Organometallics **1986**, *5*, 2199–2205 2199

Chemistry of Cyclopentadienyl–Ruthenium and –Osmium Complexes. 1. The Preparation and Substitution Reactions of (η^4-Cycloocta-1,5-diene)(η^5-cyclopentadienyl)haloruthenium(II) Complexes. Versatile New Synthetic Precursors to "Open-Face" Cyclopentadienyl–Ruthenium(II) Chemistry

Michel O. Albers, 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 April 9, 1986

Treatment of $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ (C_8H_{12} = cycloocta-1,5-diene) with cyclopentadienylthallium in refluxing acetone affords the novel cyclopentadienyl-ruthenium(II) complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})H]$ (**1**). Reaction of **1** with halogenating agents (CCl_4, CH_2Br_2, CH_3I) in pentane gives the halo complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$ (**2**–**4**; X = Cl, Br, I), while halide metathesis on **2** using either NaBr or NaI in methanol provides alternative routes to **3** and **4**, respectively. The substitution of the cycloocta-1,5-diene and/or chloro ligands in **2** in a range of solvents and under mild reaction conditions is a rapid and facile process. Mono- and bidentate ligands [CO, PPh_3, PMe_3, 1,2-bis(diphenylphosphino)ethane, $P(OMe)_3$, PPh_2H, MeNC, *t*-BuNC, 2,6-$Me_2C_6H_3NC$, $CN(CH_2)_6NC$, 3,4,7,8-Me_4-1,10-phenanthroline] and the dienes (buta-1,3-diene, 2,3-dimethylbuta-1,3-diene, 1-methyl-4-(methoxycarbonyl)buta-1,3-diene, bicyclo[2.2.1]hepta-2,5-diene) substitute the cycloocta-1,5-diene ligand in **2**, in ethanol, acetone, or tetrahydrofuran solutions to give neutral products of the general type $[(\eta^5\text{-}C_5H_5)RuL_2Cl]$. Polyolefins (cyclohepta-1,3,5-triene, cycloocta-1,3,5-triene, cyclooctatetraene) and aromatics (benzene, hexamethylbenzene, indene, benzyl chloride, triphenylamine) react with **2** in refluxing ethanol solution to give, following anion exchange with NH_4PF_6, salts of the general formulation $[(\eta^5\text{-}C_5H_5)RuL_3]PF_6$. Sodium tetraphenylborate reacts directly with **2** in refluxing ethanol to give the zwitterionic η^6-arene complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5BPh_3)]$. Cyclopentadienylsodium reacts with **2** in tetrahydrofuran at room temperature giving ruthenocene, while sodium hydrotris(1-pyrazolyl)borate ($NaHBpz_3$) with **2** in ethanol yields the unusual "metallocene" $[(\eta^5\text{-}C_5H_5)Ru(HBpz_3)]$. These compounds are all obtained in high yield and have been characterized by a combination of elemental analysis and spectroscopic methods (IR and ^1H and ^{13}C NMR spectroscopy).

Introduction

Traditional synthetic routes to half-sandwich cyclopentadienyl–ruthenium(II) complexes have, in general, relied extensively upon the compounds $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl]$ as starting materials.[1,2] While these approaches have undoubtedly led to a fairly extensive chemistry of cyclopentadienyl–ruthenium(II) systems, certain of the now well-established reactivity patterns of these compounds, particularly the reluctance to undergo substitution of both the donor ligands, have effectively precluded the *systematic* development of cyclopentadienyl–ruthenium chemistry.[1,2]

In an attempt to elaborate the chemistry of cyclopentadienyl–ruthenium complexes along more general lines, we have sought to develop synthetic routes to a range of mononuclear complexes of ruthenium containing, in addition to the cyclopentadienyl moiety, other labile ligand groups. As the first part of our studies we wish to report on the synthesis and some of the substitution chemistry of the complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$ (C_8H_{12} = cycloocta-1,5-diene, X = halide) which contain readily displaceable cycloocta-1,5-diene ligands and react essentially as the pseudo-14-electron fragments $\{(\eta^5\text{-}C_5H_5)RuX\}$. In particular, $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ is shown to be a versatile and highly reactive precursor to a wide range of neutral and cationic cyclopentadienyl–ruthenium(II) complexes, providing for the first time a *general* synthetic route to these compounds. A preliminary account of this work has been published.[3]

Experimental Section

Materials and Methods. The complex $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ was prepared from $[\{(\eta^4\text{-}C_8H_{12})RuCl_2\}_x]$ by the published procedure.[4] The following materials were all prepared by the literature methods: cycloocta-1,3,5-triene,[5] NaC_5H_5,[6] Na[HB(1-pyrazolyl)$_3$],[7] methyl isocyanide.[8] TlC_5H_5 was purchased from Strem Chemicals and was purified by vacuum sublimation prior to use. All other chemicals were used as purchased, except for the solvents which were routinely dried and distilled under an inert atmosphere before use.[9] The preparation and the reactions of the complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})H]$ were carried out by using standard Schlenk techniques under strictly air-free conditions, while the reactions of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ were, unless otherwise stated, performed in air. Melting points were determined by using a Kofler micro-hotstage apparatus and are uncorrected. Elemental analyses were all performed by the microanalytical section of the analytical division of the NCRL, except for that of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})H]$ which was performed by Mikroanalytisches Labor Pascher, Buschstrasse 54, 5300 Bonn 1, West Germany. Infrared spectra were recorded by using a

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

(1) Bennet, M. A.; Bruce, M. I.; Matheson, T. W. in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 4, pp 775–796.

(2) Albers, M. O.; Robinson, D. J.; Singleton, E. *Coord. Chem. Rev.*, in press.

(3) Albers, M. O.; Oosthuizen, H. E.; Robinson, D. J.; Shaver, A.; Singleton, E. *J. Organomet. Chem.* **1985**, *282*, C49.

(4) Ashworth, T. V.; Singleton, E.; Hough, J. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1809.

(5) Jones, W. O. *J. Chem. Soc.* **1954**, 1808.

(6) King, R. B. *Organometallic Synthesis*; Academic Press: New York, 1965; Vol. 1, p 107.

(7) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99.

(8) Casanova, J.; Schuster, R. E.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280.

(9) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1980.

0276-7333/86/2305-2199$01.50/0

Bruker IFS 85 FT-IR spectrometer, and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 303 K by using a Bruker WM 500 or a Bruker AM 300 instrument either at 500.13, 125.72, or 121.44 MHz, respectively.

$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})H]$ (1). A suspension of $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ (10.7 g, 20.0 mmol) and TlC_5H_5 (6.0 g, 22.0 mmol) in acetone (240 mL) was heated under reflux for 30–35 min. After being cooled to room temperature, the air-sensitive solution was filtered by using a Celite filter pad and pumped to dryness. Repeated extractions of the sticky residue with deoxygenated pentane (5 × 35 mL) were performed, and the yellow solution so obtained was filtered. Solvent removal under vacuum gave the product as a pale yellow, crystalline solid sensitive to both air and light; yield 5.4 g (19.6 mmol, 98%).

$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ (2). 1 (5.51 g, 20.0 mmol) was taken up in deoxygenated pentane (150 mL), and CCl_4 (2 mL) was added. The mixture was stirred at room temperature for 5 min and then filtered, giving golden orange crystals of the analytically pure product, yield 5.1 g (16.2 mmol, 82%).

$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Br]$ (3). (a) To a solution of 1 (5.51 g, 20.0 mmol) in deoxygenated pentane (150 mL) was added CH_2Br_2 (2 mL). Stirring at room temperature for 30 min gave a dark orange precipitate. Filtration gave the analytically pure product as a dark orange crystalline solid, yield 5.31 g (15.0 mmol, 75%).

(b) 2 (0.31 g, 1.0 mmol) and NaBr (2.0 g, excess) were stirred in refluxing methanol (30 mL) for 3 h. The solvent was removed under reduced pressure and the crude product extracted with CH_2Cl_2 (10 mL) and crystallized by the addition of hexane (20 mL) and the slow evaporation of the solvent. The product was obtained by filtration and washing with cold hexane; yield 0.28 g (0.79 mmol, 79%).

$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})I]$ (4). (a) Methyl iodide (1 mL, excess) was added to a solution of **1** (1.38 g, 5.0 mmol) in pentane (50 mL) and stirred at room temperature for 1 h. Solvent removal under vacuum followed by extraction with ethanol (2 × 50 mL) gave an orange-red solution. Evaporation of this solution to dryness gave the pure product as a microcrystalline red-orange solid, yield 1.2 g (3.1 mmol, 62%).

(b) 2 (0.62 g, 2.0 mmol) and NaI (2.0 g, excess) were stirred in refluxing methanol (30 mL) for 3 h. After solvent removal the crude product was extracted with CH_2Cl_2 (10 mL) and crystallized by the addition of hexane (20 mL) and the slow removal of the solvent with cooling. The deep red crystalline product was obtained by filtration and washed with hexane; yield 0.70 g (1.8 mmol, 90%).

Substitution Reactions of 2. (a) Carbon Monoxide. A solution of 2 (0.31 g, 1.0 mmol) in CO-saturated ethanol (25 mL) was heated at 40 °C for 20 min. Solvent removal under vacuum gave $[(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl]$ (**5**) as a yellow crystalline solid, yield 0.25 g (0.95 mmol, 95%).

(b) Triphenylphosphine. A solution of **2** (0.31 g, 1.0 mmol) and PPh_3 (0.58 g, 2.2 mmol) in acetone (25 mL) was stirred at room temperature for 60 min. Solvent removal followed by recrystallization of the crude product from dichloromethane–ethanol gave analytically pure $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (**6**), yield 0.63 g (0.87 mmol, 87%).

(c) Trimethylphosphine. A solution of **2** (0.31 g, 1.0 mmol) and PMe_3 (0.20 g, 2.6 mmol) in tetrahydrofuran (15 mL) was stirred under an inert atmosphere at room temperature for 1 h. Removal of the solvent and excess phosphine under vacuum gave pure $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ (**7**) as a yellow crystalline solid, yield 0.30 g (0.85 mmol, 85%).

(d) 1,2-Bis(diphenylphosphino)ethane (dppe). A solution of **2** (0.31 g, 1.0 mmol) and dppe (0.44 g, 1.1 mmol) in ethanol (25 mL) was heated under reflux for 20 min. The solution was pumped to dryness, and the remaining yellow-orange solid was washed several times with pentane. Recrystallization of the crude product from hot ethanol yielded pure $[(\eta^5\text{-}C_5H_5)Ru(dppe)Cl]$ (**8**), yield 0.48 g (0.81 mmol, 81%).

(e) Trimethyl Phosphite. A solution of **2** (0.31 g, 1.0 mmol) and $P(OMe)_3$ (0.28 g, 2.2 mmol) in tetrahydrofuran (20 mL) was stirred at room temperature for 90 min. Solvent removal under vacuum followed by recrystallization of the crude product from acetone–ethanol gave pure $[(\eta^5\text{-}C_5H_5)Ru\{P(OMe)_3\}_2Cl]$ (**9**) as a yellow powder, yield 0.32 g (0.71 mmol, 71%).

(f) Diphenylphosphine. A solution of **2** (0.31 g, 1.0 mmol) and PPh_2H (0.39 g, 2.1 mmol) in acetone (30 mL) was stirred under an inert atmosphere at room temperature for 60 min. Solvent removal under vacuum followed by recrystallization from acetone–ethanol gave the pure product $[(\eta^5\text{-}C_5H_5)Ru(PPh_2H)_2Cl]$ (**10**) as a crystalline yellow solid, yield 0.42 g (0.74 mmol, 74%).

(g) Methyl Isocyanide (2 Molar Equiv). A solution of **2** (0.31 g, 1.0 mmol) and MeNC (0.09 g, 2.2 mmol) in acetone (30 mL) was stirred under an inert atmosphere at room temperature for 8 h. Solvent removal under vacuum followed by washing with pentane gave pure $[(\eta^5\text{-}C_5H_5)Ru(CNMe)_2Cl]$ (**11**) as a yellow crystalline solid, yield 0.24 g (0.85 mmol, 85%).

In a similar manner the compounds $[(\eta^5\text{-}C_5H_5)Ru(CN\text{-}t\text{-}Bu)_2Cl]$ (**12**) (yield 0.32 g (0.86 mmol, 86%)), $[(\eta^5\text{-}C_5H_5)Ru(CNC_6H_3Me_2\text{-}2,6)_2Cl]$ (**13**), (yield 0.39 g (0.84 mmol, 84%)), and $[(\eta^5\text{-}C_5H_5)Ru\{CN(CH_2)_6NC\}Cl]$ (**14**) (yield 0.28 g (0.83 mmol, 83%)) were obtained. Recrystallization from hot acetone gave the analytically pure products.

(h) Methyl Isocyanide (3 Molar Equiv). A solution of **2** (0.31 g, 1.0 mmol) and MeNC (0.13 g, 3.2 mmol) in ethanol (25 mL) was heated at reflux under an inert atmosphere for 20 min. Filtration of the hot solution followed by the addition of NH_4PF_6 (0.17 g, 1.0 mmol) in ethanol (5 mL), and cooling to room temperature yielded a crop of pink crystals. Filtration followed by washing with a small amount of cold ethanol and diethyl ether gave the product $[(\eta^5\text{-}C_5H_5)Ru(CNMe)_3]PF_6$ (**15**), yield 0.36 g (0.83 mmol, 83%).

(i) 3,4,7,8-Tetramethyl-1,10-phenanthroline. A solution of **2** (0.31 g, 1.0 mmol) and 3,4,7,8-tetramethyl-1,10-phenanthroline (0.26 g, 1.0 mmol) in acetone (30 mL) was stirred under an inert atmosphere at room temperature for 8 h. The purple precipitate formed in the reaction was filtered off and washed with diethyl ether (2 × 25 mL), giving, after being dried under vacuum, the analytically pure product $[(\eta^5\text{-}C_5H_5)Ru(3,4,7,8\text{-}Me_4\text{-}1,10\text{-}phen)Cl]$ (**16**) as a purple crystalline solid, yield 0.42 g (0.90 mmol, 90%).

(j) Buta-1,3-diene. A solution of **2** (0.31 g, 1.0 mmol) in ethanol (25 mL) was saturated with buta-1,3-diene and heated under reflux for 15 min. The volume of the reaction solution was reduced by half, and cooling to −5 °C overnight gave $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_4H_6)Cl]$ (**17**) as an orange, microcrystalline solid, yield 0.15 g (0.57 mmol, 57%).

Other buta-1,3-diene derivatives $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}diene)Cl]$ (**18**, 2,3-dimethylbuta-1,3-diene; **19**, 1-methyl-4-(methoxycarbonyl)-buta-1,3-diene) were obtained in a similar manner but with a **2** to diene molar ratio of 1:2. The yields of **18** and **19** were 59 and 85%, respectively.

(k) Bicyclo[2.2.1]hepta-2,5-diene. A solution of **2** (0.31 g, 1.0 mmol) and norbornadiene (0.13 mL, 1.5 mmol) in ethanol (25 mL) was heated under reflux for 20 min after which the solvent was removed under vacuum. The dark orange solid residue was washed with pentane (2 × 35 mL) and recrystallized from hot ethanol, giving the analytically pure product $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_7H_8)Cl]$ (**20**), yield 0.24 g (0.82 mmol, 82%).

(l) Cyclohepta-1,3,5-triene. An ethanol (30-mL) solution of **2** (0.31 g, 1.0 mmol) and cyclohepta-1,3,5-triene (0.2 mL, 1.93 mmol, excess) was heated under reflux for 25 min. Addition of NH_4PF_6 (0.17 g, 1.0 mmol) in ethanol (5 mL) to the pale yellow solution followed by cooling to 0 °C gave a crop of pale yellow crystals. Filtration and washing with cold ethanol followed by drying under vacuum gave the pure product $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_7H_8)]PF_6$ (**21**), yield 0.32 g (0.72 mmol, 72%).

Other cyclopentadienyl–ruthenium(II) cations containing cyclic polyolefins $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}cycloocta\text{-}1,3,5\text{-}triene)]PF_6$ (**22**) and $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}cyclooctatetraene)]PF_6$ (**23**) were prepared in a similar manner from **2** and excess of the respective polyolefin (yields 83 and 89%, respectively, based on ruthenium).

(m) Benzene. A solution of **2** (0.31 g, 1.0 mmol) and benzene (1.0 mL, 12.0 mmol, excess) in ethanol (25 mL) was heated under reflux for 30 min. Addition of NH_4PF_6 (0.17 g, 1.0 mmol) in ethanol (5 mL) to the pale yellow solution followed by cooling to 0 °C gave a crop of pale yellow crystals. Filtration and washing with cold ethanol (5 mL) gave the pure product $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$ (**24**), yield 0.32 g (0.82 mmol, 82%).

Other cyclopentadienyl–ruthenium(II) cations containing η^6-arene ligands $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}hexamethylbenzene)]PF_6$ (**25**), $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}indene)]PF_6$ (**26**), and $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}benzyl$

Table I. Physical and Analytical Data for the New Complexes

no.	complex	color	yield, %	mp,[a] °C	anal.[b]			
					C	H	N	X[c]
1	$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})H]$[d]	yellow	98		56.51 (56.72)	6.51 (6.55)		
2	$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$	orange	82	230–235 dec	50.40 (50.66)	5.53 (5.47)		11.44 (11.21)
3	$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Br]$	orange	75	240–245 dec	44.08 (44.12)	4.84 (4.87)		22.56 (22.20)
4	$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})I]$	red-orange	61	240–245 dec	38.91 (38.42)	4.27 (4.11)		31.63 (30.89)
10	$[(\eta^5\text{-}C_5H_5)Ru(PPh_2H)_2Cl]$	yellow	74	133–134	60.63 (60.68)	4.86 (4.74)		5.98 (6.18)
11	$[(\eta^5\text{-}C_5H_5)Ru(CNMe)_2Cl]$	yellow	85	145–147	37.97 (38.09)	3.87 (3.91)	9.64 (9.87)	12.21 (12.49)
12	$[(\eta^5\text{-}C_5H_5)Ru(CN\text{-}t\text{-}Bu)_2Cl]$	yellow	86	183–184	48.97 (49.14)	6.30 (6.54)	7.61 (7.72)	9.64 (10.06)
14	$[(\eta^5\text{-}C_5H_5)Ru\{CN(CH_2)_6NC\}Cl]$	yellow	83	>250	46.22 (46.54)	5.07 (5.20)	8.29 (8.09)	10.49 (10.19)
15	$[(\eta^5\text{-}C_5H_5)Ru(CNMe)_3]PF_6$	pink	83	203–205	30.46 (30.42)	3.13 (3.25)	9.62 (9.67)	
16	$[(\eta^5\text{-}C_5H_5)Ru(3,4,7,8\text{-}Me_4\text{-}1,10\text{-}phen)Cl]$[e]	purple	90	>250	57.24 (57.60)	4.95 (4.83)	6.44 (6.40)	8.74 (8.10)
17	$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_4H_6)Cl]$	orange	57	225–230 dec	42.27 (42.35)	4.34 (4.29)		13.86 (13.74)
18	$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_4H_4Me_2\text{-}2,3)Cl]$	orange	59	160–165 dec	46.56 (46.40)	5.33 (5.43)		12.49 (12.54)
19	$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_4H_4Me\text{-}1\text{-}CO_2Me\text{-}4)Cl]$	red-orange	85	160–165 dec	43.97 (43.95)	4.61 (4.67)		10.82 (10.98)
20	$[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_7H_8)Cl]$	orange	92	145–146	49.06 (48.99)	4.46 (4.42)		12.07 (11.68)
21	$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_7H_8)]PF_6$	pale yellow	72	>250	35.72 (35.82)	3.25 (3.27)		
22	$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_{10})]PF_6$	cream	83	>250	37.52 (37.41)	3.64 (3.62)		
23	$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_8)]PF_6$	pale yellow	89	>250	37.60 (37.56)	3.16 (3.05)		
26	$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_9H_8)]PF_6$	white	79	200–205 dec	39.35 (39.32)	3.07 (3.49)		
27	$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5CH_2Cl)]PF_6$	pale yellow	66	210–211	32.93 (32.89)	2.76 (2.90)		8.10 (8.16)
28	$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5NPh_2)]PF_6$	cream	58	>250	49.64 (49.63)	3.62 (3.57)	2.52 (2.65)	
31	$[(\eta^5\text{-}C_5H_5)Ru\{(pz)_3BH\}]$	golden yellow	83	>250	44.27 (44.34)	3.92 (3.99)	21.89 (22.15)	

[a] Uncorrected. [b] Required values are given in parentheses. [c] X = respective halogen. [d] % Ru = 37.3 (required 37.7). [e] λ_{max} = 469 nm (ϵ 6.5 × 10^3).

chloride)]PF_6 (**27**) were prepared in a similar manner (yields 70–80%).

(**n**) **Triphenylamine.** A solution of **2** (0.31 g, 1.0 mmol) and triphenylamine (0.26 g, 1.1 mmol) in ethanol (30 mL) was heated under reflux for 20 min. Addition of NH_4PF_6 (0.17 g, 1.0 mmol) in ethanol (5 mL) to the yellow solution followed by cooling gave yellow crystals. Filtration followed by washing with diethyl ether and drying under vacuum gave the analytically pure product $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5NPh_2)]PF_6$ (**28**), yield 0.31 g (0.58 mmol, 58%).

(**o**) **Sodium Tetraphenylborate.** A solution of **2** (0.31 g, 1.0 mmol) and $NaBPh_4$ (0.38 g, 1.1 mmol) in ethanol (30 mL) was heated under reflux for 10 min. When cooled to room temperature, the pale yellow solution deposited colorless crystals of the analytically pure product $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5BPh_3)]$ (**29**), yield, 0.38 g (0.78 mmol, 78%).

(**p**) **Cyclopentadienylsodium.** A solution of **2** (0.31 g, 1.0 mmol) and NaC_5H_5 (1.2 mmol) in air- and peroxide-free tetrahydrofuran (30 mL) was stirred at 25 °C under an inert atmosphere for 1 h. Solvent removal under reduced pressure followed by extraction with pentane and cooling of the extracts to −5 °C gave very pale yellow crystals of ruthenocene $[Ru(\eta^5\text{-}C_5H_5)_2]$ (**30**), yield 0.15 g (0.65 mmol, 65%).

(**q**) **Sodium Hydrotris(1-pyrazolyl)borate ($NaHBpz_3$).** **2** (0.31 g, 1.0 mmol) in boiling ethanol (30 mL) was treated with $NaHBpz_3$ (0.19 mg, 1.1 mmol) and the mixture heated under reflux for 35 min. The reaction solution was pumped to dryness and then extracted with diethyl ether (150 mL). The volume of the ether extract was reduced to 30 mL, which on cooling to −5 °C gave crystals of the product $[(\eta^5\text{-}C_5H_5)Ru(HBpz_3)]$ (**31**), yield 0.32 g (0.83 mmol, 83%).

Results and Discussion

Synthesis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$ (1–4, X = H, Cl, Br, and I, Respectively; C_8H_{12} = Cycloocta-1,5-diene). The general lack of substitutive reactivity which characterizes the compounds $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl]$, the traditional synthetic precursors to cyclopentadienyl–ruthenium chemistry,[1,2] may be attributed to a combination of thermodynamic and kinetic factors which make the triphenylphosphine and the carbonyl ligands difficult to displace. This severely restricts the synthetic utility of these complexes. In efforts to overcome these limitations and develop rational synthetic routes to a large range of cyclopentadienyl–ruthenium complexes, we sought to synthesize, in high yield, complexes which incorporate, in addition to the cyclopentadienyl ligand, readily displaceable ligand systems. Diolefins, the archetype being cycloocta-1,5-diene, fulfill this requirement in ruthenium chemistry, and hence our endeavours were aimed at the synthesis of cyclopentadienyl–ruthenium complexes containing the cycloocta-1,5-diene ligand.

Treatment of $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ (C_8H_{12} = cycloocta-1,5-diene)[4] with freshly sublimed cyclopentadienylthallium (mole ratio 1.0:1.1) in boiling acetone for 30 min, gives, after pentane extraction and solvent removal, high yields of the air- and light-sensitive crystalline solid $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})H]$ (**1**).[10] The hydrido ligand in **1** is readily replaced by halo ligands on treatment with a variety of halogenating agents. For instance, the addition of CCl_4 to a pentane solution of **1** affords, in essentially quantitative yield, $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ (**2**) as a golden orange, air- and light-stable solid. In a similar manner, treatment of **1** with either CH_2Br_2 or MeI has given a convenient synthesis of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$ (X = Br and I, **3** and **4**, respectively), both possessing similar physical properties to **2**. Halide metathesis on **2** using either NaBr of NaI in boiling methanol provides alternative routes to **3** and **4**, respectively.

Complexes **1**–**4** have been completely characterized by a combination of elemental analysis and ^1H and ^{13}C NMR spectroscopy (see Tables I–III). Complex **1** has a ^1H NMR spectrum consisting of the expected singlet at 4.97 ppm (5 H) for the cyclopentadienyl ligand, characteristic multiplets at 3.75 (2 H), 3.15 (2 H), 2.10 (2 H), and 1.80 ppm (6 H) for the cycloocta-1,5-diene ligand and a signal at −5.78 ppm (1 H) for the hydrido ligand. Complexes **2**–**4** have altogether similar, characteristic cyclopentadienyl and cycloocta-1,5-diene signals in the ^1H NMR specta and will not be further discussed. Characteristic $^{13}C\{^1H\}$ NMR signals are observed for the cycloocta-1,5-diene ring[11] in **2**–**4**; the olefinic carbons appear in the range 76–86 ppm and the methylene carbons between 26 and 34 ppm. The cyclopentadienyl ring carbons resonate in the narrow range 85–88 ppm.

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[10] Liles, D. C.; Oosthuizen, H. E.; Shaver, A.; Singleton, E.; Wiege, M. B. *Organometallics* **1986**, *5*, 591.

[11] Ashworth, T. V.; Chalmers, A. A.; Oosthuizen, H. E.; Singleton, E. *Organometallics* **1984**, *3*, 1485.

Table II. ^{1}H NMR Spectral Data for the New Complexes (δ)[a]

complex	^{1}H NMR data[b]
1	4.97 (5 H, s, C_5H_5), 3.75 (2 H, m, CH), 3.15 (2 H, m, CH), 2.10 (2 H, m, CH_2), 1.80 (6 H, m, CH_2), −5.78 (1 H, s, Ru–H)
2[c]	5.32 (2 H, m, CH), 4.95 (5 H, s, C_5H_5), 4.40 (2 H, m, CH), 2.62 (2 H, m, CH_2), 2.03 (6 H, m, CH_2)
3[c]	5.18 (2 H, m, CH), 4.96 (5 H, s, C_5H_5), 4.44 (2 H, m, CH), 2.64 (2 H, m, CH_2), 2.05 (6 H, m, CH_2)
4	5.18 (5 H, s, C_5H_5), 5.11 (2 H, m, CH), 4.35 (2 H, m, CH), 2.68 (2 H, m, CH_2), 2.22 (6 H, m, CH_2)
10[d]	8.09 (1 H, m, Ph), 7.81 (1 H, m, Ph), 7.51 (8 H, m, Ph), 7.36 (2 H, m, Ph), 7.30 (4 H, m, Ph), 7.24 (4 H, m, Ph), 6.49 [2 H, d, J(HP) = 359 Hz, PH], 4.52 (5 H, s, C_5H_5)
11	4.73 (5 H, s, C_5H_5), 3.54 (6 H, s, Me)
12	5.19 (5 H, s, C_5H_5), 1.48 (18 H, s, Me)
14	4.78 (5 H, s, C_5H_5), 1.71–1.68 (12 H, m, CH_2)
15	5.27 (5 H, s, C_5H_5), 3.57 (9 H, s, Me)
16[e]	9.68 (2 H, s, H_A), 8.03 (2 H, s, H_D), 4.25 (5 H, s, C_5H_5), 2.71 (6 H, s, Me), 2.60 (6 H, s, Me)
17[c]	5.33 [2 H, m, $J(H_aH_c)$ = 10.1, $J(H_aH_b)$ = 8.5, H_a], 4.95 (5 H, s, C_5H_5), 4.08 [2 H, m, $J(H_bH_a)$ = 8.5, $J(H_bH_c)$ = 1.7, H_b], 1.35 [2 H, m, $J(H_cH_a)$ = 10.1, $J(H_cH_b)$ = 1.7, H_c]
18[c]	4.85 (5 H, s, C_5H_5), 4.05 [2 H, d, $J(H_bH_c)$ = 2.8, H_b], 2.10 (6 H, s, Me), 1.22 [2 H, d, $J(H_cH_b)$ = 2.8, H_c]
19[c]	5.88 [1 H, m, $J(H_{a'}H_{c'})$ = 9.0, $J(H_{a'}H_a)$ = 5.6, $H_{a'}$], 5.50 [1 H, m, $J(H_aH_c)$ = 10.3, $J(H_aH_{a'})$ = 5.6, H_a], 4.97 (5 H, s, C_5H_5), 3.69 (3 H, s, Me), 2.45 [1 H, m, $J(H_cH_a)$ = 10.3, $J(H_c\mathrm{Me})$ = 6.5, H_c], 1.97 [1 H, d, $J(H_{c'}H_{a'})$ = 9.0], 1.81 [3 H, d, $J(\mathrm{Me}H_c)$ = 6.5, Me]
20	4.98 (5 H, s, C_5H_5), 4.86 (2 H, m, CH), 4.26 (2 H, m, CH), 3.66 (1 H, m, CH), 3.51 (1 H, m, CH), 1.20 [2 H, t, J = 3.9, CH_2]
21	6.80 (2 H, m, H_a), 5.67 (2 H, m, H_b), 5.56 (5 H, s, C_5H_5), 4.07 [2 H, M, $J(H_cH_{endo})$ = 9.0, $J(H_cH_{exo})$ = 4.4, Hc], 3.04 [1 H, m, $J(H_{endo}H_{exo})$ = 13.4, $J(H_{endo}H_c)$ = 9.0, H_{endo}], 1.31 [1 H, m, $J(H_{exo}H_{endo})$ = 13.4, $J(H_{exo}H_c)$ = 4.4, H_{exo}]
22	6.81 [2 H, m, $J(H_aH_b)$ = 5.0, $J(H_aH_c)$ = 2.1, H_a], 5.94 [2 H, m, $J(H_cH_b)$ = 8.6, $J(H_cH_a)$ = 2.1, H_c], 5.80 [2 H, m, $J(H_bH_c)$ = 8.6, $J(H_bH_a)$ = 5.0, H_b], 5.56 (5 H, s, C_5H_5), 2.21 (2 H, m, CH_2), 0.91 (2 H, m, CH_2)
23	6.92 [2 H, m, $J(H_aH_b)$ = 4.5, H_a], 6.04 [2 H, m, $J(H_bH_c)$ 8.4, $J(H_bH_a)$ = 4.5, H_b], 5.95 [2 H, m, $J(H_cH_b)$ 8.4, $J(H_cH_d)$ = 2.3, H_c], 5.69 (5 H, s, C_5H_5), 5.11 [2 H, m, $J(H_dH_c)$ = 2.3, H_d]
26	6.88 (3 H, m, CH), 6.76 (1 H, m, CH), 6.18 (2 H, m, CH), 5.28 (5 H, s, C_5H_5), 3.65 (2 H, m, CH_2)
27	6.52–6.48 (5 H, m, CH), 5.61 (5 H, s, C_5H_5), 4.76 (2 H, s, CH_2)
28	7.55 [4 H, m, $J(H_bH_c)$ = 7.7, $J(H_bH_a)$ = 7.3, H_b], 7.49 [4 H, d, $J(H_cH_b)$ = 7.7, H_c], 7.39 [2 H, t, $J(H_aH_b)$ = 7.3, H_a], 6.12 [2 H, m, $J(H_{b'}H_{c'})$ = 6.6, $J(H_{b'}H_{a'})$ 5.5, $H_{b'}$], 6.02 [1 H, t, $J(H_{a'}H_{b'})$ 5.5, $H_{a'}$], 5.73 [2 H, d, $J(H_{c'}H_{b'})$ = 6.6, $H_{c'}$], 5.51 (5 H, s C_5H_5)
31[c]	8.00 [3 H, d, $J(H_aH_b)$ = 2.2, H_a], 7.54 [3 H, d, $J(H_cH_b)$ = 2.2, H_c], 6.12 [3 H, t, $J(H_bH_a)$ = 2.2, $J(H_bH_c)$ = 2.2, H_b], 4.23 (5 H, s, C_5H_5)

[a] Recorded in acetone-d_6 unless stated otherwise, J values in Hz. [b] Recorded at 500.13 MHz at 303 K; s = singlet, d = doublet, t = triplet, m = multiplet. [c] Recorded in $CDCl_3$. [d] $^{31}P\{^1H\}$ (acetone-d_6, 303 K, 121.44 MHz) δ 37.31. [e] Recorded in CD_2Cl_2.

Table III. $^{13}C\{^1H\}$ NMR Spectral Data for Some of the New Complexes (δ)[a]

complex	^{13}C NMR data[b]
2[c]	87.5 (C_5H_5), 85.9, 78.6 (CH), 33.4, 27.6 (CH_2)
3[c]	85.5 (C_5H_5), 84.6, 77.6 (CH), 32.0, 26.9 (CH_2)
4	86.0 (C_5H_5), 79.4, 76.3 (CH), 31.5, 31.4 (CH_2)
10	134.2, 133.1, 132.2, 132.0, 130.3, 129.9, 129.1, 128.7 ($C_{aromatic}$), 80.5 (C_5H_5)
11[d]	80.9 (C_5H_5), 30.5 (Me)
12[d]	158.5 (Ru–C), 82.8 (C_5H_5), 59.3 (C), 33.0 (Me)
15[d]	84.5 (C_5H_5), 30.6 (Me)
16[e]	155.4 (C_a), 146.6 (C^f), 141.3 (C_c), 132.9 (C_b), 128.5 (C^f), 122.9 (C_α), 68.2 (C_5H_5), 17.9, 14.5 (Me)
18[c]	101.7 (CMe), 86.0 (C_5H_5), 56.6 (CH_2), 56.6 (CH_2), 21.3 (Me)
20	85.4 (C_5H_5), 72.6, 61.6, 50.7, 49.4 (CH), 48.2 (CH_2)
21	96.6, 91.0 (CH), 84.5 (C_5H_5), 28.2 (CH), 22.4 (CH_2)
22	101.0, 89.0, 87.7 (CH), 85.9 (C_5H_5), 33.8 (CH_2)
23[g]	136.2 (C_d), 104.9 (C_a), 95.1 (C_b), 88.5 (C_5H_5), 84.6 (C_c)
26	143.0, 129.4, 85.0, 84.6, 84.1, 83.7, 83.4 (C^h), 81.6 (C_5H_5), 81.4 (C^h), 40.3 (CH_2)
27	102.4, 87.4, 86.8, 86.5 ($C_{aromatic}$), 82.1 (C_5H_5), 44.5 (CH_2)
28	143.6, 131.4, 128.7, 128.5, 126.6, 84.7, 81.8 ($C_{aromatic}$), 80.5 (C_5H_5), 71.7 ($C_{aromatic}$)

[a] Recorded in acetone-d_6 unless stated otherwise. [b] Recorded at 125.72 MHz at 303 K. [c] Recorded in $CDCl_3$. [d] Ru–C represents isocyanide carbon bonded to ruthenium (not observed for complexes **11** and **15**). [e] Recorded in CD_2Cl_2. [f] Ring-shared carbon atoms. [g] $^{13}C\{^1H\}$ assignment made possible by using ^{1}H and ^{13}C heteronuclear shift correlation spectrum (Figure 1). [h] CH and/or ring-shared carbon atoms.

The Substitution Chemistry of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ (2). The substituion of the cycloocta-1,5-diene and/or halo ligands in **2**–**4** in a range of solvents and under mild reaction conditions is generally a rapid and facile process. The substitution chemistry of **2**–**4** is qualitatively the same but differs markedly from that of **1**.[10] Preliminary kinetic studies[12] have indicated that the rate of substitution of the cyclooctadiene ligand in **2**–**4** by neutral donor molecules falls in the sequence **2** > **3** > **4**. Thus, the following discussion is confined to the most convenient representative of the series, **2**.

The reactivity of **2** is, as expected, largely dictated by factors which include the reaction solvent, the reaction temperature, the potential denticity of the entering ligand(s), and the stability of the final substitution products under the experimental conditions. Generally speaking, alcohol solvents favor the labilization of both the cycloocta-1,5-diene and the chloro ligands giving cationic products, while solvents such as acetone and tetrahydrofuran can generally be used to obtain neutral substitution products. In acetone solution, the rate-determining step in the substitution of **2** by a variety of donor ligands, e.g., 3,4,7,8-tetramethyl-1,10-phenanthroline (see below), is the scission of a ruthenium–olefin bond,[12,13] thus mitigating against cationic intermediates (arising from initial ionization of the chloro ligand) under these conditions. Presumably in alcohol solvents halide labilization is an important feature of the substitution process, and this is currently under investigation.

In order to fully illustrate the synthetic utility of **2**, a range of substitutive reactions are discussed below.

Neutral Substitution Products $[(\eta^5\text{-}C_5H_5)RuL_2Cl]$. Heating of **2** in CO-saturated ethanol gives $[(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl]$ (**5**),[14] the reaction proceeding to completion within minutes at 40 °C. Treatment of **2** with 2 molar equiv of PPh_3 in acetone at 30 °C rapidly gives the substitution product $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (**6**)[15] (isolated yield 87%). The spectroscopic (IR and ^{1}H NMR) properties of both **5** and **6** are in agreement with literature values,[14,15] and analytical data support their formulation.

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(12) Albers, M. O.; De Waal, D. J. A.; Robinson, D. J.; Singleton, E., unpublished results.

(13) Albers, M. O.; Robinson, D. J.; Singleton, E. *J. Organomet. Chem.*, in press.

(14) (a) Haines, R. J.; Du Preez, A. L. *J. Am. Chem. Soc.* **1971**, *93*, 2820. (b) Haines, R. J.; Du Preez, A. L. *J. Chem. Soc., Dalton Trans.* **1972**, 944.

(15) (a) Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc.* **1969**, 1749. (b) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376. (c) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601.

Table IV. Infrared Data for the New Isocyanide Complexes

complex	$\nu(N{\equiv}C)^{a,b}$
11	2165 (s), 2120 (s), 2050 (sh)
12[c]	2144 (s), 2110 (s), 2075 (sh)
14[d]	2160 (s), 2095 (s)
15[e]	2255 (m), 2220 (s), 2180 (sh)

[a] Peak positions in cm^{-1}. [b] Recorded as Nujol mulls unless otherwise stated. [c] Recorded in chloroform. [d] Recorded in dichloromethane. [e] ν(P–F) = 840 cm^{-1}.

Of more interest in relation to phosphorus donor ligand substituted complexes of the type $[(\eta^5\text{-}C_5H_5)RuL_2Cl]$ are the facile reactions of **2** with PMe_3 (tetrahydrofuran, 30 °C), with a chelating diphosphine, 1,2-bis(diphenylphosphino)ethane (dppe) (ethanol at reflux), a phosphite, $P(OMe)_3$ (tetrahydrofuran, 30 °C), and a secondary phosphine PPh_2H (acetone, 30 °C), giving the products $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2Cl]$ (**7**),[16] $[(\eta^5\text{-}C_5H_5)Ru(dppe)Cl]$ (**8**),[17] $[(\eta^5\text{-}C_5H_5Ru\{P(OMe)_3\}_2Cl]$ (**9**),[17] and $[(\eta\text{-}C_5H_5)Ru(PPh_2H)_2Cl]$ (**10**), respectively. The reactions all proceed essentially quantitatively to the products. Phosphine and phosphite derivatives of the type $[(\eta^5\text{-}C_5H_5)RuL_2Cl]$ have previously been obtained by ligand exchange on $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and more recently by the thermally induced decomposition of the ruthenium(IV) alkyl complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-allyl})(CH_3)X]$ in the presence of donor ligands.[18] Both these procedures, however, lack the generality of the route via **2**, where the mild conditions under which the reactions are performed make the synthesis of compounds containing relatively sensitive or reactive ligand systems, here exemplified by PPh_2H, a trivial matter.

Compounds **7–9** have spectroscopic characteristics consistent with the literature values[16,17] and analytical data consistent with their formulation. Compound **10** has been characterized by ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectroscopy and by elemental analysis. The data bear no remarkable features and will not be considered further.

The reaction of **2** with 2 molar equiv of monodentate alkyl or aryl isocyanides proceeds smoothly in acetone solution at room temperature to afford the neutral bis(isocyanide) complexes $[(\eta^5\text{-}C_5H_5)Ru(CNR)_2Cl]$ (**11–13**, R = Me, *t*-Bu, 2,6-$Me_2C_6H_3$, respectively) in yields in excess of 80%. The bidentate isocyanide 1,6-diisocyanohexane reacts with **2** in acetone at 25 °C to afford $[(\eta^5\text{-}C_5H_5)Ru\{CN(CH_2)_6NC\}Cl]$ (**14**). Compounds **11–14** are yellow, crystalline air- and light-stable solids and have been characterized by a combination of IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by elemental analysis (Tables I–IV). The compounds show two ν(NC) bands in the IR spectrum (except for **12** which has three, a similar effect having been noted by Coville and co-workers[19] for $[(\eta^5\text{-}C_5H_5)Ru(CN\text{-}t\text{-}Bu)_2I]$). Further, **11**, **12**, and **14** have the expected higher ν(NC) stretching frequencies.[20] The ^1H NMR spectra of **11–14** bear no unusual features except that the cyclopentadienyl ring signals (all singlets) exhibit a consistent upfield shift which parallels the isocyanide ligand donor strengths. The synthesis of several $[(\eta^5\text{-}C_5H_5)Ru(CNR)_2X]$ (X = Cl, I) derivatives from $[(\eta^5\text{-}C_5H_5)Ru(CO)_2X]$ has been achieved in the presence of carbonyl substitution catalysts,[19] while the only other report in the literature[21] incorrectly formulates a white unstable solid (obtained from the reaction of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with *tert*-butyl isocyanide at 180 °C for 12 h) as $[(\eta^5\text{-}C_5H_5)Ru(CN\text{-}t\text{-}Bu)_2Cl]$.

It is interesting to note that under the experimental conditions described here, only the neutral complexes $[(\eta^5\text{-}C_5H_5)Ru(CNR)_2Cl]$ are obtained. However, under different conditions i.e., excess isocyanide in ethanol solution, cationic complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(CNR)_3]Cl$ are readily obtained. These reactions may proceed directly from **2** with 3 molar equivs of isocyanide in ethanol or via the neutral disubstituted product $[(\eta^5\text{-}C_5H_5)Ru(CNR)_2Cl]$ with one further molar equivalent of isocyanide in ethanol solution. In both cases, anion exchange with NH_4PF_6 is readily achieved giving, high yields of the hexafluorophosphate salts. A representative complex cation, $[(\eta^5\text{-}C_5H_5)Ru(CNMe)_3]PF_6$ (**15**), has been prepared to illustrate the procedure.

It is remarkable that to date there has been no reported synthesis of neutral diamine complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(diamine)Cl]$.[13,22] This may be related to the synthetic routes currently available; for instance $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ reacts with 1,10-phenanthroline in methanol to give the cation $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(1,10\text{-phenanthroline})]^+$.[23] We were thus interested to determine whether the facile displacement of the cycloocta-1,5-diene ligand in **2** by donor ligands would include diamine ligands. Indeed, 3,4,7,8-tetramethyl-1,10-phenanthroline reacts smoothly with **2** in acetone at 25 °C, giving the neutral substitution product $[(\eta^5\text{-}C_5H_5)Ru(3,4,7,8\text{-}Me_4\text{-}1,10\text{-phen})Cl]$ (**16**) as a purple crystalline solid in 84% yield. Complex **16** has been completely characterized by a combination of elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and has a charge-transfer absorption band at 469 nm with an extinction coefficient of 6.5×10^3. Interestingly, **16** has in common with **11–14** a marked tendency to form cations of the type $[(\eta^5\text{-}C_5H_5)RuL_3]^+$, many reactions of which mirror those of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$. These results will, however, be discussed elsewhere.

Perhaps the most remarkable illustration of the lability of the cycloocta-1,5-diene ligand in **2** relates to the substitution of this ligand by 1,3-dienes (specifically buta-1,3-diene and buta-1,3-diene derivatives), a relatively rare observation in ruthenium chemistry.[24] Thus, treatment of **2** with excess diene in boiling ethanol solution affords, in good yield, $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_4H_6)Cl]$ (**17**), $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_4H_4Me_2\text{-}2,3)Cl]$ (**18**), and $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_4H_4Me\text{-}1\text{-}CO_2Me\text{-}4)Cl]$ (**19**). Bicyclo[2.2.1]hepta-2,5-diene also replaces the cyclooctadiene ligand in **2** under similar conditions giving $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_7H_8)Cl]$ (**20**) in 92% yield. Compounds **17–20** are all orange, crystalline, air- and light-stable solids, soluble in most organic solvents. Characterization of these compounds has been by elemental analysis and particularly ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (Tables I–III). The terminal olefinic protons of the butadiene ligand in **17** resonate at 4.08 and 1.35 ppm

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(16) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398.

(17) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003.

(18) Nagashima, H.; Yamaguchi, K.; Mukai, K.; Itoh, K. *J. Organomet. Chem.* **1985**, *291*, C20.

(19) Boeyens, J. C. A.; Coville, N. J.; Soldenhoff, K. *S. Afr. J. Chem.* **1984**, *37*, 153.

(20) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*; Wiley: London, 1969; p 7.

(21) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1981**, *34*, 209.

(22) The field desorption mass spectrum of $[(\eta^5\text{-}C_5H_5)Ru(2,2'\text{-bpy})Cl]$ has been reporated although no preparative details for this compound have to date been reported: Cerney, R. I.; Sullivan, B. P.; Bursey, M. M.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 397.

(23) Usôn, R.; Oro, L. A.; Ciriano, M. A.; Naval, M. M.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H.; Garcia-Blanco, S. *J. Organomet. Chem.* **1983**, *256*, 331.

(24) Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2288.

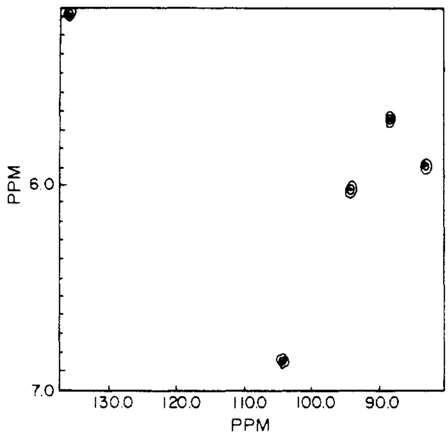

Figure 1. Heteronuclear shift correlation spectrum for $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_8)]PF_6$ (**23**).

while the remaining protons of the butadiene ligand resonate at 5.33 ppm; the signal for the cyclopentadienyl ligand appears at 4.95 ppm. Similar spectra are observed for **18** and **19**. The protons of the norbornadiene ligand in **20** appear as olefinic signals at 4.86 and 4.26 ppm, protons on the ring shared carbons at 3.66 and 3.51 ppm, and the protons of the CH_2 group resonating as the expected triplet at 1.20 ppm.

It is notable that it is only recently that the first cyclopentadienyl–ruthenium diolefin complexes $[(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-diolefin})Cl]$ (diolefin = norbornadiene, cycloocta-1,5-diene) were reported.[25] Grubbs and co-workers[26] obtained $[(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}C_7H_8)Cl]$ (C_7H_8 = norbornadiene), albeit in low yield, by reacting the polymer $[\{(\eta^4\text{-}C_7H_8)RuCl_2\}_x]$ with LiC_5Me_5 in tetrahydrofuran, while Suzuki and co-workers[25] obtained both the norbornadiene and cycloocta-1,5-diene compounds by the treatment of the unusual ruthenium(III) polymer $[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_x]$ with excess diene in ethanol solution. Little has been reported on the reactivity of these compounds, but in broad outline their chemistry, and that of the diene complexes **17–20**, parallels that of **2**.[27]

Cationic Substitution Products $[(\eta^5\text{-}C_5H_5)RuL_3]^+$. In boiling ethanol, one of the principle features of the chemistry of **2** relates to the formation of cationic complexes by the substitution of both the cyclooctadiene and chloro ligands. Polyolefins (cyclohepta-1,3,5-triene, cycloocta-1,3,5-triene, cyclooctatetraene) rapidly react with **2** under these conditions giving, after anion exchange with NH_4PF_6, $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_7H_8)]PF_6$ (**21**), $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_{10})]PF_6$ (**22**), and $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_8)]PF_3$ (**23**), respectively. The characteristic ^1H and $^{13}C\{^1H\}$ NMR spectra of these complexes were assigned by comparison with published data for similar complexes[28] or (in the case of **23**) by heteronuclear (^1H, ^{13}C) correlation spectroscopy (Figure 1). The η^6-cyclooctatetraene ligand in **23** is, surprisingly, static at room temperature, an observation in marked contrast to other compounds containing the $\eta^6\text{-}C_8H_8$ ligand, e.g., $[(\eta^6\text{-}C_8H_8)M(CO)_3]$ (M = Cr, Mo, W).[29] Nevertheless, there is some evidence for fluxionality at high temperatures (e.g., at 148 °C in dimethylformamide-d_7), occurring by a 1,3-hydrogen shift process.[30]

The facile displacement of both the chloro and cyclooctadiene ligands in **2** by triene ligands would suggest that a similar process should occur with aromatics yielding cations of the type $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$. Indeed, benzene reacts readily with **2** in boiling ethanol, giving, following anion exchange with NH_4PF_6, a high yield of $[(\eta^6\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$[2,31] (**24**). Of greater interest though are the reactions of **2** with hexamethylbenzene, indene, and other functionalized aromatic compounds (benzyl chloride, triphenylamine) which also occur rapidly in boiling ethanol, giving, in the presence of NH_4PF_6, $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]PF_6$ (**25–28**, arene = hexamethylbenzene, indene, benzyl chloride, triphenylamine) in high yield. Of particular note here is the remarkable ease with which these products are formed, contrasting directly with the established procedures for the preparations of cyclopentadienyl–ruthenium–arene cations.[32] The new compounds **26–28** have been characterized by elemental analysis and by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (Tables I–III). **26** has a proton NMR spectrum consistent with the η^6-indene ligand with the aromatic protons appearing as multiplets between 6.7 and 6.9 ppm, while the protons on the uncoordinated ring resonate as multiplets at 6.18 and 3.65 ppm. The singlet at 5.28 ppm in the ^1H NMR spectrum of **26** is assigned to the cyclopentadienyl ring. Complex **28** shows the expected two sets of phenyl protons, the high field sets assigned to the ruthenium bound arene ring of the triphenylamine molecule. The high affinity of **2** for arene coordination in alcohol solvents is most graphically illustrated by the reaction between **2** and $NaBPh_4$ in warm ethanol which gives the arene-bound, zwitterionic complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5BPh_3)]$ (**29**)[33] characterized by elemental analysis and by ^1H NMR spectroscopy.

Treatment of **2** with a single equivalent of sodium cyclopentadienide in tetrahydrofuran at 25 °C produces ruthenocene, $[Ru(\eta^5\text{-}C_5H_5)_2]$ (**30**), in high yield, a route we are currently further exploring to obtain mixed-ligand metallocenes.[34] However, one example, the unusual "sandwich" compound $[(\eta^5\text{-}C_5H_5)Ru(HBpz_3)]$ (**31**), is obtained in good yield from **2** and sodium hydrotris(1-pyrazolyl)borate in ethanol solution. The ^1H NMR spectrum of **31** is characteristic of the tridentate hydrotris(1-pyrazolyl)borato ligand, with the cyclopentadienyl ligand contributing only the expected sharp singlet at 4.23 ppm.

Conclusion

The ease of synthesis of **2** and its high lability provides a general synthetic precursor to neutral and cationic cyclopentadienyl–ruthenium(II) complexes which is exceptional in terms of its versatility and simplicity. The most striking aspects of the reactivity of **2** relate to the facile substitution of the cycloocta-1,5-diene ligand (such that **2** can be considered to react essentially as the pseudo-14-electron fragment $\{(\eta^5\text{-}C_5H_5)RuCl\}$) and the combined

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[25] Oshima, N.; Suzuki, M; Moro-Oka, Y. *Chem. Lett.* **1984**, 1161.

[26] Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274.

[27] Albers, M. O.; Dewhurst, S. F. A.; Robinson, D. J.; Singleton, E., unpublished results.

[28] For example, comparisons with data for the complexes $[(\eta^6\text{-}C_7H_8)Mn(CO)_2L]^+$ (L = CO, PPh_3) aided in the assignment of the ^1H NMR data for **21**: Honig, E. D.; Quin-Jin, M.; Robinson, W. T.; Willard, P. G.; Sweigart, D. A. *Organometallics* **1985**, *4*, 871.

[29] (a) Mann, B. E. *J. Chem. Soc., Chem. Commun.* **1977**, 626. (b) Gibson, J. A.; Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1979**, 1021.

[30] Mann, B. E., personal communication.

[31] Robertson, I. W.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1982**, *228*, 171.

[32] (a) Sutherland, R. G. *J. Organomet. Chem. Libr.* **1977**, *3*, 311. (b) Roman, E.; Astruc, D. *Inorg. Chim. Acta* **1979**, *37*, L465. (c) Nesmeyanov, A. N.; Vol'kenau, N. A.; Blesova, I. N.; Sul'pina, L. S. *J. Organomet. Chem.* **1979**, *182*, C36. (d) Vol'kenau, N. A.; Bolesova, I. N.; Shul'pina, L. S.; Kitaigorodskii, A. N.; Krautsov, D. N. *J. Organomet. Chem.* **1985**, *288*, 341.

[33] Haines, R. J.; Du Preez, A. L. *J. Organomet. Chem.* **1975**, *84*, 357.

[34] Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Boeyens, J. C. A.; Levendis, D. C. *Organometallics*, in press.

displacement of the chloro and cycloocta-1,5-diene ligands such that the entire one face of the complex is receptive to entering ligand systems. These patterns of reactivity are in marked contrast to those of the traditional synthetic precursors in cyclopentadienyl–ruthenium(II) chemistry and will be elaborated upon in greater detail in future publications.[35]

Acknowledgment. Western Platinum Refinery (Lonrho) (Pty) Ltd is thanked for a generous loan of ruthenium trichloride which made this work possible. A.S. gratefully acknowledges an International Scientific Collaboration Award from the Science and Engineering Research Council of Canada.

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[35] (a) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1986**, 645. (b) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Singleton, E. *J. Chem. Soc., Chem. Commun.*, in press.

Cobalt(I) Complexes: Synthesis and Molecular and X-ray Structures of Group 14 (η^4-Metallole)tris(trimethylphosphine)cobalt Tetraphenylborate Complexes

L. C. Ananias de Carvalho, M. Dartiguenave,* F. Dahan, and Y. Dartiguenave

Laboratoire de Chimie de Coordination du CNRS, 31400 Toulouse, France

J. Dubac, A. Laporterie, G. Manuel, and H. Iloughmane

Laboratoire des Organométalliques, UA au CNRS No. 477, Université Paul Sabatier, 31062 Toulouse-Cedex, France

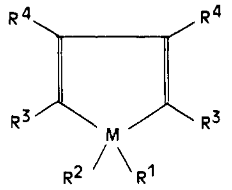
Received March 3, 1986

Reaction of $CoBr(PMe_3)_3$ (**4**) with 1,1,3,4-tetramethylmetalloles (Si, **2**; Ge, **3**) in presence of $NaBPh_4$ yielded $[Co(metallole)(PMe_3)_3]BPh_4$ complexes (Si, **5**; Ge, **6**). The crystal structures of **5** and **6** have been determined by X-ray diffraction techniques. They are isomorphous and crystallize in the orthorhombic system $P2_12_12_1$. Crystal data: for **5**, a = 16.064 (2) Å, b = 10.304 (2) Å, c = 25.680 (4) Å; for **6**, a = 16.088 (2) Å, b = 10.272 (2) Å, c = 25.805 (3) Å, Z = 4. R = 0.050 in **5** for 2726 "observed" reflections, while R = 0.056 in **6** for 2911 "observed" reflections. The structures consist of independent BPh_4 anions and Co cations. In both complexes the cobalt is in a distorted square-pyramidal environment with an apical and two basal PMe_3 ligands. The difference between the apical and basal Co–P bond lengths is greater in **5** ($Co-P_a$ = 2.298 (1) Å compared to $Co-P_b$ = 2.229 (2) and 2.230 (2) Å) than in **6** (2.251 (3) Å compared to 2.206 (3) and 2.225 (3) Å). The metalloles are η^4-coordinated by their dimethylbutadiene moiety, which is roughly planar and makes an angle of 77.1° in **5** and of 78.5° in **6** to the basal plane. Bending of the metallole ring after coordination is 41.2° in **5** and 44.5° in **6**. Co is located 0.706 Å above the equatorial plane in **5** and 0.664 Å in **6**. The Co–metallole double-bond distance is shorter in **6** (average 2.059 (10) Å) than in **5** (average 2.102 (7) Å). Multinuclear NMR spectra (183–297 K) indicate that both complexes are stereononrigid.

The reaction of group 14 metalloles (siloles and germoles) with transition-metal complexes have already afforded several coordination compounds. But these reactions have so far been limited to the C-phenylated metalloles (**1**: $R^3 = R^4 = Ph$; $R^3 = Ph$, $R^4 = H$). Coordination occurs through the butadiene part of the ring, and compounds with Fe, Co, Ru, Mo, Ni, Cr, or Rh and 2,3,4,5-tetraphenyl- or 2,5-diphenylmetalloles bearing different groups on Si and Ge have been reported[1,2] (Chart I).

The unstable C-unsubstituted siloles[3-6] or germoles[6,7] ($R^3 = R^4 = H$) were identified as monomers in 1981[4,7] and stabilized as carbonyl iron, nickel, or molybdenum complexes.[8,9] The chemistry of these complexes is still not well-developed despite their interest as (i) cyclic conjugated dienes and (ii) sources of η^5-metallacyclopentadienyl species.[10]

Chart I



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[1] Si Chemistry: McMahon, R. J. *Coord. Chem. Rev.* **1982**, *47*, 1 and references therein.

[2] Ge Chemistry: (a) Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1977**, *128*, 57. (b) Jutzi, P.; Karl, A.; Burschka, C. *Ibid.* **1981**, *215*, 27.

[3] Barton, T. J.; Burns, G. T. *J. Organomet. Chem.* **1979**, *179*, C17.

[4] Laporterie, A.; Dubac, J.; Mazerolles, P.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *206*, C25; **1981**, *216*, 321.

[5] Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *209*, C25.

[6] Laporterie, A.; Iloughmane, H.; Dubac, J. *J. Organomet. Chem.* **1983**, *244*, C12.

[7] Laporterie, A.; Manuel, G.; Dubac, J.; Mazerolles, P.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *210*, C33.

[8] Burns, G. T.; Colomer, E.; Corriu, R. J. P. *Organometallics* **1983**, *2*, 1901.

[9] Dubac, J.; Iloughmane, H.; Laporterie, A.; Carré, F.; Colomer, E.; Corriu, R. J. P.; Lheureux, M. 5th Fechem Conference on Organometallic Chemistry, Cap d'Agde, 1984.

[10] Transients free of η^5-silacyclopentadienyl species are formed in the mass spectrometer during the fragmentation of η^4-complexes of siloles.[1] The C-unsubstituted silacyclopentadienide anion[11] is still not identified although benzo or C-phenylated forms are known.[12]

[11] Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972.

[12] (a) Ishikawa, M.; Tabohashi, T.; Ohashi, H.; Kumada, M.; Iyoda, J. *Organometallics* **1983**, *2*, 351. (b) Corriu, R. J. P.; Guérin, C.; Kolani, B. *Bull. Soc. Chim. Fr.* **1985**, 973.