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Reactions of $[Ru(C_5Me_5)Cl]_4$ with Enones and Enals: $Ru(C_5Me_5)$ as a "Carboxophile"

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The reaction of $[Ru(C_5Me_5)Cl]_4$ with enones and enals can lead to pale yellow half-open ruthenocenes incorporating oxo dienyl ligands. In addition to these products, it is possible in some cases to isolate significant quantities of other compounds, in which CO has been abstracted from the oxo dienyl ligand, and coordinates to one or more ruthenium centers, along with the remaining fragment of the oxo dienyl ligand. Isolated in this fashion were $Ru(C_5Me_5)(2\text{-}CH_3C_3H_4)(CO)$, $Ru_2(C_5Me_5)_2(\mu_2\text{-}HC_2CH_3)(\mu_2\text{-}CO)$, and the closo "methylcyclopropenyl" cluster $Ru_3(C_5Me_5)_3[C_3H_2(CH_3)](\mu_3\text{-}CO)$. Single crystal structural determinations have been carried out for the last two compounds. For the dimetallic compound, the space group is $P\bar{1}$, with a = 9.247(3) Å, b = 10.208(3) Å, c = 13.729(2) Å, α = 72.96(2)°, β = 98.73(2)°, γ = 114.92(2)°, and V = 1123.1 Å^3, for Z = 2, while for the trimetallic compound, the space group is $P\bar{1}$ with a = 8.605(1) Å, b = 11.076(1) Å, c = 18.051(2) Å, α = 89.33(1)°, β = 95.55(1)°, γ = 108.09(1)°, and V = 1627.6 Å^3 for Z = 2.

It has been demonstrated that reactions of the $Ru(C_5Me_5)Cl$ tetramer with a wide variety of dienes or dienyl anions can be used to obtain the appropriate half-open ruthenocenes, $Ru(C_5Me_5)(Pdl)$, in which Pdl may be pentadienyl itself or a variety of alkylated, arylated, and even CF_3-substituted pentadienyl ligands.[1] In addition, the use of certain enones or enals in such reactions has allowed for oxo dienyl ligands to be incorporated, such as $2,4\text{-}OC_6H_9$ or $3,5\text{-}OC_6H_9$, in which the oxygen atom has formally replaced a terminal CH_2 group of a pentadienyl ligand (essentially giving a hybrid between a pentadienyl and an acac ligand). However, it was found that attempts to prepare oxo dienyl ligands with fewer methyl groups did not lead to the desired products. Instead, scission of a carbon–carbon bond seemed to occur, leading to carbonyl extrusion and coordination and incorporation of the remaining organic fragment as an additional ligand.[1a] We now report on the natures of these products.

Experimental Section

All hydrocarbon, aromatic, and ethereal solvents were thoroughly dried and deoxygenated by distillation under nitrogen from Na/K benzophenone ketyl immediately before use. Deuterated benzene was degassed over potassium and stored in a glass bulb under nitrogen. Infrared mulls were prepared in a glovebox with dry, degassed Nujol, and representative peaks are given for unobscured regions only. All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen using a Schlenk apparatus or in a glovebox. Solvents and solutions were added by glass syringes with stainless steel needles. Spectroscopic studies were carried out as previously described.[2] Analytical data were obtained by Beller Laboratories and Oneida Research Labs. $[Ru(C_5Me_5)Cl]_4$ was prepared as previously described,[3] while crotonaldehyde, *trans*-2-methyl-2-butenal, *trans*-3-methyl-2-butenal, *trans*-2-pentenal, and acetaldehyde were purchased from Aldrich Chemical Co.

Reaction of $[Ru(C_5Me_5)Cl]_4$ with Crotonaldehyde: $Ru_2(C_5Me_5)_2(\mu_2\text{-}HC_2CH_3)(\mu_2\text{-}CO)$. To a THF solution (25 mL) containing 0.28 g (1.0 mmol) of (pentamethylcyclopentadienyl)ruthenium(II) chloride and 0.19 g (1.4 mmol) of potassium carbonate was added 0.080 g (1.2 mmol) of crotonaldehyde. The original dark brown solution immediately turned red. After overnight stirring, the solvent was removed from the red solution, and the remaining red-brown residue was extracted with 2 × 25 mL of pentane or hexane. The red extract was filtered through a short alumina column, with diethyl ether as eluent. A green upper band and a red-brown lower band which eluted together were combined to give a red solution. A second filtering through alumina (with diethyl ether as eluent) gave only a green solution which was concentrated and cooled to −30 °C, resulting in the formation of dark green crystals in 65% yield (0.16 g, mp 270 °C dec). Single crystals could be grown by slowly cooling a saturated pentane solution to −20 °C.

^1H NMR (benzene-d_6, ambient): δ 8.37 (s, 1H), 2.67 (s, 3H, CH_3), 1.64 (s, 15H, C_5Me_5). ^{13}C NMR (benzene-d_6, ambient): δ 232.0 (CO), 146.3 (C=CH), 127.0 (C=CH), 92.4 (C_5Me_5), 21.4 (CH_3), 9.7 (C_5Me_5). IR (Nujol mull): 1994 (w), 1937 (m), 1926 (w), 1905 (w, br), 1722 (s), 1481 (w), 1260 (s), 1245 (w), 1150 (m), 1057 (m), 1024 (s), 945 (w), 888 (ms), 875 (m), 796 (s, br) cm^{-1}. Mass spectrum (EI, 17 eV), m/z (relative intensity): 544 (70), 543 (52), 542 (100), 541 (98), 540 (73), 539 (74), 538 (50), 537 (26), 536 (29), 514 (49), 513 (40), 512 (76), 511 (72), 510 (83), 509 (74), 508 (78), 468 (21), 466 (29), 465 (25), 464 (30). Anal. Calc for $C_{24}H_{34}Ru_2O$: C, 53.31; H, 6.34. Found: C, 54.15; H, 6.53.

Reaction of $[Ru(C_5Me_5)Cl]_4$ with *trans*-2-Pentenal: $Ru_2(C_5Me_5)_2(\mu_2\text{-}HC_2C_2H_5)(\mu_2\text{-}CO)$. This green compound was made by an analogous procedure using *trans*-2-pentenal. The yield was 50%, mp 250 °C dec.

^1H NMR (benzene-d_6, ambient): δ 8.34 (s, 1H), 2.92 (q, 2H, CH_2, J = 7.3 Hz), 1.64 (s, 15H, C_5Me_5), 1.30 (t, 3H, CH_3, J = 7.3 Hz). IR (Nujol mull): 1722 (s), 1286 (w), 1150 (m), 1057 (m, br), 1024 (ms), 918 (m), 859 (w), 790 (w) cm^{-1}. Mass spectrum (EI, 17 eV), m/z (relative intensity): 558 (28), 557 (22), 556 (38), 555 (39), 554 (31), 553 (31), 528 (71), 527 (54), 526 (95), 525 (100), 524 (84), 523 (83), 522 (61), 521 (35), 520 (39). Anal. Calc for $C_{25}H_{36}Ru_2O$: C, 54.13; H, 6.54. Found: C, 54.61; H, 6.57.

Reaction of $[Ru(C_5Me_5)Cl]_4$ with *trans*-2-Methyl-2-butenal: $Ru_2(C_5Me_5)_2(\mu_2\text{-}H_3CC_2CH_3)(\mu_2\text{-}CO)$ (A), $Ru(C_5Me_5)(3\text{-}OC_5H_7)$ (B). A THF solution (25 mL) containing 0.28 g (1.0 mmol) of (pentamethylcyclopentadienyl)ruthenium(II) chloride, 0.19 g (1.4 mmol) of potassium carbonate, and 0.10 g (1.2 mmol) of *trans*-2-methyl-2-butenal was refluxed at 75 °C for 10 h. The

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solvent was removed from the dark red-brown solution, and the residue was extracted with 2 × 25 mL of pentane and filtered through a pad of Celite. The dark orange filtrate was concentrated and cooled to −30 °C, resulting in the formation of dark green (A) and yellow (B) crystals. The yellow air-stable crystals (mp 67–68 °C) were picked out (0.11 g, 35%). After that, the solids were redissolved in pentane and filtered through a short alumina column, and the green filtrate so isolated was concentrated and cooled to −30 °C, resulting in moderately air-sensitive green crystals (0.10 g, 36%; mp 360 °C dec).

(A) $Ru_2(C_5Me_5)_2(\mu_2\text{-}H_3CC_2CH_3)(\mu_2\text{-}CO)$. ^1H NMR (benzene-d_6, ambient): δ 2.56 (s, 3H, CH_3), 1.64 (s, 15H, C_5Me_5). ^{13}C NMR (benzene-d_6, ambient): δ 230.0 (s, CO), 136.1 (s, C=C), 92.2 (s, C_5Me_5), 19.4 (q, CH_3, J = 127 Hz), 9.6 (q, $C_5\mathit{Me}_5$, J = 127 Hz). IR (Nujol mull): 1721 (s), 1269 (m), 1159 (m), 1137 (m), 1067 (w), 1031 (ms), 805 (w) cm^{-1}. Mass spectrum (EI, 17 eV), m/z (relative intensity): 556 (53), 555 (52), 554 (41), 553 (41), 528 (67), 527 (54), 526 (99), 525 (95), 524 (87), 523 (81), 522 (62), 320 (36), 292 (87), 290 (100), 289 (59), 288 (48), 236 (63). High resolution MS: calc mass = 556.0840 amu; obsd = 556.0831 amu.

(B) $Ru(C_5Me_5)(3\text{-}OC_6H_7)$. ^1H NMR (benzene-d_6, ambient): δ 6.82 (s, 1H), 4.20 (dd, 1H, H-4, J = 10.8, 8.5 Hz), 3.32 (d, 1H, H-5, J = 8.5 Hz), 2.29 (d, 1H, H-5, J = 10.8 Hz), 1.60 (s, 3H, CH_3), 1.58 (s, 15H, C_5Me_5). ^{13}C NMR (benzene-d_6, ambient): δ 123.6 (d, CH, J = 177 Hz), 96.1 (s, C-3), 91.6 (d, CH, J = 158 Hz), 88.7 (s, C_5Me_5), 54.4 (t, C-5, J = 151 Hz), 16.8 (q, CH_3, J = 123 Hz), 10.5 (q, $C_5\mathit{Me}_5$, J = 127 Hz). IR (Nujol mull): 1490 (m), 1330 (w), 1265 (s), 1222 (m), 1174 (m), 1161 (w), 1068 (m), 1027 (s), 980 (m), 883 (w), 844 (ms), 831 (m), 818 (w), 760 (m), 746 (w), 700 (w) cm^{-1}. Mass spectrum (EI, 17 eV), m/z (relative intensity): 320 (47), 319 (28), 318 (25), 317 (25), 294 (27), 292 (85), 291 (43), 290 (100), 289 (58), 288 (54), 287 (43), 286 (36), 236 (64), 235 (36), 234 (41), 233 (36). Anal. Calc for $C_{15}H_{22}RuO$: C, 56.40; H, 6.94. Found: C, 56.56; H, 6.96.

Reaction of $[Ru(C_5Me_5)Cl]_4$ with *trans*-3-Methyl-2-butenal: $Ru(C_5Me_5)(2\text{-}CH_3C_3H_4)(CO)$ (A), $Ru_3(C_5Me_5)_3[C_3H_2(CH_3)](\mu_3\text{-}CO)$ (B). A THF solution (25 mL) containing 0.50 g (1.8 mmol) of (pentamethylcyclopentadienyl)ruthenium(II) chloride, 0.25 g (1.8 mmol) of potassium carbonate, and 0.15 g (1.8 mmol) of *trans*-3-methyl-2-butenal was refluxed at 80 °C for 4 h. The solvent was removed from the dark red solution, the red residue was dissolved in pentane, and the solution was passed through a short alumina column. The yellow lower and red upper bands were eluted with diethyl ether, collected together, and pumped to dryness. The yellow compound (A) was sublimed out at 85 °C (0.17 g, 30% yield based on $Ru(C_5Me_5)Cl$; mp 129–131 °C), while left behind was the orange compound (B) (0.20 g, 42% yield; mp 200 °C dec). Both compounds are air-stable as solids. Single crystals of the orange compound were grown by slowly cooling a saturated pentane–ether solution to ca. −20 °C.

(A) $Ru(C_5Me_5)(2\text{-}CH_3C_3H_4)(CO)$. ^1H NMR (benzene-d_6, ambient): δ 2.21 (s, 2H, CH_2(exo)), 1.68 (s, 15H, C_5Me_5), 1.65 (s, 3H, CH_3), 1.58 (s, 2H, CH_2(endo)). ^{13}C NMR (benzene-d_6, ambient): δ 210.6 (s, CO), 94.4 (s, C_5Me_5), 88.8 (s, C), 34.3 (t, CH_2, J = 156 Hz), 24.4 (q, CH_3, J = 125 Hz), 10.8 (q, $C_5\mathit{Me}_5$, J = 127 Hz). IR (Nujol mull): 2007 (m), 1966 (m), 1920 (vs), 1267 (ms), 1257 (m, sh), 1064 (w), 1016 (s), 924 (w), 887 (ms), 859 (w), 839 (ms), 803 (m) cm^{-1}. Mass spectrum (EI, 17 eV), m/z (relative intensity): 320 (29), 319 (17), 294 (60), 293 (22), 292 (100), 291 (61), 290 (56), 289 (45), 238 (42), 237 (23), 236 (89), 235 (49), 234 (54), 233 (40). High resolution MS: calcd mass = 320.0707 amu; obsd = 320.0700 amu.

(B) $Ru_3(C_5Me_5)_3[C_3H_2(CH_3)](\mu_3\text{-}CO)$. ^1H NMR (benzene-d_6, ambient): δ 5.95 (s, 2H), 2.14 (s, 3H, CH_3), 1.75 (s, 15H, C_5Me_5), 1.74 (s, 30H, C_5Me_5). ^{13}C NMR (benzene-d_6, ambient): δ 207.6 (s, CO), 144.3 (s, C), 142.3 (d, CH, J = 177 Hz), 92.3 (C_5Me_5), 10.7 ($C_5\mathit{Me}_5$, Me coincident, J = 125 Hz), 10.5 ($C_5\mathit{Me}_5$, J = 125 Hz). IR (Nujol mull) ν(CO): 1618 cm^{-1}. Mass spectrum (EI, 17 eV), m/z (relative intensity): 794 (62), 793 (68), 792 (91), 791 (100), 790 (91), 789 (85), 788 (78), 787 (61), 786 (50), 785 (34). High resolution MS: calc mass = 792.0973 amu; obsd = 792.0939 amu.

Table 1. Crystallographic Data for $Ru_2(C_5Me_5)_2(\mu_2\text{-}HC_2CH_3)(\mu_2\text{-}CO)$ and $Ru_3(C_5Me_5)_3(\mu_3\text{-}C_3H_2CH_3)(\mu_3\text{-}CO)$

	(a) Crystal Parameters	
formula	$C_{24}H_{34}Ru_2O$	$C_{35}H_{50}Ru_3O$
fw	540.7	790.0
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.247(3)	8.605(1)
b, Å	10.208(3)	11.076(1)
c, Å	13.729(2)	18.051(2)
α, deg	72.96(2)	89.33(1)
β, deg	98.73(2)	95.55(1)
γ, deg	114.92(2)	108.09(1)
V, Å^3	1123.1	1627.6
Z	2	2
cryst dimens, mm	0.31 × 0.25 × 0.22	0.37 × 0.20 × 0.07
cryst color	green	orange
D(calcd), g cm^{-3}	1.60	1.61
μ(Mo Kα), cm^{-1}	13.3	13.7
temp, K	293	293
T(max)/T(min)	1.157	1.205
	(b) Data Collection	
diffractometer	Enraf-Nonius CAD 4	
radiation (λ, Å)	Mo Kα (0.710 73)	
2θ scan range, deg	4–50	3–46
no. of rflns collcd	4179	4578
no. of indpt rflns	3915	4531
no. of indpt obsd rflns, $F_o \geq 3\sigma(F_o)$	3206	3939
var in stds, %	no decay	
	(c) Refinement	
$R(F)$, %	0.032	0.038
$R(wF)$, %	0.037	0.061
Δ/σ(max)	0.001	0.015
ρ_{max}, e Å^{-3}	0.93	0.76
N_o/N_v	12.7	11.0

Reaction of $[Ru(C_5Me_5)Cl]_4$ with Acetaldehyde: $Ru(C_5Me_5)(CH_3)(CO)_2$. To a THF mixture (25 mL) containing $[Ru(C_5Me_5)Cl]_4$ (0.28 g, 1.0 mmol) and potassium carbonate (0.25 g, 1.8 mmol) was added 0.13 mL (2.2 mmol) of acetaldehyde. The mixture became red within 2 h and was stirred overnight. The solvent was removed from the red solution. The solid residue was extracted with 2 × 25 mL of pentane and filtered through a pad of Celite. The red filtrate was pumped dry and sublimed at ca. 50 °C. The sublimable yellow air-stable compound was collected from the cold finger (0.12 g, 38% yield, mp 85–86 °C), leaving behind a red, air-sensitive solid (IR: 1795, 1261, 1093, 1028 cm^{-1}). ^1H NMR (benzene-d_6, ambient): δ 1.53 (s, 15H, $C_5\mathit{Me}_5$), 0.35 (s, 3H, CH_3). $^{13}C\{H\}$ NMR (benzene-d_6, ambient): δ 204.6 (CO), 98.9 (C_5Me_5), 10.8 ($C_5\mathit{Me}_5$), −19.6 (CH_3). IR (Nujol mull): 2000 (s), 1940 (s), 1178 (m), 1070 (w), 1030 (mw) cm^{-1}. Mass spectrum (EI, 17 eV), m/z (relative intensity): 308 (31), 307 (18), 295 (18), 293 (32), 292 (18), 267 (24), 265 (44), 264 (28), 263 (20), 239 (55), 237 (100), 236 (83), 235 (69), 234 (58), 233 (36).

X-ray Diffraction Studies. Single crystals of the studied compounds were obtained as described above and mounted in glass capillaries under nitrogen. They were then transferred to a rotating anode Enraf-Nonius CAD 4 diffractometer, on which unit cell determination and data collection were carried out. Both lattices were found to be triclinic and assumed to be $P\bar{1}$, which was confirmed by the successful refinements of the two structures. Both structures were solved by direct methods using the SDP programs, which led to the metal atom locations and locations for some of the other non-hydrogen atoms. The remaining non-hydrogen atom locations were found from difference Fourier maps. Hydrogen atoms were either included in positions suggested from difference Fourier maps or placed in calculated positions. Other pertinent data collection and refinement parameters are provided in Table 1, while selected positional and bonding parameters are given in Tables 2–5.

Table 2. Positional Coordinates for the Non-Hydrogen Atoms of $Ru_2(C_5Me_5)_2(\mu_2\text{-}HC_2CH_3)(\mu_2\text{-}CO)$

atom	*x*	*y*	*z*	*B* (Å^2)
Ru(1)	0.16604(4)	0.45267(4)	0.23170(3)	2.367(9)
Ru(2)	0.16902(4)	0.68068(4)	0.26882(3)	2.425(9)
O(1)	–0.1572(4)	0.4319(4)	0.2684(3)	3.9(1)
C(1)	–0.0166(5)	0.4918(5)	0.2590(4)	2.6(1)
C(2)	0.3428(6)	0.6692(6)	0.1941(5)	3.5(1)
C(3)	0.3568(6)	0.6117(6)	0.2910(4)	3.3(1)
C(4)	0.450(1)	0.770(1)	0.103(1)	4.2(3)
C(4′)	0.480(1)	0.605(1)	0.370(1)	5.8(4)
C(5)	0.0127(6)	0.2589(5)	0.1673(4)	3.1(1)
C(6)	0.0463(6)	0.2040(5)	0.2723(4)	3.1(1)
C(7)	0.2114(6)	0.2489(5)	0.2872(4)	3.3(1)
C(8)	0.2836(6)	0.3296(5)	0.1921(4)	3.2(1)
C(9)	0.1602(6)	0.3381(5)	0.1176(4)	3.1(1)
C(10)	–0.1515(8)	0.2273(7)	0.1187(5)	4.7(2)
C(11)	–0.0785(8)	0.1065(7)	0.3518(5)	4.8(2)
C(12)	0.2967(8)	0.2058(7)	0.3863(5)	5.1(2)
C(13)	0.4578(7)	0.3929(7)	0.1694(6)	5.6(2)
C(14)	0.1802(9)	0.4057(7)	0.0042(5)	5.4(2)
C(15)	0.1708(7)	0.9060(5)	0.2093(4)	3.4(1)
C(16)	0.0214(6)	0.8112(6)	0.2550(4)	3.2(1)
C(17)	0.0508(6)	0.7556(5)	0.3595(4)	3.1(1)
C(18)	0.2173(6)	0.8132(5)	0.3801(4)	3.1(1)
C(19)	0.2910(6))	0.9073(6)	0.2864(4)	3.4(1)
C(20)	0.194(1)	0.9967(7)	0.1000(5)	5.6(2)
C(21)	–0.1419(7)	0.7846(7)	0.2053(5)	5.1(2)
C(22)	–0.0774(7)	0.6566(7)	0.4368(5)	4.7(2)
C(23)	0.3035(8)	0.7906(7)	0.4821(5)	4.7(2)
C(24)	0.4679(8)	0.9970(8)	0.2745(6)	5.4(2)

Table 3. Pertinent Bonding Parameters for $Ru_2(C_5Me_5)_2(\mu_2\text{-}HC_2CH_3)(\mu_2\text{-}CO)$

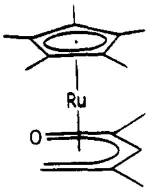
Bond Distances (Å)			
Ru(1)–Ru(2)	2.5130(6)	C(5)–C(6)	1.423(8)
Ru(1)–C(1)	2.000(5)	C(5)–C(9)	1.417(8)
Ru(1)–C(2)	2.090(6)	C(5)–C(10)	1.503(8)
Ru(1)–C(3)	2.082(5)	C(6)–C(7)	1.398(8)
Ru(1)–C(5)	2.233(5)	C(6)–C(11)	1.514(8)
Ru(1)–C(6)	2.229(5)	C(7)–C(8)	1.415(8)
Ru(1)–C(7)	2.189(5)	C(7)–C(12)	1.510(8)
Ru(1)–C(8)	2.187(5)	C(8)–C(9)	1.425(8)
Ru(1)–C(9)	2.195(5)	C(8)–C(13)	1.506(8)
Ru(2)–C(1)	1.994(5)	C(9)–C(14)	1.512(8)
Ru(2)–C(2)	2.093(6)	C(15)–C(16)	1.421(8)
Ru(2)–C(3)	2.085(5)	C(15)–C(19)	1.412(8)
Ru(2)–C(15)	2.198(6)	C(15)–C(20)	1.507(8)
Ru(2)–C(16)	2.232(5)	C(16)–C(17)	1.410(8)
Ru(2)–C(17)	2.237(5)	C(16)–C(21)	1.507(8)
Ru(2)–C(18)	2.205(5)	C(17)–C(18)	1.414(8)
Ru(2)–C(19)	2.175(6)	C(17)–C(22)	1.515(8)
O(1)–C(1)	1.189(6)	C(18)–C(19)	1.426(8)
C(2)–C(3)	1.299(8)	C(18)–C(23)	1.509(8)
C(2)–C(4)	1.54(1)	C(19)–C(24)	1.507(9)
C(3)–C(4′)	1.46(1)		
Bond Angles (degs)			
Ru(2)–Ru(1)–C(1)	50.9(2)	C(9)–C(5)–C(10)	127.2(5)
Ru(2)–Ru(1)–C(2)	53.1(2)	C(5)–C(6)–C(7)	108.5(5)
Ru(2)–Ru(1)–C(3)	53.0(2)	C(5)–C(6)–C(11)	124.8(5)
C(1)–Ru(1)–C(2)	101.3(2)	C(7)–C(6)–C(11)	126.6(5)
C(1)–Ru(1)–C(3)	100.8(2)	C(6)–C(7)–C(8)	108.4(5)
C(2)–Ru(1)–C(3)	36.3(2)	C(6)–C(7)–C(12)	125.6(6)
Ru(1)–Ru(2)–C(1)	51.1(1)	C(8)–C(7)–C(12)	125.8(6)
Ru(1)–R(2)–C(2)	53.0(2)	C(7)–C(8)–C(9)	107.7(5)
Ru(1)–Ru(2)–C(3)	52.9(1)	C(7)–C(8)–C(13)	127.7(6)
C(1)–Ru(2)–C(2)	101.4(2)	C(9)–C(8)–C(13)	124.6(6)
C(1)–Ru(2)–C(3)	101.0(2)	C(5)–C(9)–C(8)	107.8(5)
C(2)–Ru(2)–C(3)	36.2(2)	C(5)–C(9)–C(14)	125.6(6)
Ru(1)–C(1)–Ru(2)	78.0(2)	C(8)–C(9)–C(14)	126.4(6)
Ru(1)–C(1)–O(1)	140.5(4)	C(16)–C(15)–C(19)	107.6(5)
Ru(2)–C(1)–O(1)	141.4(4)	C(16)–C(15)–C(20)	125.6(6)
Ru(1)–C(2)–Ru(2)	73.9(2)	C(19)–C(15)–C(20)	126.7(6)
Ru(1)–C(2)–C(3)	71.5(4)	C(15)–C(16)–C(17)	108.0(5)
Ru(1)–C(2)–C(4)	136.4(6)	C(15)–C(16)–C(21)	127.1(6)
Ru(2)–C(2)–C(3)	71.5(4)	C(17)–C(16)–C(21)	124.7(6)
Ru(2)–C(2)–C(4)	135.5(6)	C(16)–C(17)–C(18)	108.9(5)
C(3)–C(2)–C(4)	139.2(7)	C(16)–C(17)–C(22)	124.8(5)
Ru(1)–C(3)–Ru(2)	74.2(2)	C(18)–C(17)–C(22)	126.3(5)
Ru(1)–C(3)–C(2)	72.2(3)	C(17)–C(18)–C(19)	106.9(5)
Ru(1)–C(3)–C(4′)	134.3(7)	C(17)–C(18)–C(23)	127.6(6)
Ru(2)–C(3)–C(2)	72.2(3)	C(19)–C(18)–C(23)	125.4(5)
Ru(2)–C(3)–C(4′)	135.5(7)	C(15)–C(19)–C(18)	108.7(5)
C(2)–C(3)–C(4′)	140.2(9)	C(15)–C(19)–C(24)	126.6(8)
C(6)–C(5)–C(9)	107.5(5)	C(18)–C(19)–C(24)	124.7(6)
C(6)–C(5)–C(10)	125.2(5)		

Synthetic and Spectroscopic Results and Discussion

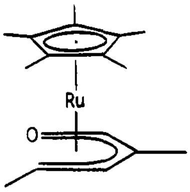
In our previous report, we described the preparation of Ru(C$_5$Me$_5$)(Odl) complexes (Odl = 2,4-OC$_6$H$_9$ (I); 3,5-OC$_6$H$_9$ (II)) from [Ru(C$_5$Me$_5$)Cl]$_4$ and the appropriate enone or enal.[1a] Although it was mentioned that similar reactions designed to prepare the analogous species with fewer methyl groups led instead to CO extrusion and coordination, we have found that it is actually possible to isolate the analogous pale yellow 3-OC$_5$H$_7$ complex (III, eq 1), utilizing *trans*-2-methyl-2-butenal. The complex

$$ {}^{1}/_{4}[Ru(C_5Me_5)Cl]_4 + CH_3CHC(CH_3)CHO \xrightarrow{K_2CO_3,\,\Delta} Ru(C_5Me_5)(3\text{-}OC_5H_7) + [Ru(C_5Me_5)]_2[(\mu_2\text{-}CH_3C_2CH_3)(\mu_2\text{-}CO)] \quad (1) $$

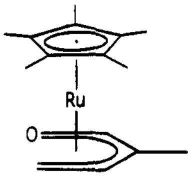
exhibits ^{1}H and ^{13}C NMR spectra which are consistent with I[4] and II, as well as mass spectral and analytical data which confirm its formulation. However, in this case a second product, IV, is also obtained (R = R′ = CH$_3$), the deep green [Ru(C$_5$Me$_5$)]$_2$[(μ_2-CH$_3$C$_2$CH$_3$)(μ_2-CO)], which



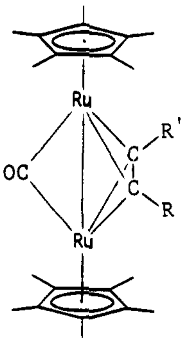
I



II



III



IV

Table 4. Positional Coordinates for the Non-Hydrogen Atoms of $Ru_3(C_5Me_5)_3(\mu_3\text{-}C_3H_2CH_3)(\mu_3\text{-}CO)$

atom	*x*	*y*	*z*	*B* (Å^2)
Ru(1)	0.14829(5)	0.22167(4)	0.33362(2)	2.596(9)
Ru(2)	0.21972(5)	0.42795(4)	0.24276(2)	2.420(9)
Ru(3)	0.19479(5)	0.19272(4)	0.18786(2)	2.557(9)
O	−0.1271(5)	0.2398(4)	0.2175(2)	3.53(9)
C(1)	0.3936(7)	0.3387(5)	0.2311(3)	3.2(1)
C(2)	0.3518(7)	0.2222(5)	0.2381(3)	3.4(1)
C(3)	0.3678(6)	0.3568(5)	0.3163(3)	2.9(1)
C(4)	0.5081(9)	0.4302(8)	0.3716(5)	5.6(2)
C(5)	0.0172(6)	0.2587(5)	0.2340(3)	2.6(1)
C(6)	−0.0424(8)	0.2058(6)	0.4118(4)	4.7(2)
C(7)	0.108(1)	0.2375(8)	0.4517(4)	6.2(2)
C(8)	0.178(1)	0.145(1)	0.4436(4)	8.2(2)
C(9)	0.073(1)	0.0507(7)	0.4006(4)	8.3(2)
C(10)	−0.069(1)	0.0856(8)	0.3789(4)	6.6(2)
C(11)	−0.159(1)	0.277(1)	0.4143(6)	15.4(3)
C(12)	0.174(2)	0.360(1)	0.4971(6)	19.4(5)
C(13)	0.339(2)	0.144(2)	0.4823(7)	25.4(5)
C(14)	0.074(2)	−0.079(1)	0.3802(7)	20.8(4)
C(15)	−0.227(2)	0.015(1)	0.3354(6)	20.6(4)
C(16)	0.2463(8)	0.5831(6)	0.1613(4)	4.3(2)
C(17)	0.3442(9)	0.6307(6)	0.2286(5)	4.9(2)
C(18)	0.2392(9)	0.6189(6)	0.2872(4)	4.7(2)
C(19)	0.0771(8)	0.5649(5)	0.2544(4)	3.9(1)
C(20)	0.0824(8)	0.5441(5)	0.1767(4)	3.9(1)
C(21)	0.311(1)	0.5933(8)	0.0878(5)	8.2(3)
C(22)	0.530(1)	0.6938(8)	0.2384(9)	10.4(4)
C(23)	0.287(1)	0.6678(8)	0.3648(5)	9.1(3)
C(24)	−0.074(1)	0.5441(7)	0.2909(5)	7.2(2)
C(25)	−0.065(1)	0.4970(7)	0.1227(5)	6.3(2)
C(26)	0.013(1)	0.0391(7)	0.1171(4)	5.8(2)
C(27)	0.145(1)	0.0003(6)	0.1430(4)	7.5(2)
C(28)	0.2878(8)	0.0926(8)	0.1102(4)	8.3(2)
C(29)	0.216(1)	0.1746(7)	0.0687(4)	6.6(2)
C(30)	0.063(1)	0.1392(7)	0.0744(4)	6.3(2)
C(31)	−0.158(2)	−0.036(1)	0.1347(7)	19.4(4)
C(32)	0.148(3)	−0.1155(9)	0.1834(7)	19.2(6)
C(33)	0.453(2)	0.079(1)	0.1189(8)	31.2(4)
C(34)	0.305(3)	0.277(1)	0.0201(6)	18.7(5)
C(35)	−0.057(2)	0.197(1)	0.0343(6)	17.9(5)

could have resulted from scission of a carbon–carbon bond in the $Ru(C_5Me_5)(3\text{-}OC_5H_7)$ oxo dienyl complex. In support of this possibility, further heating in solution of the pure oxo dienyl complex was found to bring about conversion to the green bridging alkyne species.

Similar reactions involving crotonaldehyde and *trans*-2-pentenal led to the analogous $\mu_2\text{-}HC_2CH_3$ and $\mu_2\text{-}HC_2C_2H_5$ species (eq 2). These complexes have been

$$^{1}/_{2}[Ru(C_5Me_5)Cl]_4 + RCHC(R')CHO \xrightarrow{K_2CO_3,\ \Delta} [Ru(C_5Me_5)]_2(\mu_2\text{-}RC_2R')(\mu_2\text{-}CO) \quad (2)$$

$$R = CH_3,\ R' = H,\ CH_3$$

$$R = C_2H_5,\ R' = H$$

Table 5. Pertinent Bonding Parameters for $Ru_3(C_5Me_5)_3[C_3H_2(CH_3)](\mu_3\text{-}CO)$

Bond Distances (Å)			
Ru(1)–Ru(2)	2.7429(5)	C(3)–C(4)	1.514(7)
Ru(1)–Ru(3)	2.7364(5)	C(6)–C(7)	1.364(9)
Ru(1)–C(2)	2.050(5)	C(6)–C(10)	1.407(9)
Ru(1)–C(3)	2.062(4)	C(6)–C(11)	1.459(9)
Ru(1)–C(5)	2.133(4)	C(7)–C(8)	1.36(1)
Ru(1)–C(6)	2.231(5)	C(7)–C(12)	1.52(1)
Ru(1)–C(7)	2.211(5)	C(8)–C(9)	1.34(1)
Ru(1)–C(8)	2.174(6)	C(8)–C(13)	1.49(1)
Ru(1)–C(9)	2.192(6)	C(9)–C(10)	1.42(1)
Ru(1)–C(10)	2.228(5)	C(9)–C(14)	1.49(1)
Ru(2)–Ru(3)	2.7366(5)	C(10)–C(15)	1.49(1)
Ru(2)–C(1)	2.061(4)	C(16)–C(17)	1.416(8)
Ru(2)–C(3)	2.069(4)	C(16)–C(20)	1.396(7)
Ru(2)–C(5)	2.121(4)	C(16)–C(21)	1.477(8)
Ru(2)–C(16)	2.220(5)	C(17)–C(18)	1.436(8)
Ru(2)–C(17)	2.191(5)	C(17)–C(22)	1.530(9)
Ru(2)–C(18)	2.223(5)	C(18)–C(19)	1.409(8)
Ru(2)–C(19)	2.250(5)	C(18)–C(23)	1.480(8)
Ru(2)–C(20)	2.260(5)	C(19)–C(20)	1.431(7)
Ru(3)–C(1)	2.051(5)	C(19)–C(24)	1.470(8)
Ru(3)–C(2)	2.045(5)	C(20)–C(25)	1.479(8)
Ru(3)–C(5)	2.125(4)	C(26)–C(27)	1.37(1)
Ru(3)–C(26)	2.233(6)	C(26)–C(30)	1.33(1)
Ru(3)–C(27)	2.188(5)	C(26)–C(31)	1.51(1)
Ru(3)–C(28)	2.155(5)	C(27)–C(28)	1.50(1)
Ru(3)–C(29)	2.193(6)	C(27)–C(32)	1.47(1)
Ru(3)–C(30)	2.236(6)	C(28)–C(29)	1.42(1)
O–C(5)	1.202(5)	C(28)–C(33)	1.47(1)
C(1)–C(2)	1.558(7)	C(29)–C(30)	1.27(1)
C(1)–C(3)	1.599(6)	C(29)–C(34)	1.48(1)
C(2)–C(3)	1.574(6)	C(30)–C(35)	1.50(1)
Bond Angles			
Ru(2)–Ru(1)–Ru(3)	59.93(1)	C(17)–C(16)–C(20)	107.5(5)
Ru(1)–Ru(2)–Ru(3)	59.92(1)	C(16)–C(17)–C(18)	109.0(5)
Ru(1)–Ru(3)–Ru(2)	60.15(1)	C(16)–C(17)–C(22)	126.8(7)
C(2)–C(1)–C(3)	59.8(3)	C(18)–C(17)–C(22)	124.1(7)
C(1)–C(2)–C(3)	61.4(3)	C(17)–C(18)–C(19)	106.4(5)
C(1)–C(3)–C(2)	58.8(3)	C(17)–C(18)–C(23)	127.5(7)
C(1)–C(3)–C(4)	121.6(4)	C(19)–C(18)–C(23)	125.7(7)
C(2)–C(3)–C(4)	123.7(4)	C(18)–C(19)–C(20)	108.4(5)
Ru(1)–C(5)–O	131.3(3)	C(18)–C(19)–C(24)	126.7(6)
Ru(2)–C(5)–O	132.0(3)	C(20)–C(19)–C(24)	124.6(6)
Ru(3)–C(5)–O	132.6(3)	C(16)–C(20)–C(19)	108.6(5)
C(7)–C(6)–C(10)	106.9(6)	C(16)–C(20)–C(25)	127.1(6)
C(7)–C(6)–C(11)	124.4(9)	C(19)–C(20)–C(25)	124.3(5)
C(10)–C(6)–C(11)	128.0(9)	C(27)–C(26)–C(30)	109.7(7)
C(6)–C(7)–C(8)	109.9(7)	C(27)–C(26)–C(31)	120.(1)
C(6)–C(7)–C(12)	121.(1)	C(30)–C(26)–C(31)	130.(1)
C(8)–C(7)–C(12)	129.(1)	C(26)–C(27)–C(28)	104.0(6)
C(7)–C(8)–C(9)	108.7(7)	C(26)–C(27)–C(32)	129.(1)
C(7)–C(8)–C(13)	125.(1)	C(28)–C(27)–C(32)	126.(1)
C(9)–C(8)–C(13)	126.(1)	C(27)–C(28)–C(29)	103.6(6)
C(8)–C(9)–C(10)	108.3(6)	C(27)–C(28)–C(33)	122.(1)
C(8)–C(9)–C(14)	133.(2)	C(29)–C(28)–C(33)	134.(2)
C(10)–C(9)–C(14)	119.(1)	C(28)–C(29)–C(30)	109.3(6)
C(6)–C(10)–C(9)	106.2(6)	C(28)–C(29)–C(34)	125.(1)
C(6)–C(10)–C(15)	123.(1)	C(30)–C(29)–C(34)	126.(1)
C(9)–C(10)–C(15)	131.(1)	C(26)–C(30)–C(29)	113.3(7)
C(17)–C(16)–C(21)	124.0(6)	C(26)–C(30)–C(35)	121.(1)
C(20)–C(16)–C(21)	127.9(6)	C(29)–C(30)–C(35)	125.1(1)

characterized analytically and spectroscopically, having C–O stretching frequencies around 1722 cm^{-1}, and additional support for their formulations has been obtained through an X-ray diffraction study of the R = CH_3, R′ = H complex (*vide infra*). Thus, the carbonyl extrusion process for these enals is quite general and leads to a coordinated alkyne fragment derived from what had been the enal's olefin β and γ carbon atoms (Scheme 1). In the course of this transformation, a hydrogen atom is lost from the γ carbon atom. Hence, one would expect that placement of two methyl groups at the γ position of a conjugated enal would prevent formation of an alkyne complex. This expectation has been confirmed. Thus, for the reaction of $[Ru(C_5Me_5)Cl]_4$ with senecialdehyde two alternative paths were found to be operative, as indicated by eq 3, and neither path led to an alkyne

$$[Ru(C_5Me_5)Cl]_4 + (CH_3)_2CCHCHO \xrightarrow{K_2CO_3,\ \Delta} Ru(C_5Me_5)(2\text{-}CH_3C_3H_4)(CO) + [Ru(C_5Me_5)]_3[\mu_3\text{-}C_3H_2(CH_3)](\mu_3\text{-}CO) \quad (3)$$

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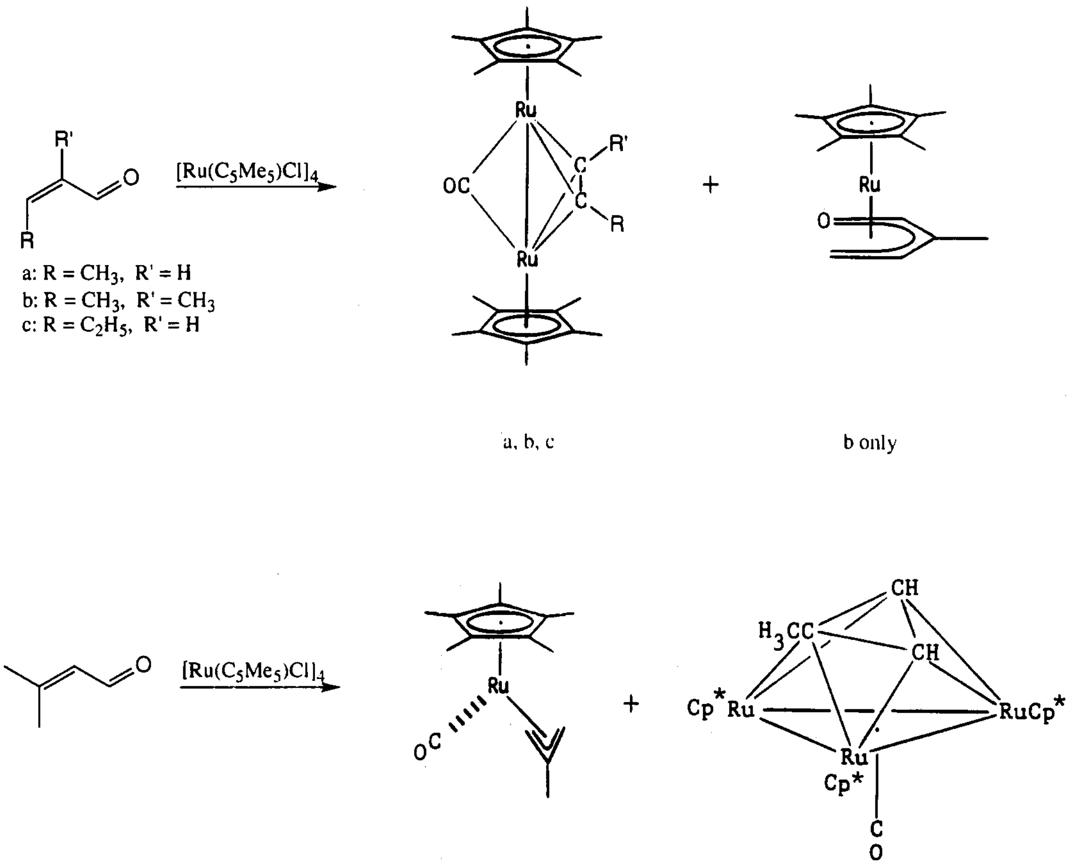
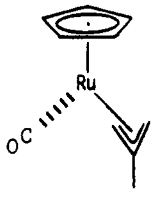
(4) An incorrect assignment of the ^{13}C NMR spectra for *I* was given earlier.[1a] The correct assignments should be δ 135.0 (s, C–O), 101.2 (s, C-4), 87.1 (s, C_5Me_5), 84.0 (d, C-3, *J* = 160 Hz), 54.8 (t, C-5, *J* = 160 Hz), 25.2 (q, CH_3, *J* = 122 Hz), 23.3 (q, CH_3, *J* = 127 Hz), 10.7 (q, C_5Me_5, *J* = 127 Hz).

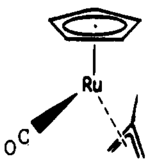
Scheme 1



complex (Scheme 1). From this reaction a pale yellow, monometallic, 2-methylallyl complex was isolated, along with a trimetallic complex incorporating a μ_3-CO ligand (1618 cm^{-1}) and what might be regarded as a bridging methylcyclopropenyl ligand (*vide infra*). The 2-methylallyl complex is well-precedented by its previously reported analog, Ru(C_5H_5)(2-$CH_3C_3H_4$)(CO),[5] which displays similar spectral properties, although only a single isomer was found in the present case (with ν_{CO} = 1920 cm^{-1}), whereas the latter complex exists in two isomeric forms, V (endo) and VI (exo). It seems most likely that Ru(C_5Me_5)(2-$CH_3C_3H_4$)(CO) would exist in the endo form.[5,6] For the trimetallic complex, the ^{1}H NMR spectrum revealed nonequivalent C_5Me_5 resonances in a 2:1 ratio. Coalescence of these signals could not be achieved even by heating to 80 °C, and little if any signal broadening was evident, indicating a significant barrier to site exchange. While it is not clear whether the 2-$CH_3C_3H_4$ complex is a precursor to the trimetallic cyclopropenyl complex, it can be noted that conversions of pentadienyl to cyclopentadienyl ligands have been observed.[7]



V



VI

Given the ease with which single CO molecules were extricated, it was of interest to investigate whether multiple CO extractions could be realized. It is particularly notable, then, that a reaction with acetaldehyde also occurred readily, indeed leading to the extraction of *two* carbonyl ligands, as in eq 4. The product has been found to be

$$[\mathrm{Ru}(C_5Me_5)\mathrm{Cl}]_4 + \text{excess } \mathrm{CH_3CHO} \xrightarrow{K_2CO_3,\ \Delta} \mathrm{Ru}(C_5Me_5)(CH_3)(CO)_2 \quad (4)$$

spectroscopically identical with Ru(C_5Me_5)(CH_3)(CO)$_2$,[8] which has been reported previously. Once again, the carbonyl extrusion seems very general and facile and may justify the use of the term "carboxophile" in describing the chemistry of the Ru(C_5Me_5) fragment. Of course, other examples of such CO extrusions have long been known, such as in the preparation of Vaska's compound utilizing alcohols or aldehydes as solvents,[9] and a more recent CO extrusion from furan, involving an oxo dienyl intermediate, has also been observed.[10] We have also found that the reaction of $^1/_4$[Ru(C_5Me_5)Cl]$_4$ with *n*-C_4H_9Li and KO(*t*-C_4H_9) in THF leads to a low yield (*ca.* 10%) of Ru(C_5Me_5)(CH_3)(C_2H_4)(CO).[11]

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The means by which the above reactions occur is clearly of interest. Perhaps the most common means of a carbonyl extrication involves alkyl migration from an acyl ligand,[12] and as all of the reactions reported herein utilize enals rather than enones, it would be possible to generate acyl ligands, either prior or subsequent to coordination of the enal. However, other examples of C–C bond activation utilizing the $Ru(C_5Me_5)$ fragment have been reported, although more forcing conditions generally seem to be used.[13] There is, in fact, reason to believe that more than one pathway is available for these reactions. Thus, if one subjects previously isolated oxo dienyl complex $Ru(C_5Me_5)(3\text{-}OC_5H_7)$ to the reaction conditions used for its preparation (which also resulted in formation of the alkyne complex), one does indeed observe conversion of the oxo dienyl complex to the alkyne complex, at a rate which could be similar to the rate of formation of alkyne complex from the initial reaction of $[Ru(C_5Me_5)Cl]_4$ with the enal. On the other hand, a reaction of $[Ru(C_5Me_5)Cl]_4$ with acetaldehyde was also found to occur readily, leading to $Ru(C_5Me_5)(CH_3)(CO)_2$. Hence, formation of an oxo dienyl is not required for these reactions to occur, although an oxoallyl species could certainly be formed. Additional information bearing on these points was sought through the attempted isolation of a presumed initially formed enal adduct of $Ru(C_5Me_5)Cl$. Several of the enals appeared to react with $[Ru(C_5Me_5)Cl]_4$ under mild conditions (mixing at room temperature), yielding reddish or purplish solutions, but the products could not be isolated cleanly, being accompanied by the other products reported above. However, infrared spectra of the mixtures contained new peaks attributable to carbonyl ligands, indicating that the initially observed products are themselves not simple enal adducts. It is clear, then, that carbonyl extrication occurs very readily, although there are probably several pathways which are operative. Interestingly, unsaturated nitriles seem to undergo similar reactions.[14]

Structural Results and Discussion

The structure of $Ru_2(C_5Me_5)_2(\mu_2\text{-}HC_2CH_3)(\mu_2\text{-}CO)$ is presented in Figure 1, and representative bonding parameters are provided in Tables 2 and 3. It can be seen that the two $Ru(C_5Me_5)$ units are bridged symmetrically by both the CO and the (disordered) HC_2CH_3 ligands, quite similar to the situation for the previously reported $Ru_2(C_5H_5)_2[\mu_2\text{-}C_2(C_6H_5)_2](\mu_2\text{-}CO)$.[15] In the absence of any metal–metal interaction, the ruthenium centers would have 16 electron configurations, suggesting the presence of a Ru–Ru double bond. The length, 2.5130(6) Å, is quite consistent with this formulation and similar to the length 2.505(1) Å in $Ru_2(C_5H_5)_2[C_2(C_6H_5)_2](\mu_2\text{-}CO)$.[16] The Ru–C($C_5Me_5$) bonds average 2.208(7) Å, although they really appear to fall in two different categories. The two C_5Me_5 ligands are nearly eclipsed, and some slippage of each toward the carbonyl ligand is apparent, which leads to an average Ru–C(5,6,16,17) bond length of 2.233(3) Å, vs 2.192(3) Å for the other six positions. The delocalized C–C bonds for these ligands appear uniform, averaging 1.416(3) Å. The bridging ligand carbon atoms each formally donate one electron to each attached metal center (as is also the case for each carbon atom of the C_5Me_5 ligands), and one observes a slightly shorter average Ru–C bond length for the carbonyl group relative to the alkyne, 1.997(4) vs 2.087(3) Å. This could be in accord with the clear affinity of the $Ru(C_5Me_5)$ fragment for CO and is consistent with the corresponding distances for the $C_2(C_6H_5)_2$ complex, 2.002(7) vs 2.106(5) Å. The respective C–O and alkyne C–C bond lengths, 1.189(6) and 1.299(8) Å, are lengthened somewhat relative to what was found for the free species, 1.128[16] and ca. 1.20–1.21 Å.[17] The C(2)–C(3)–C(4) and C(2)–C(3)–C(4′) bond angles are bent significantly from linearity, as is expected,[18] averaging 139.7(6)°.

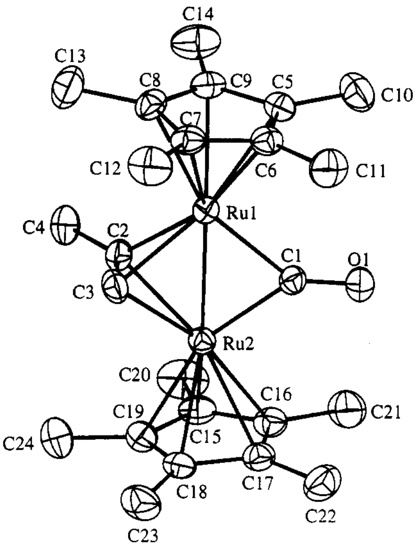

Figure 1. Perspective view and numbering scheme for $Ru_2(C_5Me_5)_2(\mu_2\text{-}HC_2CH_3)(\mu_2\text{-}CO)$. The alkyne methyl group is actually disordered over both sites nearly equally.

The structure of the trimetallic complex, $Ru_3(C_5Me_5)_3[C_3H_2(CH_3)](\mu_3\text{-}CO)$, is depicted in Figures 2 and 3. As the organic ligands can donate a total of 20 electrons for the three metal atoms, it would be difficult to treat this complex in terms of the 18 electron rule. Thus, it appears more reasonable to treat this complex as a cluster species. Indeed, according to Wade's rules,[19] the Ru_3C_3 cluster possesses seven skeletal electron pairs $(n + 1)$[20] and, hence, is a closo species, in agreement with the observed geometry. Interestingly, other $Ru_3(C_3R_3)$ clusters have been found which are nido and arachno species.[21]

Not surprisingly in this light, the average Ru–Ru distance of 2.739(2) Å is significantly longer than that found in the previous dimetallic species. Actually, two of the Ru–Ru lengths are even more similar than the above would

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[11] Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. Unpublished results. In addition to analytical and spectral data, a single crystal X-ray diffraction study was carried out; however, the quality of the study has been seriously affected by a disorder problem.

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[20] A total of 36 valence electrons are contributed by the six cluster atoms, 3 more from the cyclopropenyl substituents, and 17 more from the C_5Me_5 and CO ligands, giving a total of 56 electrons. Subtracting 2 electrons per cluster carbon atom and 12 per ruthenium atom leaves 14 skeletal electrons, or 7 electron pairs.

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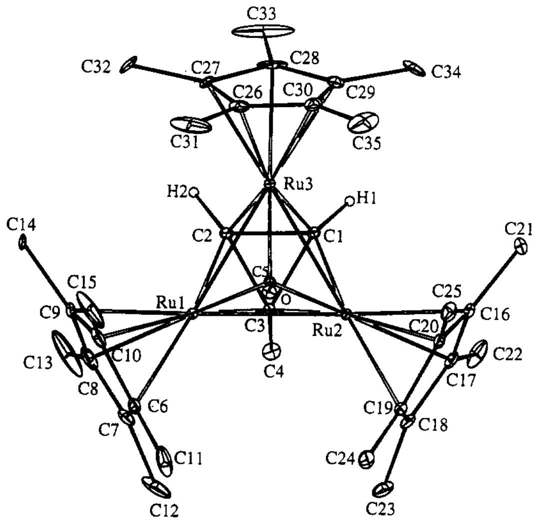

Figure 2. Perspective view and numbering scheme for $Ru_3(C_5Me_5)_3[\mu_3\text{-}C_3H_2(CH_3)](\mu_3\text{-}CO)$.

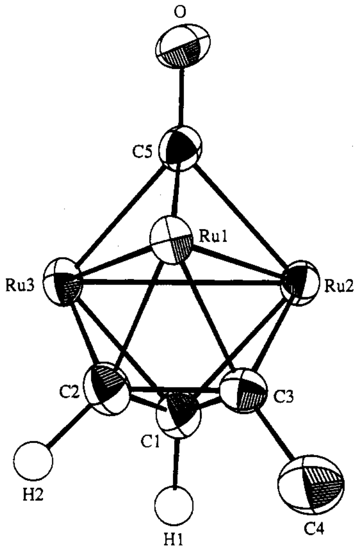

Figure 3. Alternate view of $Ru_3(C_5Me_5)_3[\mu_3\text{-}C_3H_2(CH_3)][\mu_3\text{-}CO)$. The three C_5Me_5 ligands have been deleted for clarity.

indicate, averaging 2.7365(4) vs 2.7429(5) Å for the Ru(1)–Ru(2) bond. A small steric or electronic effect brought on by the single methyl group on the cyclopropenyl fragment would seem to be responsible. The average Ru–CO distance is 2.126(2) Å, while the C–O distance is 1.202(5) Å. The remaining "ligand", the methylcyclopropenyl fragment, is characterized by some unusual bonding parameters. First, C(4) is bent below the "cyclopropenyl" plane by 1.188 Å, or 51.7°, which is perhaps reasonable given the cluster formulation. Similar tilts of 49.7 and 47.1°, respectively, were observed for H(1) and H(2), whose positional parameters had been refined. The most surprising observation is the length of delocalized cyclopropenyl C–C bonds, which range from 1.558(7) to 1.599(6) Å, seemingly longer than normal C–C single bonds. This reveals a rather strong interaction with the Ru_3 centers and could be regarded as indicating that each of the three carbon centers is essentially functioning as a μ_2-carbanion; i.e., a cyclopropenyl trianion is staggered with the Ru_3 triangle. A strong Ru_3–cyclopropenyl interaction is consistent with the observation of a high barrier to interconversion for the three C_5Me_5 ligands (*vide supra*) and is also supported by the relevant Ru–C bond lengths, which average 2.056(2) Å. This is rather short compared to the Ru–C bond lengths for the C_5Me_5 ligands, which are quite irregular and range from 2.155(5) to 2.260(5) Å.

It can be seen in Figure 2 that the two lower C_5Me_5 groups seem to be adjusting to the orientation of the upper C_5Me_5 ligand (on Ru(3)), in an attempt to stagger their methyl groups. There appears to be nearly a vertical mirror plane of symmetry relating the orientations of the lower two C_5Me_5 ligands, which perhaps are prevented by their own mutual steric interaction from better staggering themselves relative to the upper C_5Me_5 ligand. In any event, the range of Ru–C(C_5Me_5) bond lengths is consistent with the average Ru–C(C_5Me_5) length found in the dimeric complex, 2.208(7) Å. An examination of the C–C distances, however, reveals some problem with the bonding parameters of the upper C_5Me_5 ligand, which may explain in part the widely ranging Ru–C(C_5Me_5) bond lengths. In particular, the C(27)–C(28) and C(29)–C(30) lengths of 1.500(12) and 1.269(10) Å are clearly significantly outside the range of C–C distances for the other two C_5Me_5 ligands, 1.345(13)–1.436(8) Å, and appear to suffer from a disorder problem. Hence, their bonding parameters must be treated cautiously.

It is apparent that CO is extruded from a wide variety of organic molecules very readily by the Ru(C_5Me_5) fragment, and that at least some nitriles seem to undergo similar reactions. Given these observations, it can be expected that a large number of other interesting transformations can be effected by this and other related metal systems.

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Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms, positional and thermal parameters for the hydrogen atoms, and selected least squares planes (13 pages). Ordering information is given on any current masthead page.

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