Organometallics 1987, *6*, 2347-2354

Chemistry of Cyclopentadienyl–Ruthenium and –Osmium Complexes. 4. The Facile Synthesis of Cyclopentadienyl–Ruthenium(IV) and –Osmium(IV) Allyl Complexes and the Characterization of a Novel Ruthenium(IV) Intermediate in the Dehydrohalogenation and Dehydrogenation of 3-Bromocyclohexene. The X-ray Crystal Structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^3\text{-C}_4\text{H}_4\text{OMe})\text{Cl}_2]$

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Received March 2, 1987

The labile cyclopentadienyl–ruthenium(II) complexes $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})\text{X}]$ (R = H, Me; C_8H_{12} = cycloocta-1,5-diene; X = Cl, Br, I) undergo facile oxidative addition reactions with allyl halides in alcohol solvents to give the ruthenium(IV)–allyl complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^3\text{-allyl})\text{X}_2]$ (X = Cl, allyl = C_3H_5, $\text{C}_3\text{H}_4\text{Me-1}$, $\text{C}_3\text{H}_4\text{Me-2}$, $\text{C}_3\text{H}_4\text{CH}_2\text{Cl-1}$, $\text{C}_3\text{H}_4\text{Ph-1}$, $\text{C}_3\text{H}_4\text{Cl-2}$; X = Br, allyl = C_3H_5, $\text{C}_3\text{H}_4\text{CH}_2\text{Br-1}$, $\text{C}_3\text{H}_4\text{Br-2}$; X = I, allyl = C_3H_5) and $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Ru}(\eta^3\text{-allyl})\text{X}_2]$ (X = Cl, allyl = C_3H_5, $\text{C}_3\text{H}_4\text{Me-1}$, $\text{C}_3\text{H}_4\text{Me-2}$, $\text{C}_3\text{H}_4\text{CH}_2\text{Cl-1}$, $\text{C}_3\text{H}_4\text{Ph-1}$; X = Br, allyl = C_3H_5; X = I, allyl = C_3H_5). The reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})\text{Cl}]$ with 3,4-dichlorocyclobutene in methanol or ethanol solution gives in good yield the η^3-cyclobutenyl complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^3\text{-C}_4\text{H}_4\text{OR})\text{Cl}_2]$ (R = Me, Et), the alkoxy ring substituent arising from solvolysis of the intermediate chlorocyclobutenyl ligand system. With 1-chloro-2-methylprop-1-ene $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})\text{Cl}]$ reacts to give the ruthenium(IV)–allyl compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^3\text{-C}_3\text{H}_4\text{Me-2})\text{Cl}_2]$, representing a rare example of vinyl halide oxidative addition outside d^{10} transition-metal systems. This oxidative addition/rearrangement process is approximately 100 times slower than the reaction of the corresponding allyl chloride, 1-chloro-2-methylprop-2-ene, with $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})\text{Cl}]$. The thermal rearrangement of η^1-vinyl to η^3-allyl ligands has previously been proposed to occur via hydrido allene intermediates; however, the lack of β-vinylic or β-allylic protons in this system would tend to implicate an alternate mechanism such as η^1-vinyl to η^1-allyl conversion via a 1,3-hydrogen shift. The oxidative addition of 3-bromocyclohexene in $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})\text{Br}]$ rapidly gives the cyclohexenyl complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^3\text{-C}_6\text{H}_9)\text{Br}_2]$, which, on further warming in ethanol, converts to the ruthenium(II)–arene cation $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^6\text{-C}_6\text{H}_6)]^+$, isolated as the hexafluorophosphate salt. This sequence represents the only example of the spontaneous dehydrohalogenation and dehydrogenation of an organic moiety at a ruthenium(II) center for which a ruthenium(IV) intermediate has unequivocally been proven. Another, possible, intermediate in this process is the η^4-cyclohexa-1,3-diene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^4\text{-C}_6\text{H}_8)\text{Br}]$, which, when independently synthesized and warmed in ethanol, spontaneously dehydrogenates to $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^6\text{-C}_6\text{H}_6)]^+$. The pentamethylcyclopentadienyl–osmium(II) complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\eta^4\text{-C}_8\text{H}_{12})\text{Cl}]$ and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{Cl}]$ also oxidatively add allyl and vinyl halides giving osmium(IV)–allyl complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\eta^3\text{-allyl})\text{Cl}_2]$ (allyl = C_3H_5, $\text{C}_3\text{H}_4\text{Me-1}$, $\text{C}_3\text{H}_4\text{Me-2}$). The reactions, however, occur with considerably greater difficulty than in the ruthenium systems. The new cyclopentadienyl–ruthenium(IV) and –osmium(IV) complexes have all been characterized by elemental analysis and by spectroscopic (^{1}H and, where possible, $^{13}\text{C}\{^1\text{H}\}$ NMR) techniques. The crystal and molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^3\text{-C}_4\text{H}_4\text{OMe})\text{Cl}_2]$ has been determined by single-crystal X-ray diffraction. The complex crystallizes in the orthorhombic space group *Pnma* (No. 62) with a = 11.4550 (16) Å, b = 9.3380 (13) Å, c = 9.8942 (12) Å, U = 1058.4 (3) Å^3, and Z = 4. The structure refined to a conventional R = 0.0380 by using 1306 reflections and 96 parameters. The complex has crystallographic mirror symmetry. The Ru–C(allyl) distances [2.116 (6) Å central, 2.181 (4) Å outer carbons] are significantly shorter than those observed in Ru(II)–allyl systems.

Introduction

The organometallic chemistry of ruthenium in the lower (O, +I, and +II) oxidation states is well-established as one of the cornerstones of the coordination chemistry of this metal.[1-3] In contrast, comparatively little is known of higher oxidation state organoruthenium chemistry,[1-3] apparently despite a quite extensive inorganic chemistry of the +III to +VIII states,[1] and also, the implication of high oxidation state organometallics in a range of ruthenium-catalyzed transformations of organic molecules including isomerization and dehydrogenation reactions.[4] With particular regard to the ruthenium(IV) oxidation state, organometallic complexes appear to fall into certain well-defined classes of compounds that include oxidized metallocenes, polyhydride phosphine derivatives, bis(allyl) complexes, nitrosyl complexes, and a range of species containing cyclopentadienyl or allyl groups.[1-3] A survey[5]

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Table I. Physical and Microanalytical Data for the New Ruthenium(IV) Complexes[a]

complex	color	yield, %	anal.[b] C	H	X
3 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_5)Cl_2]$	orange	94	34.53 (34.55)	3.61 (3.62)	25.20 (25.49)
4 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4Me\text{-}1)Cl_2]$	red-orange	92	36.59 (36.99)	4.23 (4.14)	24.35 (24.27)
5 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4Me\text{-}2)Cl_2]$	orange	92	36.92 (36.99)	4.21 (4.14)	24.35 (24.27)
6 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4CH_2Cl\text{-}1)Cl_2]$	orange	83	32.98 (33.09)	3.23 (3.39)	32.27 (32.56)
7 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4Ph\text{-}1)Cl_2]$	orange	90	47.66 (47.47)	4.06 (3.98)	20.11 (20.02)
8 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4Cl\text{-}2)Cl_2]$	orange	86	30.48 (30.73)	2.62 (2.90)	34.42 (34.02)
9 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_5)Br_2]$	red-orange	90	26.28 (26.18)	2.64 (2.75)	41.43 (43.54)
10 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4CH_2Br\text{-}1)Br_2]$	red-orange	94	23.26 (23.50)	2.38 (2.41)	52.60 (52.11)
11 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4Br\text{-}2)Br_2]$	red	84	21.69 (21.54)	1.91 (2.03)	54.20 (53.75)
12 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_5)I_2]$	red-purple	81	20.73 (20.84)	2.12 (2.19)	56.48 (55.05)
13 $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-}C_3H_5)Cl_2]$	orange	75	36.59 (36.99)	4.18 (4.14)	24.06 (24.27)
14 $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-}C_3H_4Me\text{-}1)Cl_2]$	red-orange	91	38.74 (39.23)	4.45 (4.61)	23.00 (23.16)
15 $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-}C_3H_4Me\text{-}2)Cl_2]$	red-orange	74	38.91 (39.23)	4.64 (4.61)	23.05 (23.16)
16 $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-}C_3H_4CH_2Cl\text{-}1)Cl_2]$	red-orange	78	35.25 (35.26)	3.99 (3.85)	30.25 (31.22)
17 $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-}C_3H_4Ph\text{-}1)Cl_2]$	red-orange	97	48.61 (48.92)	4.31 (4.38)	19.49 (19.25)
18 $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-}C_3H_5)Br_2]$	red	71	27.73 (28.37)	3.28 (3.17)	41.82 (41.94)
19 $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-}C_3H_5)I_2]$	purple	59	22.99 (22.75)	2.68 (2.55)	54.30 (53.43)
20 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_4H_4OMe)Cl_2]$	red-orange	91	37.55 (37.51)	3.82 (3.78)	22.19 (22.14)
21 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_4H_4OEt)Cl_2]$	red-orange	90	39.54 (39.53)	4.20 (4.22)	21.29 (21.21)
22 $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_6H_9)Br_2]$	orange	84	31.68 (32.44)	3.33 (3.46)	39.46 (39.25)
25 $[(\eta^5\text{-}C_5Me_5)Os(\eta^3\text{-}C_3H_5)Cl_2]$	yellow	43	36.98 (35.70)	4.71 (4.61)	15.20 (16.21)
26 $[(\eta^5\text{-}C_5Me_5)Os(\eta^3\text{-}C_3H_4Me\text{-}1)Cl_2]$	yellow	53	37.09 (37.25)	4.78 (4.91)	15.93 (15.71)
27 $[(\eta^5\text{-}C_5Me_5)Os(\eta^3\text{-}C_3H_4Me\text{-}2)Cl_2]$	yellow	47	37.06 (37.25)	5.04 (4.91)	15.65 (15.71)

[a] None of complexes **3–22** and **25–27** melted below 250 °C. [b] Found (calculated in parentheses).

of these systems reveals, however, that there are few systematic syntheses of ruthenium(IV) organometallics and, as far as we are aware, no generalized statements concerning the factors that influence the formation, stability and reactivity of these compounds. We recently reported the synthesis of several new classes of cyclopentadienyl–ruthenium and –osmium complexes including $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$[6] and $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})X]$[7] ($C_8H_{12}$ = cycloocta-1,5-diene; X = H, halide). Herein we wish to report on the facile oxidative addition reactions of thermolabile cyclic allyl halides at the ruthenium(II) center in $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$, results which pertain to the dehydrohalogenation[8] of organic halides at a transition-metal center. Also we report generalized studies on the oxidative addition of allyl and vinyl halides in $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$ and $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})X]$ which for the first time allow conclusions to be drawn about some of the factors that influence the formation and stability of ruthenium(IV) and osmium(IV) organometallics. A preliminary account of some of this work has already appeared.[9]

Experimental Section

All the reactions were routinely performed under an inert atmosphere of nitrogen or argon always by using freshly dried and distilled solvents. 2,3-Dibromoprop-2-ene (Ega Chemie, West Germany), 3-chloroprop-1-ene, *trans*-3-chloro-1-phenylprop-1-ene (Merck), 3-chlorobut-1-ene, 3,4-dichlorocyclobutene (Fluka AG, Switzerland), and all other organo halides (Aldrich) were used as purchased. The compounds $[(\eta^5\text{-}C_5H_4R)Ru(\eta^4\text{-}C_8H_{12})X]$ (R = H, Me; X = Cl, Br, I) were prepared by the literature procedures[6] or by modifications thereof. $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})Cl]$ was obtained by the treatment of $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})H]$[7] with CCl_4, and $[(\eta^5\text{-}C_5Me_5)Os(CO)_2Cl]$ was obtained by reacting $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})Cl]$ with excess carbon monoxide in decane. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded by using a Bruker WM500 instrument at 500.13 and 125.72 MHz, respectively, and a probe temperature of 303 K. Microanalyses were performed by the microanalytical section of the Analytical Division of the NCRL. Physical, microanalytical, and NMR spectral data for all new compounds are given in Tables I–III.

Preparation of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-allyl})X_2]$ (3–8, X = Cl, Allyl = C_3H_5, C_3H_4Me-1, C_3H_4Me-2, $C_3H_4CH_2Cl$-1, C_3H_4Ph-1, C_3H_4Cl-2; 9–11, X = Br, Allyl = C_3H_5, $C_3H_4CH_2Br$-1, C_3H_4Br-2; 12, X = I, Allyl = C_3H_5). A solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$ (**1**, X = Cl, Br, I) (1.0 mmol) in ethanol (30 mL) was treated with the respective allyl halide (1.5 mmol; 3-chloroprop-1-ene, 3-chlorobut-1-ene, 1-chloro-2-methylprop-2-ene, 3,4-dichlorobut-1-ene, *trans*-3-chloro-1-phenylprop-1-ene, 2,3-dichloroprop-1-ene, 3-bromoprop-1-ene, 1,4-dibromo-2-ene, 2,3-dibromoprop-1-ene, 3-iodoprop-1-ene), and the mixture was heated under reflux for 20 min. The reaction mixture was filtered hot in air and then cooled to room temperature. The resulting orange to red crystalline precipitate was collected by filtration and washed with ethanol (5 mL) and diethyl ether (2 × 10 mL). Analytically pure compounds were obtained by recrystallization from either acetone–ethanol or dichloromethane–ethanol mixtures. Yield: 81–94%.

Preparation of $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-allyl})X_2]$ (13–17, X = Cl, Allyl = C_3H_5, C_3H_4Me-1, C_3H_4Me-2, $C_3H_4CH_2Cl$-1, C_3H_4Ph-1; 18, X = Br, Allyl = C_3H_5; 19, X = I, Allyl = C_3H_5). A procedure similar to that described above for the compounds **3–12** was used except that the greater solubility of **13–19** necessitated the use of less ethanol solvent (15 mL) and the washing of the crystalline products with a chilled ethanol–diethyl ether mixture (1:1, 2 × 10 mL). Yield: 71–97%.

Preparation of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_4H_4OR)Cl_2]$ (20, R = Me; 21, R = Et). A solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ (0.31 g, 1.0 mmol) in alcohol (methanol or ethanol, 30 mL) was treated with 3,4-dichlorocyclobutene (0.37 g, 3.0 mmol) and heated under reflux for 20 min. Following filtration and subsequent cooling to room temperature, the resulting orange-red crystalline product was separated by filtration and washed with ethanol (5 mL) and diethyl ether (2 × 10 mL). Yield: **20**, 0.29 g (0.91 mmol, 91%); **21**, 0.32 g (0.90 mmol, 90%).

Reaction of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ with 1-Chloro-2-methylprop-1-ene. A solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Cl]$ (0.31 g, 1.0 mmol) in ethanol (30 mL) was treated with 1-chloro-2-methylprop-1-ene (0.27 g, 3.0 mml) and the resulting mixture heated under reflux for 2 h. After filtration of the hot reaction mixture followed by cooling to room temperature, the orange

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

complex	data
3	5.68 (5 H, s, C_5H_5), 4.97 [1 H, tt, $J(H_aH_c)$ = 10.6, $J(H_aH_b)$ = 6.1, H_a], 4.44 [2 H, d, $J(H_bH_a)$ = 6.1, H_b], 3.71 [2 H, d, $J(H_cH_a)$ = 10.6, H_c]
4	5.55 (5 H, s, C_5H_5), 4.71 [1 H, td, $J(H_aH_c)$ = 10.2, $J(H_aH_b)$ = 6.1, H_a], 4.52 [1 H, dq, $J(H_{c'}H_a)$ = 10.2, $J(H_{c'}Me)$ = 6.4, $H_{c'}$], 4.44 [1 H, d, $J(H_bH_a)$ = 6.1, H_b], 3.54 [1 H, d, $J(H_cH_a)$ = 10.2, H_c], 1.74 [3 H, d, $J(MeH_{c'})$ = 6.4, Me]
5[b]	5.26 (5 H, s, C_5H_5), 4.04 (2 H, s, H_b), 3.69 (2 H, s, H_c), 2.21 (3 H, s, Me)
6	5.87 (5 H, s, C_5H_5), 4.71 [1 H, td, $J(H_aH_c)$ = 10.1, $J(H_aH_b)$ = 6.2, H_a], 4.52 (1 H, m, $H_{c'}$), 4.22 [1 H, d, $J(H_bH_a)$ = 6.2, H_b], 4.05 [2 H, d, $J(CH_2H_{c'})$ = 4.2, CH_2Cl], 3.92 [1 H, d, $J(H_cH_a)$ = 10.1, H_c]
7	7.45 (1 H, m, Ph), 7.39 (2 H, m, Ph), 7.33 (2 H, m, Ph), 5.56 (5 H, s, C_5H_5), 5.43 [1 H, d, $J(H_{c'}H_a)$ = 11.4, $H_{c'}$], 5.29 [1 H, ddd, $J(H_aH_{c'})$ = 11.4, $J(H_aH_c)$ = 9.8, $J(H_aH_b)$ = 6.2, H_a], 4.59 [1 H, d, $J(H_bH_a)$ = 6.2, H_b], 3.84 [1 H, d, $J(H_cH_a)$ = 9.8, H_c]
8	5.76 (5 H, s, C_5H_5), 4.53 (2 H, s, H_b), 4.11 (2 H, s, H_c)
9	5.66 (5 H, s, C_5H_5), 5.01 [1 H, tt, $J(H_aH_c)$ = 10.3, $J(H_aH_b)$ = 6.2, H_a], 4.57 [2 H, d, $J(H_bH_a)$ = 6.2, H_b], 3.52 [2 H, d, $J(H_cH_a)$ = 10.3, H_c]
10[b]	5.89 (5 H, s, C_5H_5), 4.79 [1 H, td, $J(H_aH_c)$ = 10.2, $J(H_aH_b)$ = 6.2, H_a], 4.50 (1 H, m, $H_{c'}$), 4.41 [1 H, d, $J(H_bH_a)$ = 6.2, H_b], 3.99 [2 H, d, $J(CH_2H_{c'})$ = 3.6, CH_2], 3.82 [1 H, d, $J(H_cH_a)$ = 10.2, H_c]
11	5.76 (5 H, s, C_5H_5), 4.53 (2 H, s, H_b), 4.11 (2 H, s, H_c)
12	5.66 (5 H, s, C_5H_5), 4.97 [1 H, tt, $J(H_aH_c)$ = 11.0, $J(H_aH_b)$ = 6.0, H_a], 4.76 [2 H, d, $J(H_bH_a)$ = 6.0, H_b], 3.21 [2 H, d, $J(H_cH_a)$ = 11.0, H_c]
13	5.47 (2 H, m, $C_5\mathit{H}_4Me$), 5.20 (2 H, m, $C_5\mathit{H}_4Me$), 5.04 [1 H, tt, $J(H_aH_c)$ = 10.4, $J(H_aH_b)$ = 6.1, H_a], 4.37 [2 H, d, $J(H_bH_a)$ = 6.1, H_b], 3.53 [2 H, d, $J(H_cH_a)$ = 10.4, H_c], 2.11 (3 H, s, Me)
14	5.35 (1 H, m, $C_5\mathit{H}_4Me$), 5.32 (1 H, m, $C_5\mathit{H}_4Me$), 5.09 (2 H, m, $C_5\mathit{H}_4Me$), 4.78 [1 H, ddd, $J(H_aH_{c'})$ = 10.1, $J(H_aH_c)$ = 10.0, $J(H_aH_b)$ = 6.0, H_a], 4.36 [1 H, d, $J(H_bH_a)$ = 6.0, H_b], 4.32 [1 H, dq, $J(H_{c'}H_a)$ = 10.1, $J(H_{c'}Me)$ = 6.3, $H_{c'}$], 3.38 [1 H, d, $J(H_cH_a)$ = 10.0, H_c], 2.06 (3 H, s, $C_5H_4\mathit{Me}$), 1.69 [3 H, d, $J(MeH_{c'})$ = 6.3, Me]
15	5.42 (2 H, m, $C_5\mathit{H}_4Me$), 5.19 (2 H, m, $C_5\mathit{H}_4Me$), 3.96 (2 H, s, H_b), 3.49 (2 H, s, H_c), 2.28 (3 H, s, Me_a), 2.09 (3 H, s, $C_5H_4\mathit{Me}$)
16	5.58 (1 H, m, $C_5\mathit{H}_4Me$), 5.44 (1 H, m, $C_5\mathit{H}_4Me$), 5.25 (1 H, m, $C_5\mathit{H}_4Me$), 5.21 (1 H, m, $C_5\mathit{H}_4Me$), 4.96 (1 H, m, H_a), 4.39 [1 H, d, $J(H_bH_a)$ = 5.8, H_b], 4.21 (1 H, m, $H_{c'}$), 4.08 [2 H, d, $J(CH_2H_{c'})$ = 10.0, CH_2Cl], 3.46 [1 H, d, $J(H_cH_a)$ = 10.1, H_c], 2.10 (3 H, s, Me)
17	7.43 (1 H, m, Ph), 7.39 (2 H, m, Ph), 7.31 (2 H, m, Ph), 5.38 (1 H, m, H_a), 5.36 (1 H, m, $C_5\mathit{H}_4Me$), 5.33 (1 H, m, $C_5\mathit{H}_4Me$), 5.25 [1 H, d, $J(H_{c'}H_a)$ = 11.3, $H_{c'}$], 5.13 (2 H, m, $C_5\mathit{H}_4Me$), 4.50 [1 H, d, $J(H_bH_a)$ = 6.1, H_b], 3.65 [1 H, d, $J(H_cH_a)$ = 9.2, H_c], 1.99 (3 H, s, Me)
18	5.42 (2 H, m, $C_5\mathit{H}_4Me$), 5.33 (2 H, m, $C_5\mathit{H}_4Me$), 5.05 [1 H, tt, $J(H_aH_c)$ = 10.5, $J(H_aH_b)$ = 6.1, H_a], 4.49 [2 H, d, $J(H_bH_a)$ = 6.1, H_b], 3.36 [2 H, d, $J(H_cH_a)$ = 10.5, H_c], 2.22 (3 H, s, Me)
19	5.59 (2 H, m, $C_5\mathit{H}_4Me$), 5.32 (2 H, m, C_5H_4Me), 4.98 [1 H, tt, $J(H_aH_c)$ = 10.6, $J(H_aH_b)$ = 5.9, H_a], 4.68 [2 H, d, $J(H_bH_a)$ = 5.9, H_b], 3.01 [2 H, d, $J(H_cH_a)$ = 10.6, H_c], 2.24 (3 H, s, Me)
20[c]	5.94 (1 H, m, H_a), 5.86 (5 H, s, C_5H_5), 5.28 (2 H, m, H_b), 3.59 (1 H, m, $C\mathit{H}OMe$), 2.72 (3 H, s, Me)
21[b]	5.94 (1 H, m, H_a), 5.87 (5 H, s, C_5H_5), 5.28 (2 H, m, H_b), 3.66 (1 H, m, $C\mathit{H}OEt$), 3.59 (2 H, q, J = 6.9, CH_2), 1.15 (3 H, t, J = 6.9, Me)
22[c]	6.04 (2 H, m, H_b), 5.27 (5 H, s, C_5H_5), 5.23 [1 H, t, $J(H_aH_b)$ = 6.1, H_a], 2.73 (2 H, m, CH_2), ~~1.60 (4~~ H, m, CH_2)
25	4.75 [1 H, tt, $J(H_aH_c)$ = 8.2, $J(H_aH_b)$ = 5.6, H_a], 3.84 [2 H, d, $J(H_bH_a)$ = 5.6, H_b], 2.75 [2 H, d, $J(H_cH_a)$ = 8.2, H_c], 1.64 (15 H, s, C_5Me_5)
26	4.71 [1 H, td, $J(H_aH_c)$ = 7.8, $J(H_aH_b)$ = 5.6, H_a], 3.82 [1 H, d, $J(H_bH_a)$ = 5.6, H_b], 3.31 [1 H, dq, $J(H_{c'}H_a)$ = 7.8, $J(H_{c'}Me)$ = 6.1, $H_{c'}$], 2.60 [1 H, d, $J(H_cH_a)$ = 7.8, H_c], 1.56 (15 H, s, C_5Me_5), 1.18 [3 H, d, $J(MeH_{c'})$ = 6.1, Me]
27	3.41 (2 H, s, H_b), 2.87 (2 H, s, H_c), 2.70 (3 H, s, Me), 1.59 (15 H, s, C_5Me_5)

[a] Spectra recorded at 303 K and 500.13 MHz by using $CDCl_3$ solutions unless stated otherwise; positions given in ppm; H_a, H_b, and H_c represent the allyl protons on the central carbon atom and on the terminal carbon atom (in the anti and syn positions), respectively; J values in Hz. [b] Recorded in acetone-d_6. [c] Recorded in CD_2Cl_2.

crystalline precipitate $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4Me\text{-}2)Cl_2]$ (**5**) that formed was collected by filtration and washed firstly with ethanol (5 mL) and then with diethyl ether (2 × 10 mL). Yield: 0.21 g (0.72 mmol, 72%).

Preparation of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_6H_9)Br_2]$ (22). A solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Br]$ (0.36 g, 1.0 mmol) in ethanol (30 mL) was warmed to 40 °C and treated with 3-bromocyclohexene (0.48 g, 3.0 mmol). After 2 min the reaction mixture was filtered and rapidly cooled to 0 °C. The resulting orange crystalline precipitate was separated by filtration in air and washed with ethanol (5 mL) and diethyl ether (2 × 10 mL). Yield: 0.24 g (0.84 mmol, 84%).

Conversion of 22 to $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$. This reaction may be effected either with preformed **22** or directly from **1** (X = Br) and 3-bromocyclohexene.

(a) A suspension of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_6H_9)Br_2]$ (0.41 g, 1.0 mmol) in ethanol (30 mL) was heated under reflux for 5 min giving a pale yellow solution. Filtration followed by treatment with NH_4PF_6 (0.17 g, 1.1 mmol) in ethanol (5 mL) and cooling to 0 °C gave a pale yellow crystalline precipitate. Filtration followed by washing with ethanol (10 mL) and diethyl ether (2 × 10 mL) gave the product $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$ as a pale yellow crystalline solid. Yield: 0.37 g (0.94 mmol, 94%).

(b) A solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Br]$ (0.36 g, 1.0 mmol) and 3-bromocyclohexene (0.48 g, 3.0 mmol) in ethanol (30 mL) was heated under reflux for 10 min giving a pale yellow solution of the arene cation. With use of a similar procedure as detailed in (a) above, the product $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$ was obtained in similar yield.

Preparation of $[(\eta^5\text{-}C_5Me_5)Os(\eta^3\text{-allyl})Cl_2]$ (25–27, Allyl = C_3H_5, C_3H_4Me-1, C_3H_4Me-2). (a) A solution of $[(\eta^5\text{-}C_5Me_5)Os(CO)_2Cl]$ (0.20 g, 0.48 mmol) in *n*-decane (40 mL) was treated with excess allyl halide (2.0 mL; 3-chloroprop-1-ene, 3-chlorobut-1-ene, 1-chloro-2-methylprop-2-ene) and heated under reflux for 14–15 h. After being cooled to room temperature, the mixture was adsorbed on a silica gel column and the *n*-decane eluted with hexane. Subsequent elution with hexane–diethyl ether mixtures gave two fractions, the first being unreacted $[(\eta^5\text{-}C_5Me_5)Os(CO)_2Cl]$ (typically 45–55% recovery) and the second being the required products **25–27**. Yield: typically 40–55%.

(b) A solution of $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})Cl]$ (0.20 g, 0.43 mmol) in *n*-decane (40 mL) was treated with excess 3-chloroprop-1-ene (2.0 mL) and heated under reflux for 30 h. With use of procedures similar to those detailed in (a) above, $[(\eta^5\text{-}C_5Me_5)Os(\eta^3\text{-}C_3H_5)Cl_2]$ (**25**) was obtained as a yellow crystalline solid. Yield: 0.07 g (0.17 mmol, 39%).

Reaction of $[(\eta\text{-}C_5Me_5)Os(CO)_2Cl]$ with 1-Chloro-2-methylprop-1-ene. A solution of $[(\eta^5\text{-}C_5Me_5)Os(CO)_2Cl]$ (0.20 g, 0.48 mmol) in *n*-decane (40 mL) was treated with 1-chloro-2-methylprop-1-ene (2.0 mL, excess) and heated under reflux for 15 h. Following a workup procedure as detailed for **25–27** in (a) above, **27** was obtained in 26% yield based on consumed starting material.

X-ray Data Collection, Solution, and Refinement of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_4H_4OMe)Cl_2]$ (20). Dark red rhomboid shaped crystals of **20** were grown from acetone solution. A crystal of dimensions 0.18 × 0.15 × 0.10 mm was used for the structure determination.

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

complex	data
3	96.6 (C_5H_5), 93.6 (C_a), 65.8 (C_b)
5[b]	96.9 (C_5H_5), 93.8 (C_a), 63.8 (C_b), 15.9 (Me)
13	101.1 (*C*Me), 99.4, 95.1 (*C*$_5$H$_4$Me), 88.9 (C_a), 65.4 (C_b), 13.3 (Me)
14	103.1 (*C*Me), 99.0, 94.9, 94.0 (*C*$_5$H$_4$Me), 88.6 (C_a), 85.4 ($C_{b'}$), 61.5 (C_b), 18.6 (Me), 13.0 (C$_5$H$_4$*Me*)
15	100.1 (*C*Me), 95.6 (*C*$_5$H$_4$Me), 92.1 (C_a), 89.9 (*C*$_5$H$_4$Me), 61.9 (C_b), 17.4 (Me), 13.3 (C$_5$H$_4$*Me*)
16	97.8 (*C*$_5$H$_4$Me), 97.0 (*C*Me), 96.0, 94.9 (*C*$_5$H$_4$Me), 89.9 (C_a), 88.6 ($C_{b'}$), 62.6 (C_b), 44.8 (*C*H$_2$Cl), 13.3 (Me)
17	133.8, 131.1, 130.2, 128.0 (Ph), 97.2 (*C*Me), 96.0, 92.6, 92.4 (*C*$_5$H$_4$Me), 90.0 (C_a), 88.9 ($C_{b'}$), 60.4 (C_b), 13.0 (Me)
18	98.2 (*C*Me), 97.9, 94.3 (*C*$_5$H$_4$Me), 89.3 (C_a), 62.6 (C_b), 13.9 (Me)
19	105.7 (*C*Me), 94.8, 92.1 (*C*$_5$H$_4$Me), 88.8 (C_a), 57.0 (C_b), 14.7 (Me)
22[c]	96.2 (C_5H_5), 95.5 (C_a), 83.4 (C_b), 27.8, 17.4 (CH_2)
25	100.3 (*C*$_5$Me$_5$), 84.9 (C_a), 49.4 (C_b), 9.3 (C$_5$*Me*$_5$)
26	99.5 (*C*$_5$Me$_5$), 86.8 (C_a), 63.0 ($C_{b'}$), 47.4 (C_b), 15.7 (Me), 9.0 (C$_5$*Me*$_5$)
27	100.1 (*C*$_5$Me$_5$), 96.5 (C_a), 45.8 (C_b), 16.3 (Me), 9.2 (C$_5$*Me*$_5$)

[a] Chemical shifts in ppm. Spectra recorded at 303 K and 125.76 MHz by using $CDCl_3$ solutions unless stated otherwise; C_a and C_b represent the central and outer allylic carbon atoms. [b] Recorded in acetone-d_6. [c] Recorded in CD_2Cl_2.

Crystal data: $C_{10}H_{12}Cl_2ORu$, *M*, 320.18; orthorhombic, space group *Pnma* (No. 62), $a = 11.4550$ (16) Å, $b = 9.3380$ (13) Å, $c = 9.8942$ (12) Å, $U = 1058.4$ (3) Å^3, $Z = 4$, $D_{calcd} = 2.009$ Mg m^{-3}, $F(000) = 632$, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 1.797 mm^{-1}, $T = 293 \pm 1$ K.

The unit cell parameters were determined by a least-squares fit to the setting angles of 25 accurately centered reflections with $9.2 \leqslant \theta \leqslant 22.3°$ using an Enraf-Nonius CAD4F diffractometer with graphite-crystal-monochromatized Mo Kα radiation. A total of 1782 reflections with $3 \leqslant \theta \leqslant 30°$ (*h*, 0–16, *k*, 0–13, *l*, 0–13) were measured by using the ω-scan mode with a variable scan speed: maximum 0.0915° s^{-1}, maximum time 60 s per reflection, and a scan width of (0.58 + 0.25 tan θ). The scan width was extended by 25% on each side for background measurements. Three standard reflections (220, 331, and 008) were measured every 60 min and showed no significant changes in intensity. Semi-empirical absorption corrections,[10] based on azimuth scans of nine reflections, were applied to the data; corrections: maximum 0.9993, minimum 0.9271, average 0.9713. The structure was solved by using Patterson and difference Fourier methods and was refined by using SHELX.[11] The complex has crystallographic mirror symmetry with the mirror plane bisecting Ru, the methoxycyclobutenyl, and the cyclopentadienyl groups. Anisotropic temperature factors were used for all non-hydrogen atoms. All hydrogen atom positions were located and refined with d_{C-H} constrained to equal 0.95 Å.[12] Complex neutral-atom scattering factors[13] were used for all atoms. Full-matrix-weighted least-squares refinement [$\sum w|\Delta F|^2$ minimized, $w = \sigma^{-2}(F)$] converged with R [$= \sum|\Delta F|/\sum F_o$] = 0.0380 and wR [$= (\sum w|\Delta F|^2/\sum wF_o^2)$] = 0.0322 for 1306 reflections with $F_0 \geqslant 4\sigma(F_o)$ and 96 refined parameters. The final atom fractional coordinates and equivalent isotropic temperature factors are given in Table IV. Bond lengths and bond angles are given in Table V.

Table IV. Fractional Coordinates (×10^4, ×10^5 for Ru and Cl, ×10^3 for H) and Equivalent Isotropic Temperature Factors (Å^2, ×10^3, ×10^4 for Ru and Cl) for 20

	x/a	*y/b*	*z/c*	*U*(eq)
Ru	22867 (4)	25000	3949 (5)	319 (2)
Cl(1)	12328 (10)	42580 (12)	16823 (12)	445 (6)
C(11)	2048 (5)	2500	−2384 (7)	37 (3)
C(12)	1549 (4)	1432 (5)	−1370 (5)	37 (2)
C(13)	785 (5)	2500	−850 (6)	37 (3)
O(11)	1396 (4)	2500	−3608 (4)	44 (3)
C(14)	2076 (7)	2500	−4802 (6)	48 (4)
C(21)	3981 (3)	3264 (5)	−436 (4)	37 (2)
C(22)	3868 (4)	3722 (5)	893 (5)	41 (2)
C(23)	3795 (6)	2500	1730 (7)	41 (4)
H(11)	283 (2)	250	−272 (6)	48 (10)[a]
H(12)	152 (4)	42 (1)	−131 (4)	48 (10)[a]
H(13)	8 (3)	250	−34 (5)	48 (10)[a]
H(14A)	153 (6)	250	−553 (6)	158 (22)[a]
H(14B)	240 (4)	344 (3)	−471 (5)	158 (22)[a]
H(21)	404 (5)	390 (5)	−118 (4)	124 (12)[a]
H(22)	381 (5)	474 (1)	99 (6)	124 (12)[a]
H(23)	361 (4)	250	266 (1)	124 (12)[a]

[a] Isotropic temperature factor.

Table V. Bond Lengths and Bond Angles for 20

	Bond Lengths (Å)		
Ru–Cl(1)	2.403 (1)	Ru–C(12)	2.181 (4)
Ru–C(13)	2.116 (6)	Ru–C(21)	2.225 (4)
Ru–C(22)	2.197 (4)	Ru–C(23)	2.175 (6)
C(11)–C(12)	1.526 (6)	C(11)–O(11)	1.422 (7)
C(12)–C(13)	1.423 (6)	O(11)–C(14)	1.415 (8)
C(21)–C(21′)	1.426 (9)	C(21)–C(22)	1.388 (6)
C(22)–C(23)	1.412 (6)		
	Bond Angles (deg)		
Cl(1)–Ru–C(12)	122.8 (1)	Cl(1)–Ru–C(13)	84.3 (1)
C(12)–Ru–C(13)	38.6 (2)	Cl(1)–Ru–C(21)	114.5 (1)
C(12)–Ru–C(21)	100.9 (2)	C(13)–Ru–C(21)	119.6 (2)
Cl(1)–Ru–C(22)	86.6 (1)	C(12)–Ru–C(22)	137.4 (2)
C(13)–Ru–C(22)	143.2 (2)	C(21)–Ru–C(22)	36.6 (2)
Cl(1)–Ru–C(23)	94.4 (1)	C(12)–Ru–C(23)	142.6 (2)
C(13)–Ru–C(23)	178.2 (3)	C(21)–Ru–C(23)	62.0 (2)
C(22)–Ru–C(23)	37.7 (2)	Cl(1)–Ru–Cl(1′)	86.2 (1)
C(12)–C(11)–O(11)	111.3 (4)	Ru–C(12)–C(11)	94.7 (3)
Ru–C(12)–C(13)	68.2 (3)	C(11)–C(12)–C(13)	90.6 (4)
C(12)–Ru–C(12′)	54.4 (2)	C(12)–C(11)–C(12′)	81.6 (4)
C(12)–C(13)–C(12′)	89.0 (5)	Ru–C(13)–C(12)	73.2 (3)
C(11)–O(11)–C(14)	115.0 (5)	Ru–C(21)–C(22)	70.6 (3)
C(21)–Ru–C(21′)	37.4 (2)	Ru–C(22)–C(21)	72.8 (3)
Ru–C(22)–C(23)	70.3 (3)	C(21)–C(22)–C(23)	108.1 (4)
C(22)–Ru–C(22′)	62.6 (2)	C(22)–C(23)–C(22′)	107.8 (6)
Ru–C(23)–C(22)	72.0 (3)	C(22)–C(21)–C(21′)	107.8 (5)

Results and Discussion

There are to date, few systematic syntheses of organoruthenium(IV) complexes.[1-3] Rather, the rare examples of such compounds that are known have usually been the outcome of a diversity of synthetic procedures many having in common only the strategy of oxidation of a convenient ruthenium(II) precursor. Since this oxidation process usually takes the form of an oxidative addition, which by implication also involves ligand replacement, it is likely that for most of these systems, it is the lack of substitutive reactivity on the part of the ruthenium(II) precursor rather than any inherent instability of the ruthenium(IV) product that tends to restrict the generalized applications of the synthetic procedures.[1-3]

Perhaps the most prevalent ligand in organoruthenium(IV) chemistry is the cyclopentadienyl group. This ligand possibly acts as a blocking group to reductive elimination/decomposition processes and, electronically also, appears particularly suited to playing a stabilizing role in these complexes. Another ligand system of importance is the allyl group that may apparently arise in some most unusual ways during the formal oxidation processes Ru(II) → Ru(IV)[14] and Ru(III) → Ru(IV)[15] and, once formed, is

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surprisingly stable when compared to ruthenium(II)–allyl complexes. Notable examples of allyl formation in ruthenium(IV) chemistry include the oxidative cyclization of 1,3-dienes[15] and the novel oxidative dehydrogenation of cycloocta-1,5-diene,[14] reactions which, at present, remain mechanistically obscure.

We recently reported[6] the synthesis of the novel cyclopentadienyl–ruthenium(II) complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-diene})X]$ (diene = typically cycloocta-1,5-diene, X = halide) that contain readily displaceable, poorly competing diolefin ligands. On the basis of the aforegoing we reasoned that these complexes should function as ready precursors to ruthenium(IV) organometallics and, further, that they might provide an ideal opportunity to study the chemistry associated with the formation and reactivity of allyl groups in organoruthenium(IV) chemistry. As the first part of our studies we have investigated (i) the facile oxidative addition of allyl halides at the ruthenium(II) centers in $[(\eta^5\text{-}C_5H_4R)Ru(\eta^4\text{-}C_8H_{12})X]$ (R = H, Me; X = Cl, Br, I) leading to the generalized synthesis of neutral ruthenium(IV) complexes of the type $[(\eta^5\text{-}C_5H_4R)Ru(\eta^3\text{-allyl})X_2]$,[16] (ii) the oxidative addition of vinyl halides in these same complexes providing a rare example of vinyl halide addition at a formally d^8 metal center, (iii) the oxidative addition of 3-bromocyclohexene in $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})Br]$, a reaction which gives an insight into the dehydrohalogenation of organic halides at a transition-metal center, and (iv) a comparison between the oxidative addition of allyl and vinyl halides in cyclopentadienyl–ruthenium systems and in the cyclopentadienyl–osmium(II) complexes $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})Cl]$ and $[(\eta^5\text{-}C_5Me_5)Os(CO)_2Cl]$.

Treatment of $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}C_8H_{12})X]$[6] (**1**, X = Cl, Br, I) with excess allyl halide in boiling ethanol solution rapidly gives the neutral ruthenium(IV)–allyl complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-allyl})X_2]$ (**3**–**8**, X = Cl, allyl = C_3H_5, C_3H_4Me-1, C_3H_4Me-2, $C_3H_4CH_2Cl$-1, C_3H_4Ph-1, C_3H_4Cl-2; **9**–**11**, X = Br, allyl = C_3H_5, $C_3H_4CH_2Br$-1, C_3H_4Br-2; **12**, X = I, allyl = C_3H_5) while the corresponding reactions of $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^4\text{-}C_8H_{12})X]$ (**2**, X = Cl, Br, I) have given $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^3\text{-allyl})X_2]$ (**13**–**17**, X = Cl, allyl = C_3H_5, C_3H_4Me-1, C_3H_4Me-2, $C_3H_4CH_2Cl$-1, C_3H_4Ph-1; **18**, X = Br, allyl = C_3H_5; **19**, X = I, allyl = C_3H_5). In methanol or ethanol solution **1** (X = Cl) reacts with 3,4-dichlorocyclobutene to give in good yield the η^3-cyclobutenyl complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_4H_4OR)Cl_2]$ (**20**, R = Me; **21**, R = Et). Compounds **3**–**21** are all exceptionally crystalline solids ranging in color from orange to red. They are generally only sparingly soluble in most common organic solvents (acetone and dichloromethane have proven the best) and are stable to air in the solid state and also for extended periods in solution. **3**–**21** have been completely characterized by a combination of elemental analysis (Table I) and ^1H NMR spectroscopy (Table II). Where solubility has permitted (**3**, **5**, **13**–**19**), $^{13}C\{^1H\}$ NMR spectra have been recorded (Table III). The ^1H NMR spectra of **3**–**12** all show the expected singlet resonance for the cyclopentadienyl ring appearing in the range 5.26–5.89 ppm, while characteristic multiplet resonances assignable to the allyl ligands are observed in the expected ranges. Similar allyl resonance patterns are observed for the methylcyclopentadienyl complexes **13**–**19** together with a singlet appearing between 1.99 and 2.24 ppm for the cyclopentadienyl ring methyl substituent. The cyclopentadienyl ring protons resonate either as two multiplets (as observed in **13**, **15**, **18**, and **19**) or as three or four complex resonances (as observed for **14**, **16**, and **17**). These latter effects are interpretable in terms of the coordination of an unsymmetrically substituted allyl ligand in **14**, **16**, and **17** which introduces a magnetic inequivalence of the cyclopentadienyl ring protons. The $^{13}C\{^1H\}$ NMR spectra of **3**, **5**, and **13**–**19** contain no surprising features, suffice it to point out the marked low-field chemical shifts indicative of the higher oxidation state of the ruthenium ion and the magnetic inequivalence of cyclopentadienyl ring carbon atoms in **14**, **16**, and **17** which parallel the ^1H NMR results.

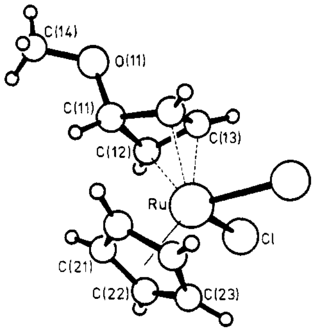

Figure 1. A perspective view of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_4H_4OMe)Cl_2]$ (**20**) showing the atom numbering scheme.

The X-ray Structure of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_4H_4OMe)Cl_2]$ (20). The cyclobutenyl complexes **20** and **21** have no precedent in ruthenium chemistry[1-3] (although related cyclobutenyl ligand systems have been observed, for instance, in palladium–acetylene chemistry[19]) and closely resemble the proposed intermediate in the formation of cyclobutadiene complexes via the dihalocyclobutene route.[20] For this reason the X-ray crystal structure of **20** has been determined.

The structure of **20** is shown in Figure 1. The complex has crystallographic mirror symmetry with the mirror plane bisecting the methoxycyclobutenyl and cyclopentadienyl ligands and the ruthenium atom. The enyl function of the cyclobutenyl ligand is symmetrically bonded to the metal with the Ru–C bond to the central carbon atom [2.116 (6) Å] being shorter than those to the outer carbon atoms [2.181 (4) Å]. This bonding pattern is similar to those found in most other complexes containing cyclobutenyl ligands.[21-23] The Ru–C(allyl) bonds are consistently shorter than the range observed for ruthenium(II)–allyl bond lengths[24] (2.130–2.143 Å central, 2.188–2.258 Å outer) and also shorter than those found in the ruthenium(IV) complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_{10})]PF_6$[14]

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(16) While this work was underway, Nagashima et al.[17] communicated the synthesis of complexes of this type obtained by the oxidative addition of allyl halides in $[(\eta^5\text{-}C_5R_5)Ru(L)_2X]$ (L = CO, PPh_3, X = halide) and, in a subsequent publication,[18] the use of the ruthenium(III) polymer $[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_x]$ as an alternative precursor.

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(2.179 Å central, 2.264 and 2.288 Å outer). (However, the geometric requirements involved in coordinating the two enyl functions of the C_8H_{10} ligand in the latter complex may preclude a closer approach of the ligand to the ruthenium atom.) The Ru–C(cyclopentadienyl) bond length range of 2.175 (6)–2.225 (4) Å in **20** lies within the range of 2.156–2.230 Å found in $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_8H_{10})]PF_6$.[14] However, the large spread of Ru–C bond lengths found in ruthenium(II)–cyclopentadienyl complexes[25] allows no distinction to be made between ruthenium(IV)– and ruthenium(II)–cyclopentadienyl coordination. In common with other cyclobutenyl complexes, the cyclobutenyl ring in **20** is puckered with a dihedral angle between the plane of the allylic carbons C(12), C(13), and C(12′) and the plane containing C(11), C(12), and C(12′) of 29.9(4)°. This compares to the range of 22–27° observed for the equivalent dihedral angle in other cyclobutenyl ligands where the nonallylic carbon atom of the ring is also sp^3-hybridized and is considerably larger than the range of 11–16° found in cyclobutenyl ligands where the non-allylic carbon atom is oxo-substituted.[22] The puckering of the ring allows a reasonable nonbonded distance between the metal atom and the noncoordinated ring carbon atom. In **20** the Ru···C(11) distance is 2.763 (6) Å. For ligands where the non-allylic carbon atom is sp^2-hybridized, electron density is donated to the ring, as reflected by the ring single bond length range of 1.45–1.50 Å[22,23] compared to a range of 1.52–1.60 Å involving an sp^3 carbon atom.[21] The increased electron density within the ring partially inhibits the puckering of the ring.

Perhaps the most remarkable feature of the reactions leading to the ruthenium(IV) complexes **3–21** relate to the ease of the oxidative addition of the allyl halide at the ruthenium(II) center. This, we believe, is directly interpretable in terms of the documented[6,26] facile substitution of the cyclooctadiene ligand in **1** and its congeners, a feature that effectively enables these complexes to react as the "open face", formally 14-electron fragments $\{(\eta^5\text{-}C_5H_4R)RuX\}$. Oxidative addition, which by implication involves ligand displacement in octahedral d^6 systems, would thus be expected to be a rapid process under these circumstances. It is, however, interesting to note that we have encountered, in these studies, no evidence that would suggest that halide labilization in **1** may be involved in the substitution/oxidative addition process. A kinetic investigation of these reactions is, however, underway to confirm this.[27]

The facility of the oxidative addition reactions in **1** and **2** contrast directly with the relatively severe reaction conditions recently employed by Itoh and co-workers[17] in preparing similar compounds by the oxidative addition of allyl halides in $[(\eta^5\text{-}C_5R_5)Ru(L)_2X]$ (R = H, Me; L = CO, PPh_3). On the basis of the present studies, the high temperatures needed to effect reaction in Itoh's systems can be attributed to the well-documented difficulty in achieving multiple-ligand substitutions in half-sandwich complexes of the type $[(\eta^5\text{-}C_5R_5)Ru(L)_2X]$.[2b,3] It is also interesting to note that the carbonyl complexes $[(\eta^5\text{-}C_5R_5)Ru(CO)_2X]$ provided the best yields in Itoh's reactions, presumably because the displaced carbonyl ligand is readily lost from the reaction system, whereas in the case of $[(\eta^5\text{-}C_5R_5)Ru(PPh_3)(L)X]$ (L = PPh_3, CO) as precursor to the ruthenium(IV) complexes, the significantly lower yields of product may be attributed to ligand competition between displaced PPh_3 and entering allyl halides. Support for this comes from the observation[17] that the oxidative addition process in Itoh's systems may formally be reversed with excess carbon monoxide (and presumably also with other donor ligands such as PPh_3) giving good (albeit not quantitative) yields of $[(\eta^5\text{-}C_5R_5)Ru(CO)_2X]$ and the starting allyl halides. Thus, another feature that emerges to emphasize the novelty of the oxidative addition reactions in **1** and **2** relates to the cyclooctadiene ligand being an exceptionally poor competitor for coordination sites at the ruthenium center. Visible spectroscopy has been used to confirm that the formation of the ruthenium(IV) products in our systems is essentially quantitative in hot ethanol, and we have obtained no evidence for the subsequent conversion back to ruthenium(II) complexes as a result of cyclooctadiene intervention. (See below, however, for one possible exception.)

Together these results lead us to conclude that an important criterion in the formation of ruthenium(IV) organometallics from ruthenium(II) precursors by a process of oxidative addition relates to the ease of the ligand substitution process implicit in the oxidative addition and to ligand competition effects within the coordination sphere of the metal ion. The latter is particularly relevant in terms of the apparent stability of the ruthenium(IV) product under the conditions of its synthesis. Perhaps the most remarkable illustration of the propensity of **1** to form ruthenium(IV)–allyl compounds is the reaction with 1-chloro-2-methylprop-1-ene. In boiling ethanol (reaction time 2 h) a high yield of orange crystalline $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_3H_4Me\text{-}2)Cl_2]$ is obtained. The analytical and spectroscopic properties of this compound are identical with those of compound **5** obtained independently by the "direct" reaction of **1** (X = Cl) with 1-chloro-2-methylprop-2-ene (see above). Under comparative conditions the oxidative addition of the vinyl halide to **1** to give **5** is 100 times slower than that of 1-chloro-2-methylprop-2-ene to give **5**. Gas chromatographic analysis of both the reaction solutions revealed a complete conversion of the 1,5-cod to the 1,3-isomer and no evidence of isomerized products derived from the vinyl or allyl chlorides. The isomerization of excess 1,5-cod added to the reaction solutions to mixtures of 1,4- and 1,3-cod indicates that isomerizations in these systems are kinetically faster than the oxidative addition reactions, and one would therefore expect some evidence of the formation of 1-chloro-2-methylprop-2-ene from 1-chloro-2-methylprop-1-ene should an isomerization step play a significant role in the oxidative addition pathway. The results therefore suggest that the formation of **5** from **1** and 1-chloro-2-methylprop-1-ene proceeds via a σ-vinyl intermediate, and consequently the approximately 100 times slower rate is in keeping with the general observation that while allyl halides readily oxidatively add at a wider range of transition-metal centers to give either η^1- or η^3-allyl complexes,[28] vinyl halides are not especially reactive and rare examples of oxidative additions (giving η^1-vinyl complexes) are generally to be found only in electron-rich d^{10} systems.[29] The thermal rearrangement of η^1-vinyl ligands to η^3-allyl ligands has been observed to occur at iridium,[30] zirconium,[31] and molybdenum[32] centers.

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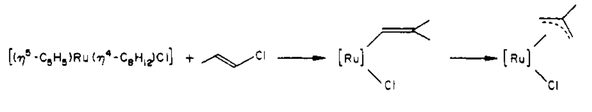
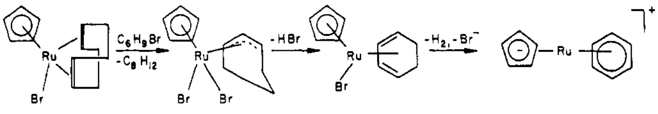
Scheme I



([Ru] = (η^5-C_5H_5) RuCl)

Scheme II



22 23

In each case hydride–allene intermediates have been implicated, but it is noteworthy that the lack of β-vinylic and β-allylic protons in this ruthenium system would preclude such a mechanism for the conversion of a presumed η^1-vinyl intermediate to the η^3-allyl ligand in **5**. However, a 1,3-hydrogen shift could produce an η^1-allyl moiety from the η^1-alkenyl ligand that would then be expected to rapidly convert to the η^3-coordination mode giving **5** (Scheme I).

Treatment of **1** (X = Br) with excess 3-bromocyclohexene in ethanol (40 °C, 2 min) rapidly gives the ruthenium(IV)–cyclohexenyl complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}C_6H_9)Br_2]$ (**22**) (Scheme I) as an air-stable, orange crystalline solid in 84% isolated yield. In the ^{1}H NMR spectrum of **22** (Table II), a sharp singlet at 5.27 ppm is observed for the cyclopentadienyl ligand; the expected triplet for the central allyl proton appears at 5.23 ppm while the remaining ring protons resonate as multiplets at 6.04 (2 H), 2.73 (2 H), and 1.60 ppm (4 H). However, it is the $^{13}C\{^1H\}$ NMR spectrum (Table III) which, on the basis of the characteristic[33] four-signal pattern appearing at 95.50 (C_α), 83.39 ($2C_\beta$), 27.82 ($2C_\gamma$), and 17.44 ppm (C_δ), uniquely defines the cyclohexenyl ligand system. The cyclopentadienyl ring carbons resonate at 96.23 ppm.

Refluxing an orange solution of **22** rapidly (ca. 5 min) gives a pale yellow solution which, on addition of NH_4PF_6 followed by cooling, deposits a crystalline precipitate of the arene–ruthenium(II) complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$[34] (**23**) in high yield (Scheme II). A similar transformation of **22** to **23** can also be effected in ethanol at room temperature over a period of several hours. Compound **23** has been identified on the basis of its characteristic ^{1}H NMR spectrum and by an independent synthesis from **1** (X = Br) and benzene in ethanol solution.[6]

The dehydrohalogenation of organic halides is a commercially important reaction for which a range of reagents and catalysts are currently in use.[8] It is notable, however, that while a number of transition metals[35] and metal oxides[36] function as catalysts, relatively few transition-metal complexes have been reported to participate in this reaction,[37] and little is known about their mode of functioning. The sequence **22** → **23** thus represents, as far as we are aware, the only example of the spontaneous dehydrohalogenation and dehydrogenation of an organic moiety at a ruthenium(II) center and for which a ruthenium(IV) intermediate has unequivocally been proven. With regard to the mechanism of this transformation, **23** has also been obtained in quantitative yield by the treatment of **1** (X = Br) with cyclohexa-1,3-diene in warm ethanol for a few minutes suggesting the sequence of steps shown in Scheme II. The formal elimination of HBr would be envisaged to be a facile process in ethanol whereas one means of attaining the formal elimination of dihydrogen would involve the displaced cyclooctadiene as hydrogen acceptor. Indeed, the rate of the conversion **22** → **23** is markedly increased in the presence of excess cyclooctadiene, converted during the reaction to a mixture of cyclooctene and cyclooctadiene isomers.

Whereas **1** and **2** provide a ready entry to the ruthenium(IV)–allyl complexes $[(\eta^5\text{-}C_5H_4R)Ru(\eta^3\text{-allyl})X_2]$, the cyclopentadienyl–osmium complex $[(\eta^5\text{-}C_5Me_5)Os(\eta^4\text{-}C_8H_{12})Cl]$ (**24**) is oxidized by allyl chloride giving the corresponding osmium(IV)–allyl species $[(\eta^5\text{-}C_5Me_5)Os(\eta^3\text{-}C_3H_5)Cl_2]$ (**25**) only with considerable difficulty (refluxing decane, 30 h). Indeed, such are the combined effects of the relatively stabilizing pentamethylcyclopentadienyl ligand and the well-known kinetic inertness of osmium coordination compounds when compared to ruthenium, that there appears to be no advantage in the use of **24** over the more readily available $[(\eta^5\text{-}C_5Me_5)Os(CO)_2Cl]$, which, under similar reaction conditions, gives $[(\eta^5\text{-}C_5Me_5)Os(\eta^3\text{-allyl})Cl_2]$ (**25–27**, allyl = C_3H_5, C_3H_4Me-1, C_3H_4Me-2). Complexes **25–27** are crystalline, air-stable solids sparingly soluble in common organic solvents. They have been characterized by elemental analysis (Table I) and by ^{1}H NMR spectra (Table II); the spectra bear no remarkable features and will not be discussed further.

Conclusion

The results presented here lead us to suggest that perhaps the most important criterion in the formation and isolation of stable organometallic ruthenium(IV) complexes from ruthenium(II) precursors relates to ligand competition in the coordination sphere of the metal. Specifically complex **1** and its congeners, containing readily displaceable, poorly competing diene ligands (and therefore reacting essentially as the pseudo 14-electron fragments $\{(\eta^5\text{-}C_5H_5)RuX\}$), present a facile entry to the virtually unexplored organometallic chemistry of the ruthenium(IV) oxidation state.

Acknowledgment. We wish to thank Johnson Matthey Chemicals, Sonning Common, England, for a generous loan of ruthenium trichloride which made this work possible. We also thank M. B. Wiege for experimental assistance with the osmium(IV) chemistry. A.S. gratefully acknowledges an International Scientific Collaboration Award from the National Sciences and Engineering Research Council of Canada.

Registry No. 1 (X = Cl), 97913-63-8; 1 (X = Br), 101163-29-5; 1 (X = I), 103883-95-0; 3, 91083-16-8; 4, 110096-85-0; 5, 91083-17-9; 6, 110096-86-1; 7, 110097-05-7; 8, 110096-87-2; 9, 91083-15-7; 10, 110096-88-3; 11, 110096-89-4; 12, 110096-90-7; 13, 110096-91-8; 14, 110096-92-9; 15, 110096-93-0; 16, 110096-94-1; 17, 110097-06-8; 18, 110096-95-2; 19, 110096-96-3; 20, 105302-92-9; 21, 110097-04-6; 22, 106771-00-0; 23, 72812-91-0; 24, 100603-31-4; 25, 110096-97-4;

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26, 110096-98-5; **27**, 110096-99-6; $[(\eta^5\text{-}C_5Me_5)OS(\eta^4\text{-}C_8H_{12})H]$, 100603-30-3; $[(\eta^5\text{-}C_5Me_5)OS(CO)_2Cl]$, 110097-00-2; $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^4\text{-}C_8H_{12})Cl]$, 110097-01-3; $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^4\text{-}C_8H_{12})Br]$, 110097-02-4; $[(\eta^5\text{-}({}_5H_4Me)Ru(\eta^4\text{-}C_8H_{12})I]$, 110097-03-5; 3-chloroprop-1-ene, 107-05-1; 3-chlorobut-1-ene, 563-52-0; 1-chloro-2-methylprop-2-ene, 563-47-3; 3,4-dichlorobut-1-ene, 760-23-6; *trans*-3-chloro-1-phenylprop-1-ene, 21087-29-6; 2,3-dichloroprop-1-ene, 78-88-6; 3-bromoprop-1-ene, 106-95-6; 1,4-dibromobut-2-ene, 6974-12-5; 2,3-dibromoprop-1-ene, 513-31-5; 3-iodoprop-1-ene, 556-56-9; 3,4-dichlorocyclobutene, 41326-64-1; 1-chloro-2-methylprop-1-ene, 513-37-1; 3-bromocyclohexene, 1521-51-3; cyclohexa-1,3-diene, 592-57-4.

Supplementary Material Available: Tables of anisotropic temperature factors, crystal data, and selected least-squares planes (3 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Paramagnetic Monocyclopentadienyl Hydrocarbyl and Borohydride Compounds of Vanadium(II) and Vanadium(III): Synthesis, Structure, and Reactivity

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Received March 5, 1987

Paramagnetic high-spin d^2 and d^3 monocyclopentadienyl vanadium hydrocarbyl complexes $CpV^{III}R_2(PMe_3)_2$ (R = Me, Ph) and $CpV^{II}R(dmpe)$ (R = Me, Pr, Ph) have been prepared from their corresponding halide precursors. From $CpV(Me)Cl(PMe_3)_2$, prepared by ligand exchange, the mixed hydrocarbyl complex $CpV(\eta^3\text{-}C_3H_5)Me(PMe_3)$ could be obtained. The V(II) borohydride complex $CpV(\eta^2\text{-}BH_4)dmpe$ is shown by EPR and solution magnetic measurements to have a low-spin ($S = {}^1/_2$) d^3 configuration. X-ray structures of CpVMe(dmpe) ($P2_12_12_1$, $a = 12.526$ (3) Å, $b = 9.285$ (2) Å, and $c = 12.772$ (3) Å at −158 °C, $Z = 4$) and $CpV(BH_4)dmpe$ ($P2_1/m$, $a = 8.198$ (2) Å, $b = 13.435$ (3) Å, $c = 13.987$ (4) Å, and $\beta = 102.09$ (1)° at −160 °C, $Z = 4$) have been determined. Several structural and electronic features are correlated to EHMO calculations. Both V(II) and V(III) alkyl compounds have been reacted with molecular hydrogen. Although catalytic activity in hydrogenation and isomerization of olefins has been observed, no stable V(III) hydrido species could be obtained, reductive elimination processes probably precluding their isolation. Reaction of $CpVMe_2(PMe_3)_2$ with H_2 generates active CpV fragments that can bind ligands like benzene and 2,3-dimethyl-1,3-butadiene.

Introduction

The organometallic chemistry of V(II) and V(III) has for a long time been centered around the metallocene derivatives $Cp_2V^{II}\cdot L$[2a-c] and $Cp_2V^{III}R$[2d-g] (Cp = $\eta^5\text{-}C_5H_5$). In recent years two main approaches to monocyclopentadienyl complexes of vanadium have been developed: elimination of CpK from $K[Cp_2V]$[3] and reaction of Cp_2Mg with $VCl_3\cdot 2PR_3$ to form $CpVCl_2(PR_3)_2$,[4] from which CpVCl(dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane) can be obtained by reduction.[5] Here we wish to report the synthesis of monocyclopentadienyl V(II) and V(III) alkyl, aryl, and borohydride complexes from their halide precursors (a preliminary report has been published[6]). The hydrogenolysis of these hydrocarbyl complexes was investigated as a possible route to the yet unknown paramagnetic CpV hydrides.

Table I. ^1H NMR Data for $CpVX_2(PMe_3)_2$[a]

X_2	$\delta(PMe_3)$	$\Delta\nu_{1/2}$,[b] Hz
Me_2[c] (3)	−4.1	780
Ph_2 (4)	−10.8	1200
MeCl[c] (5)	−9.1	1180
Cl_2 (1)	−16.9	1030
Br_2	−18.3	490
I_2	−19.6	520

[a] Data recorded at 200 MHz, 20 °C, in toluene-d_8, except 4 (360 MHz, 20 °C, benzene-d_6). Chemical shifts in parts per million relative to Me_4Si (δ 0) with downfield shifts positive. [b] Full width of half maximum. [c] In a range of ±300 ppm no α-alkyl protons could be observed.

Results and Discussion

Synthesis of Alkyl and Borohydride Complexes. The vanadium halide complexes $CpV^{III}Cl_2(PMe_3)_2$[4] (1) and

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