrogen was added 6.9 mL (11.0 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was stirred for 1 h, dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer (1.54 g, 5.0 mmol) was added, and the mixture was stirred under nitrogen for 24 h. The solvent was evaporated under a steady stream of dry nitrogen to give a brown-black solid, which was extracted with two 100-mL portions of pentane. The pentane extracts were concentrated under a stream of nitrogen to a volume of ca. 5 mL and chromatographed on a 15-cm column of activity III neutral alumina. Elution with chloroform, followed by removal of solvent, afforded a light brown solid. Low-temperature recrystallization from pentane gave 1.44 g (81% yield) of **1** as a tan solid: mp 76–78 °C; ^1H NMR ($CDCl_3$) δ 1.95 (s, 6 H), 1.73 (s, 15 H), and 1.69 ppm (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 102.08, 88.94, 84.02, 12.78, 10.12, 9,10 ppm; mass spectrum *m/e* (%) 359 (100) [m^+, ^{102}Ru], 344 (48) [$m^+ - CH_3$], 237 (26) [$m^+ - C_4Me_4N$]. Anal. Calcd for $C_{18}H_{27}NRu$: C, 60.31; H, 7.59; N, 3.91. Found: C, 60.36; H, 8.01; N, 3.81.

Further elution with chloroform–acetone (1:1) afforded a brown solid which after low-temperature recrystallization from pentane gave 0.06 g (3% yield) of **2** as a light brown solid: mp 63–66 °C; ^1H NMR ($CDCl_3$) δ 2.18 (s, 12 H), 1.94 ppm (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 103.70, 89.04, 13.91, 8.25 ppm; mass spectrum *m/e* (%) 346 (100) [M^+, ^{102}Ru], 331 (17) [$M^+ - CH_3$], 224 (18) [$M^+ - C_4Me_4N$]. Anal. Calcd for $C_{16}H_{24}N_2Ru$: C, 55.63; H, 7.00; N, 8.11.

---

[11] Anal. Calcd for $[(\eta^5\text{-}C_5Me_5)RuCl_2]_x$ $C_{10}H_{15}RuCl_2$: C, 39.09; H, 4.89; Cl, 23.13. Found: C, 38.55; H, 4.27; Cl, 23.60.

[12] Iwata, R.; Ogata, I. *Tetrahedron* **1973**, *29*, 2753.

[13] Abel, E. W.; Bennett, M. A.; Wilkinson, G. J. *J. Chem. Soc.* **1959**, 3178.

[14] Efraty, A.; Jubran, N. *Inorg. Chim. Acta* **1980**, *44*, L191.

[15] Johnson, A. W.; Price, R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 1022.

Found: C, 55.75; H, 6.97; N, 8.05.

Reaction of Lithium 2,3,4,5-Tetramethylpyrrolide with $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$. In a three-necked round-bottom flask, equipped with a bar stirrer, nitrogen inlet, and septum, was added 2,3,4,5-tetramethylpyrrole (1.23 g, 10.0 mmol) and dry tetrahydrofuran (70 mL). To the stirred solution under nitrogen was added 6.9 mL (11.0 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was stirred under nitrogen for 1 h, $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$ (1.31 g 5.0 mmol) was added, and the mixture was stirred for 15 h. The solvent was evaporaed under a steady stream of dry nitrogen to give a black solid, which was extracted with two 100-mL portions of pentane. The volume of pentane was reduced under a stream of nitrogen to a volume of 5 mL and chromatographed on a 15-cm column of activity III neutral alumina. Elution with chloroform–acetone (1:1) gave a light brown solid, which was recrystallized from pentane to give 1.37 g (78% yield) of **2** as orange-brown crystals. The complex was identified as above.

Acknowledgment. The helpful comments of Professor C. H. Winter are greatly appreciated.

Registry No. **1**, 144467-23-2; **2**, 144467-24-3; $[Cp^*RuCl_2]_x$, 96503-27-4; $[(\eta^4\text{-}C_7H_8)RuCl_2]_x$, 42740-82-9; 2,3,4,5-tetramethylpyrrole, 1003-90-3.

OM920496W

Cautions on Use of the AM1 Semiempirical Parameters for Germanium

Andrew J. Holder* and Clarke W. Earley*

Department of Chemistry, The University of Missouri—Kansas City, Kansas City, Missouri 64110

Received July 15, 1992

Summary: Caution should be exercised in the use of results employing the AM1 germanium parameters for molecules containing germanium atoms directly bonded to one another. In these cases, a smaller than expected value of the β_p parameter causes an exaggerated separation of charge. In order to demonstrate this point, a trial value of β_p was used and the results performed in the manner expected when the size of this parameter was increased. However, we *do not* recommend the replacement of the germanium β_p value. In combination with other elements, the literature values for the germanium parameters appear to perform adequately.

Introduction

In a recent AM1 investigation, we observed an unexpectedly large charge localization on germanium atoms bonded to one another. We wish to report here a more detailed analysis of the origin of this problem based on examination of the AM1 parameter values. To this end, we have examined the results of AM1 calculations on trigermapropane (germanapropane, Ge_3H_8, **1**), trigermacyclopropane (germanacyclopropane, Ge_3H_6, **2**), and tetragermacyclobutane (germanacyclobutane, Ge_4H_8, **3**).

Methodology

Semiempirical calculations were performed using the AM1[1] Hamiltonian with previously published parameter sets[2] as implemented in a slightly modified version of the AMPAC 2.1[3] computer program. A trial value for β_p on germanium was entered manually for test purposes only. Geometries were fully optimized without symmetry constraints. An examination of the matrix of second derivatives of energy with respect to atomic positions (force constants) was performed to verify that the stationary points located were minima.[4] Partial charges were calculated using the default procedure contained in the AMPAC program, which uses a Coulson analysis of the final density matrix.[5,6] In this approach, the occupancy of each atomic orbital is calculated by summing the squares of the normalized atomic orbital basis set coefficients for the occupied molecular orbitals and multiplying by the occupancy of each molecular orbital. The partial charge is then obtained by subtracting the sum of these occupancies from the number of valence electrons on each atom. Computations were carried out on the UMKC VAX 6540V from Digital Equipment Corp.

Table I. AM1 Geometries and Atomic Charges for Germanapropane (1), Germanacyclopropane (2), and Germanacyclobutane (3)

	1	2	3
Ge-Ge[a]	2.26	2.39	2.23
Ge-H	1.53	1.55	1.51, 1.54
Ge-H'[b]	1.54		
q_{Ge}[c]	+1.22	−0.10	+2.16, −2.18
$q_{Ge'}$	−1.83		
q_H	−0.20	+0.05	−0.34, + 0.35
$q_{H'}$	+0.31		

[a] Bond lengths in Å. [b] Atoms designated with a prime refer to the center GeH_2 of the propane analog. [c] Partitioned atomic charge.

Results

The AM1 geometries and charges for the germanium analogs of propane (**1**), cyclopropane (**2**), and cyclobutane (**3**) are listed in Table I. There are no experimental results available on the structure of **1**. An X-ray investigation[7] of a highly substituted analog of **2** has been published. A comparison of the Ge–Ge bond lengths obtained with AM1 and the values from experiment indicates that the AM1-calculated Ge–Ge distance is somewhat shorter than expected (2.39 vs 2.54 Å). The AM1 distance is also shorter than that predicted by ab initio calculations for unsubstituted **2** (2.50 Å).[8] AM1 also underestimates the Ge–Ge

---

(1) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* *107*, **1985**, 3902.

(2) (a) H: See ref 1. (b) Ge: Dewar, M. J. S.; Jie, C. *Organometallics* **1989**, *8*, 1544.

(3) Dewar, M. J. S. *AMPAC*; Quantum Chemistry Program Exchange: Bloomington, IN; QCPE No. 506.

(4) McIver, J. W.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 303. (b) McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

(5) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838.

(6) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970; p 67.

(7) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

(8) Rubio, J.; Illas, F. *J. Mol. Struct.* (*THEOCHEM*) **1984**, *110*, 131.

0276-7333/92/2311-4350$03.00/0