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These results establish that electronic effects can dominate steric effects in determining the regiochemistry of coupling/insertion reactions of $Cp_2Zr(pyridyl)^+$ complexes. Our efforts to utilize this concept in the regioselective preparation of potentially interesting organic intermediates and our studies of the reactions of 1 with other unsaturated substrates will be discussed in subsequent reports.[5h]

Acknowledgment. This work was supported by DOE grant DE-FG02-88ER13935, NSF grant CHE8816445, and the Iowa EARDA program. NMR spectra were obtained in the University of Iowa Highfield NMR Facility. RJF gratefully acknowledges a Sloan Foundation Research Fellowship and a Union Carbide Research Innovation Award.

Preparation and Reactions of a Cationic (μ_3-Methylidyne)ruthenium Complex

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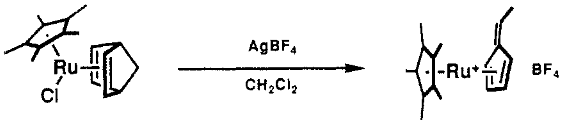
Summary: The reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (**1**) with $AgBF_4$ in ethanol yields the cationic μ_3-methylidyne complex $[((\eta^5\text{-}C_5Me_5)Ru)_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}H)(\mu_3\text{-}CH)](BF_4)$ (**2**), which undergoes reductive coupling between μ_3-methyne and μ_2-hydride ligands to give $[(\eta^5\text{-}C_5Me_5)Ru(CO)(\mu_2\text{-}CH_2)(\mu_2\text{-}Cl)Ru(CO)(\eta^5\text{-}C_5Me_5)](BF_4)$ (**4**) upon treatment with carbon monoxide. Molecular structures of **2** and **4** determined by X-ray diffraction studies are described.

The activation of C–H and C–C bonds by soluble transition-metal complexes has been a focus of recent studies in the field of organometallic chemistry. In these studies, it has been shown that coordinatively unsaturated species formed by thermal and/or photochemical excitation of transition-metal polyhydride,[1] alkyl hydride,[2] or carbonyl[3] complexes play an important role as reactive intermediates. Abstraction of halogen atoms by Ag^+ ion from transition-metal halo complexes may also become an efficient method for the generation of coordinative unsaturation. We previously found that the norbornadiene–ruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(norbornadiene)Cl$ could readily be converted to the cationic 6-methylfulvene–ruthenium complex $[(\eta^5\text{-}C_5Me_5)Ru(6\text{-methylfulvene})](BF_4)$ by treatment with $AgBF_4$ in dichloromethane (eq 1).[4]



(1)

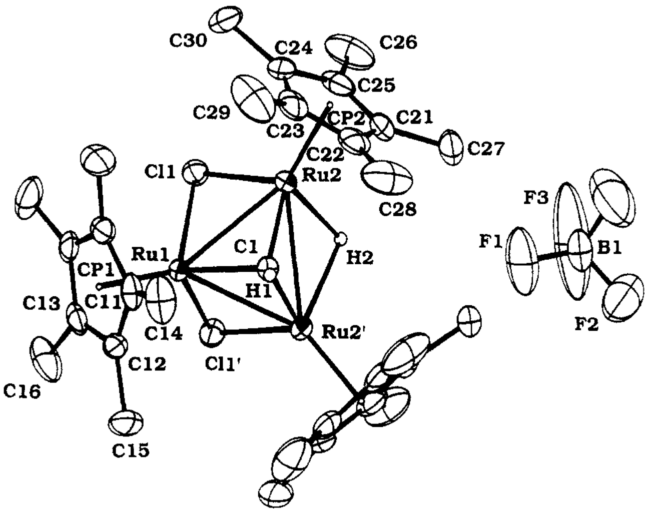


Figure 1. Molecular structure of $[((\eta^5\text{-}C_5Me_5)Ru)_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}H)(\mu_3\text{-}CH)](BF_4)$ (**2**). Bond lengths (Å) and angles (deg) of interest are as follows: Ru(1)–CP(1), 1.859 (0); Ru(2)–CP(2), 1.846 (1); Ru(1)–Ru(2), 2.757 (1); Ru(2)–Ru(2′), 2.871 (1); Ru(1)–C(1), 2.089 (7); Ru(2)–C(1), 1.997 (5); Ru(1)–Cl(1), 2.416 (1); Ru(2)–Cl(1), 2.363 (1); Ru(2)–H(2), 2.18 (7); Ru(2)–Ru(1)–Ru(2′), 62.71 (2); Ru(1)–Ru(2)–Ru(2′), 58.68 (1); Ru(1)–C(1)–Ru(2), 84.9 (3); Ru(2)–C(1)–Ru(2′), 91.9 (3); Ru(1)–Ru(2)–C(1), 49.0 (2); Ru(2)–Ru(1)–C(1), 41.2 (2); Ru(2)–Ru(2′)–C(1), 44.1 (2); Ru(1)–Cl(1)–Ru(2), 70.46 (4). CP indicates the centroid of a C_5Me_5 ring.

Several observations suggested that the skeletal rearrangement of the coordinated norbornadiene proceeded via a C–C bond activation reaction induced by an intermediary coordinatively unsaturated ruthenium species, "$[(\eta^5\text{-}C_5Me_5)Ru(norbornadiene)]^{+}$". Motivated by these results, we investigated the generation and reactions of a coordinatively unsaturated cationic ruthenium complex having only the C_5Me_5 group as an auxiliary ligand. We describe herein the formation of a novel trinuclear μ_3-methylidyne complex by the reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (1) with $AgBF_4$ in ethanol via an activation of the primary C–H bond of ethanol.

Treatment of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (1) with an equimolar amount of $AgBF_4$ in refluxing ethanol for 2 h followed by chromatographic separation on Al_2O_3 (Merck Art 1097) with CH_2Cl_2 gave a dark green solid. Crystallization from

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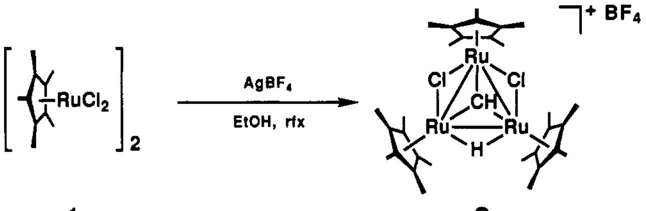
Table I. Crystallographic Data for the X-ray Diffraction Studies

	2	4
(A) Crystal Data		
formula	$Ru_3C_{31}H_{47}Cl_2BF_4$	$Ru_2C_{23}H_{32}O_2ClBF_4$
temp, °C	25	25
space group	*Pnma*	$P\bar{1}$
a, Å	15.341 (4)	11.543 (3)
b, Å	17.433 (5)	14.054 (3)
c, Å	12.423 (3)	8.652 (2)
α, deg		98.89 (2)
β, deg		98.98 (2)
γ, deg		105.21 (2)
V, Å^3	3322.4 (15)	1309.4 (5)
M_r	880.6	664.9
Z	4	2
ρ_{calc}, g/cm^3	1.760	1.686
(B) Measurement of Intensity Data		
radiation	Mo Kα	Mo Kα
monochromator	graphite	graphite
rflns measd	$+h,+k,+l$	$\pm h,\pm k,+l$
max 2θ, deg	60	60
A value for ω-scan width[a]	1.3	1.3
bkgd (count time at end of each scan)	1/3.6 scan time	1/3.6 scan time
ω-scan rate, deg/min	6.0	6.0
no. of rflns measd	4802	8116
no. of data used ($F > 3\sigma(F)$)	3545	5787
(C) Treatment of Data		
abs cor	none	none
abs coeff, cm^{-1}	15.27	12.80
P factor	0.00	0.00
final residuals		
R	0.0496	0.0495
R_w	0.0522	0.0515

[a] The scan width is equal to $A + 0.14 \tan \theta$.

CH_2Cl_2/Et_2O (2/1) afforded the trinuclear μ_3-methylidyne complex $[((\eta^5\text{-}C_5Me_5)Ru)_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}H)(\mu_3\text{-}CH)](BF_4)$ (2) in 30% yield as analytically pure dark green prisms (eq 2).[5]



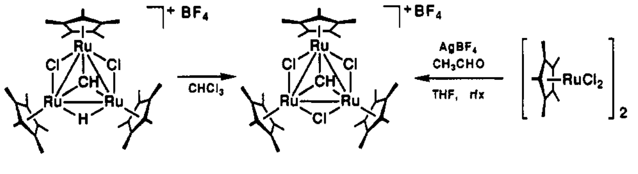
1 2

(2)

The yield of 2 was raised to 40% when 1 was treated with $AgBF_4$ in the presence of a ca. 20-fold excess of CH_3CHO. This result implied that oxidation of ethanol to give acetaldehyde occurred in the initial stage of the reaction of 1 with $AgBF_4$ in ethanol.

A notable feature in the ^1H NMR spectrum of 2 was a singlet appearing at δ 17.56 for a μ_3-methylidyne proton. The signal for the bridging hydride appeared at δ −16.77. The ^{13}C NMR spectrum revealed a doublet (J_{CH} = 164.6 Hz) for the methylidyne ligand at δ 342.2. Two singlets for the C_5Me_5 ligands observed at δ 1.73 and 1.78 in an intensity ratio of 1/2 in the ^1H NMR spectrum implied a symmetrical structure with a mirror plane.

Scheme I



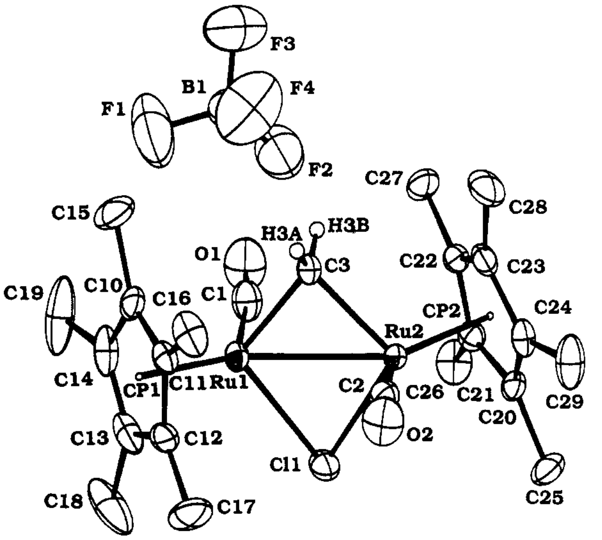


Figure 2. Molecular structure of $[(\eta^5\text{-}C_5Me_5)Ru(CO)(\mu_2\text{-}Cl)(\mu_2\text{-}CH_2)Ru(CO)(\eta^5\text{-}C_5Me_5)](BF_4)$ (4). Bond lengths (Å) and angles (deg) of interest are as follows: Ru(1)–CP(1), 1.898 (0); Ru(2)–CP(2), 1.900 (0); Ru(1)–Ru(2), 2.734 (1); Ru(1)–C(3), 2.092 (5); Ru(2)–C(3), 2.084 (6); Ru(1)–Cl(1), 2.386 (2); Ru(2)–Cl(1), 2.376 (1); Ru(1)–C(1), 1.859 (7); Ru(2)–C(2), 1.859 (7); Ru(2)–C(2), 1.859 (7); C(1)–O(1), 1.14 (1); C(2)–O(2), 1.14 (1); CP(1)–Ru(1)–Ru(2), 141.17 (2); CP(2)–Ru(2)–Ru(1), 140.35 (2); C(1)–Ru(1)–Ru(2), 93.4 (2); C(2)–Ru(2)–Ru(1), 93.5 (2); CP(1)–Ru(1)–C(1), 124.3 (3); CP(2)–Ru(2)–C(2), 124.9 (2); Ru(1)–C(3)–Ru(2), 81.8 (2); Ru(1)–Ru(2)–C(3), 49.2 (2); Ru(2)–Ru(1)–C(3), 49.0 (2); Ru(1)–Cl(1)–Ru(2), 70.10 (4); Ru(1)–Ru(2)–Cl(1), 55.12 (4); Ru(2)–Ru(1)–Cl(1), 54.78 (4). CP indicates the centroid of a C_5Me_5 ring.

The X-ray diffraction study of 2 confirmed the proposed trinuclear structure with the triply bridged methylidyne ligand.[6] The ORTEP drawing of 2 is shown in Figure 1 together with selected bond lengths and angles.

The complex has a crystallographic symmetry plane containing the C(1), C(11), C(14), H(1), H(2), and Ru(1) atoms. The Ru(1)–Ru(2) and Ru(2)–Ru(2′) distances of 2.757 (1) and 2.871 (1) Å, respectively, represent single-order metal–metal bonds. The bond distances of 2.089 (7) Å for C(1)–Ru(1) and 1.997 (5) Å for C(1)–Ru(2) are also in the range of those observed for a variety of transition-metal μ_3-carbyne complexes.[7]

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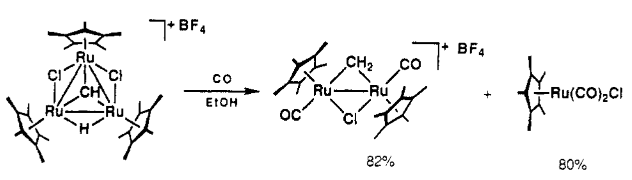
(5) 2: IR (KBr) 2945, 2894, 1808, 1487, 1460, 1430, 1377, 1366, 1282, 1093, 1051, 1014, 885, 722, 700, 529, 437, 397 cm^{-1}; ^1H NMR ($CDCl_3$) δ −16.77 (s, 1 H, Ru–H–Ru), 1.73 (s, 15 H, C_5*Me*$_5$), 1.78 (s, 30 H, C_5*Me*$_5$), 17.56 (s, 1 H, C*H*); ^{13}C NMR ($CDCl_3$) δ 11.3 (q, J_{CH} = 128.0 Hz, C_5*Me*$_5$), 11.4 (q, J_{CH} = 128.7 Hz, C_5*Me*$_5$), 97.3 (s, *C*$_5$Me$_5$), 99.5 (s, *C*$_5$Me$_5$), 342.2 (d, J_{CH} = 164.6 Hz, *C*H); mp >300 °C. Anal. Calcd for $C_{31}H_{47}Cl_2BF_4Ru_3$: C, 42.28; H, 5.38. Found: C, 41.86; H, 5.45.

(6) Complex 2 crystallized from CH_2Cl_2/Et_2O in the orthorhombic system, space group *Pnma*, with *a* = 15.341 (4) Å, *b* = 17.433 (5) Å, *c* = 12.423 (3) Å, *V* = 3322.4 (15) Å^3, and *Z* = 4. Intensity data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation in the 2° < 2θ < 60° range. Data processing was performed on a FACOM A-70 computer by using the R-CRYSTAN structure solving program library obtained from Rigaku Corp. The positions of the metal atoms were determined by direct methods. All other atom positions except for those of the hydrogen atoms of methyl groups were obtained by subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares technique. Hydrogen atoms were refined isotropically. The final *R* and R_w values are 0.0496 and 0.0522, respectively, for 3545 independent reflections with $F_o > 3\sigma(F_o)$.

A symmetrical μ_3-methylidyne complex, $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}Cl)]_3(\mu_3\text{-}CH)](BF_4)$ (**3**), was the major product upon treatment of **2** with $CHCl_3$ at ambient temperature. The complex **3** was alternatively prepared by the reaction of **1** with $AgBF_4$ in the presence of acetaldehyde in THF (Scheme I).

The symmetrical structure of **3** was confirmed by means of ^1H and ^{13}C NMR spectroscopy.[8] In the ^1H NMR spectrum of **3**, C_5Me_5 appears at δ 1.57 as a sharp singlet and the triply bridging CH appears at δ 20.03. Methyl and ring carbons of three equivalent C_5Me_5 groups are observed at δ 11.4 (q, J_{CH} = 128.9 Hz) and 97.7 (s), respectively, and the carbon of the methylidyne ligand appears at δ 340.5 (d, J_{CH} = 165.4 Hz) in the ^{13}C NMR spectrum.

Interestingly, the cationic dinuclear μ-methylene complex $(\eta^5\text{-}C_5Me_5)Ru(CO)(\mu_2\text{-}CH_2)(\mu_2\text{-}Cl)Ru(CO)(\eta^5\text{-}C_5Me_5)$ (**4**)[9] was formed via a reductive coupling between μ_3-methylidyne and μ_2-hydride ligands when complex **2** was treated with carbon monoxide (1 atm) in ethanol (eq 3). This is the reverse process of the precedented irreversible conversion of a μ_2-methylene to a μ_3-methylidyne complex caused by liberation of carbon monoxide.[10] In this reaction, one of three "$(\eta^5\text{-}C_5Me_5)Ru$" fragments of **2** was recovered as the dicarbonyl complex $(\eta^5\text{-}C_5Me_5)Ru(CO)_2Cl$.



2 **4** **5**

(3)

The structure of **4** was determined by a single-crystal X-ray diffraction study (Figure 2).[11] Two ruthenium atoms are linked by a direct metal–metal bond as well as bridging CH_2 and Cl ligands.

The key features of **4** that characterize its structural type are the ^1H and ^{13}C NMR and IR parameters associated with the μ-methylene and carbonyl ligands. In the ^{13}C NMR spectrum of **4**, the μ-methylene carbon appears at δ 166.6 (J_{CH} = 149.8 Hz) and the terminal carbonyl appears at δ 197.2. The resonance for the μ-methylene ligand is observed at δ 9.50 in the ^1H NMR spectrum. The IR spectrum reveals a strong absorption assignable to ν_{CO} at 1953 cm^{-1}.

Further mechanistic studies pertaining to the formation of **2** will be reported in due course.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates, interatomic distances and angles, and thermal parameters for **2** and **4** (12 pages); listings of calculated and observed structure factors for **2** and **4** (49 pages). Ordering information is given on any current masthead page.

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[7] (a) Aime, S.; Milone, L.; Sappa, E. *J. Chem. Soc., Dalton Trans.* **1977**, 227. (b) Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7787. (c) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63. (d) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 140. (e) Connelly, N. G.; Forrow, N. J.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 16. (f) Sailor, M. J.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6015. (g) Sailor, M. J.; Sabat, M.; Shriver, D. F. *Organometallics* **1988**, *7*, 728.

[8] **3**: IR (KBr) 2951, 2899, 1465, 1426, 1372, 1262, 1052, 1016, 890, 799, 728, 540, 505, 389 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.57 (s, 45 H, C_5Me_5), 20.03 (s, 1 H, CH); ^{13}C NMR (CD_2C_2) δ 11.4 (q, J_{CH} = 128.9 Hz), 97.7 (s, C_5Me_5), 340.5 (s, CH); mp >300 °C. Anal. Calcd for $C_{31}H_{46}Cl_3BF_4Ru_3$: C, 40.68; H, 5.07. Found: C, 40.33; H, 5.59.

[9] **4**: IR (KBr) 2909, 1953, 1450, 1380, 1362, 1277, 1152, 1092, 1051, 1019, 639, 616, 553, 517, 483, 428 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.86 (s, 30 H, C_5Me_5), 9.50 (s, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 10.2 (q, J_{CH} = 129.3 Hz, C_5Me_5), 105.2 (s, C_5Me_5), 166.6 (t, J_{CH} = 149.8 Hz, CH_2), 197.2 (s, CO); mp >300 °C. Anal. Calcd for $C_{23}H_{32}ClO_2BF_4Ru_2$: C, 41.55; H, 4.85. Found: C, 41.33; H, 4.93.

[10] Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

[11] Complex **4** crystallized from CH_2Cl_2/Et_2O in the triclinic system, space group $P\bar{1}$, with a = 11.543 (3) Å, b = 14.054 (3) Å, c = 8.652 (2) Å, α = 98.89 (2)°, β = 98.98 (2)°, δ = 105.21 (2)°, V = 1309,4 (d) $Å^3$, and z = 2. Intensity data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation in the $2° < 2\theta < 60°$ range. Data processing was performed on a FACOM A-70 computer by using R-CRYSTAN structure solving program library obtained from Rigaku Corp. The positions of the metal atoms were determined by the Patterson method. All other atom positions except for those of the hydrogen atoms of C_5Me_5 rings were obtained by subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares technique. Hydrogen atoms were refined isotropically. The final R and R^w values are 0.0495 and 0.0515, respectively, for 5787 independent reflections with $F_o > 3\sigma(F_o)$.

Synthesis of Metallacyclopentenones by Insertion of Rhodium into Cyclobutenones

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Summary: Cyclobutenones react with $ClRh(PPh_3)_3$ to give 5-rhoda-2-cyclopenten-1-ones (η^2-vinylketenes). Ligand exchange gave $(\eta^5\text{-}C_5H_5)(PPh_3)\overline{RhCH_2C(CEt){=}C(Et)CO}$, which was characterized by X-ray crystallography. Benzocyclobutenones react with $ClRh(PPh_3)_3$ to give mixtures of two regioisomeric rhodaindanones.

Metallacyclic compounds derived from insertion of transition-metal reagents into cyclobutenediones have

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[1] National Institutes of Health Postdoctoral Fellow, 1989–1991.

[2] Camille and Henry Dreyfus Foundation Teacher-Scholar, 1985–1990.

[3] Correspondence regarding the X-ray crystallography should be directed to this author.

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