Acknowledgment. Support from the Cornell National Nanofabrication Facility (NNF), the Air Force Office of Scientific Research (AFOSR-87-0103), the National Science Foundation (CHE-8714146), the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and Cornell University is gratefully acknowledged. We thank Prof. Hector D. Abruña for helpful discussions. Funding for the Cornell NMR Facility from the NIH and NSF Instumentation Programs is also acknowledged.

Registry No. **1**, 125520-06-1; **2**, 125520-07-2; **3**, 125520-08-3; **4**, 125520-09-4; **5**, 125520-10-7; **6**, 125520-11-8; **7**, 125520-12-9; **8**, 125520-13-0; **9**, 125520-14-1; (diglyme)Mo(CO)$_3$, 18177-90-7; K(dmCh), 82360-21-2; HgI$_2$, 7774-29-0; [Cp$_2$Fe]PF$_6$, 11077-24-0; [Cp$_2$Fe]BPh$_4$, 11057-46-8; ferrocene, 102-54-5; Diazald, 80-11-5.

Supplementary Material Available: Information pertaining to the X-ray structural investigation of [(dmCh)Mo(CO)$_2$]$_2$ (**5**): a summary of crystal data encompassing data collection and solution/refinement and listings of atomic coordinates, hydrogen atom coordinates, isotropic and anisotropic temperature factors, bond lengths, and bond angles (7 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Reactions of Alkynes with Coordinatively Unsaturated (η^5-C$_5$Me$_5$)Ru Derivatives. X-ray Crystal Structures of (η^5-C$_5$Me$_5$)Cl$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)Ru(η^5-C$_5$Me$_5$) and (η^5-C$_5$Me$_5$)$_3$Ru$_3$(μ_2-Cl)$_2$(μ_3-Cl)(η^2-μ_2-HC≡CSiMe$_3$)

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Reaction of acetylene with Cp*Ru(P^{i}Pr$_3$)Cl or [Cp*Ru(μ_3-Cl)]$_4$ (Cp* = η^5-C$_5$Me$_5$) gives good yields of the dinuclear ruthenacyclopentadiene complex Cp*Cl$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)RuCp* (**1**). Compound 1 crystallizes in space group $P\bar{1}$, with a = 8.673 (6) Å, b = 9.632 (7) Å, c = 16.17 (1) Å, α = 96.72 (4)°, β = 92.39 (4)°, γ = 95.95 (4)°, V = 1332 (2) Å^3, Z = 2, R_F = 4.42%, and R_{wF} = 6.53%. Alkylation of 1 with MeMgBr affords the dimethyl complex Cp*Me$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)RuCp* (**2**). Reaction of [Cp*Ru(μ_3-Cl)]$_4$ with 8 equiv of Me$_3$SiC≡CH produces the cyclobutadiene complex Cp*Ru[η^4-C$_4$H$_2$(SiMe$_3$)$_2$]Cl (**3**) as the major product (67% yield). A minor product in this reaction, formed in 5% yield, is a ruthenacyclopentadiene complex analogous to 1, Cp*Cl$_2$Ru[η^2:η^4-μ_2-C$_4$H$_2$(SiMe$_3$)$_2$]RuCp* (**4**). This species was characterized in solution by NMR spectroscopy. If [Cp*Ru(μ_3-Cl)]$_4$ is allowed to react with a limited amount of Me$_3$SiC≡CH (ca. 1 equiv), a triruthenium cluster containing one alkyne ligand may be isolated in high yield. This compound, Cp*$_3$Ru$_3$(μ_2-Cl)$_2$(μ_3-Cl)(η^2-μ_2-HC≡CSiMe$_3$) (**5**), is unstable in solution but was characterized in the solid state by X-ray crystallography. Compound 5 crystallizes in space group $P2_1/n$, with a = 12.568 (6) Å, b = 17.195 (9) Å, c = 18.307 (9) Å, β = 96.46 (3)°, V = 3931 (3) Å^3, Z = 4, R_F = 4.21%, and R_{wF} = 6.74%. Finally, [Cp*Ru(μ_3-Cl)]$_4$ and dimethyl acetylenedicarboxylate (DMAD) react to give a diruthenium complex containing DMAD and C$_6$(CO$_2$Me)$_6$ ligands, Cp*$_2$Ru$_2$Cl$_2$(MeO$_2$CC≡CCO$_2$Me)[C$_6$(CO$_2$Me)$_6$] (**6**). Possible structures for this species are discussed.

Introduction

It is well established that coordinatively unsaturated transition-metal species have a rich reaction chemistry with alkynes.[1] We have been investigating coordinatively unsaturated Cp*Ru (Cp* = η^5-C$_5$Me$_5$) species, particulary with respect to (1) eliminations in organosilicon ligands[2] and (2) the chemistry of alkoxide derivatives.[3] Convenient starting points for these studies are the 16-electron complexes Cp*Ru(PR$_3$)Cl (R = Cy, ^{i}Pr)[4] and the labile cluster [Cp*Ru(μ_3-Cl)]$_4$,[5] which serve as synthetic equivalents for the 14-electron fragment Cp*RuCl. As part of a survey of the reaction chemistry of these starting materials, we have investigated their reactions with alkynes. As expected, Cp*Ru(P^{i}Pr$_3$)Cl and [Cp*Ru(μ_3-Cl)]$_4$ are quite reactive toward alkynes, and a number of different reaction products can be observed. In this paper we report the synthesis and characterization of dinuclear ruthenacyclopentadiene complexes Cp*X$_2$Ru(η^2:η^4-μ_2-CRCHCRCH)RuCp* (X = Cl, R = H (**1**); X = Me, R = H (**2**); X = Cl, R = SiMe$_3$ (**4**)), a cyclobutadiene complex, Cp*Ru[η^4-C$_4$H$_2$(SiMe$_3$)$_2$]Cl (**3**), a triruthenium cluster with a bridging alkyne, Cp*$_3$Ru$_3$(μ_2-Cl)$_2$(μ_3-Cl)(η^2-μ_2-HC≡CSiMe$_3$) (**5**), and a dinuclear arene complex, Cp*$_2$Ru$_2$Cl$_2$(MeO$_2$CC≡CCO$_2$Me)[C$_6$(CO$_2$Me)$_6$] (**6**).

Results

Blue toluene solutions of the coordinatively unsaturated complex Cp*Ru(P^{i}Pr$_3$)Cl[4] rapidly turn red when pressurized with acetylene (15 psi) at room temperature. Workup of the reaction mixture results in isolation of the metallacyclopentadiene complex Cp*Cl$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)RuCp* (**1**), which crystallizes from toluene as red prisms. Compound 1 was characterized spectroscopically and by X-ray crystallography (vide infra). The lability of

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[1] (a) Bowden, F. L.; Lever, A. P. *Organomet. Chem. Rev.* **1968**, *3*, 227. (b) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323. (c) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[2] Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558.

[3] Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712.

[4] Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278.

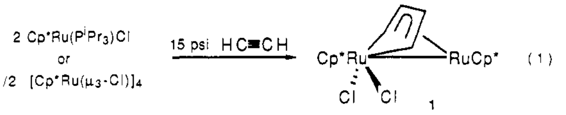
[5] Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

0276-7333/90/2309-1106$02.50/0

Table I. Crystal Data, Data Collection, and Refinement Parameters for 1•CH_2Cl_2 and 5

	1·CH_2Cl_2	**5**
	Crystal Parameters	
formula	$C_{25}H_{36}Cl_4Ru_2$	$C_{35}H_{55}Cl_3Ru_3Si$
color; habit	dark blue; block	dark red; plate
cryst size, mm	0.30 × 0.35 × 0.55	0.08 × 0.3 × 0.5
cryst syst	$P\bar{1}$	$P2_1/n$
a, Å	8.673 (6)	12.568 (6)
b, Å	9.632 (7)	17.195 (9)
c, Å	16.17 (1)	18.307 (9)
α, deg	96.72 (4)	
β, deg	92.39 (4)	96.46 (3)
γ, deg	95.95 (4)	
V, Å^3	1332 (2)	3931 (3)
Z	2	4
ρ(calcd), g cm^{-3}	1.70	1.54
μ, mm^{-1} (Mo Kα)	1.53	1.38
F(000), e$^-$	684	1848
	Data Collection	
scan type	$\theta/2\theta$	$\theta/2\theta$
2θ scan range, deg	$3 \le 2\theta \le 48$	$3 \le 2\theta \le 48$
scan speed, deg min^{-1}	variable, 1.5 to 15 in ω	variable, 1.5 to 15 in ω
index ranges	$0 \le h \le 9$ $-11 \le k \le 10$ $-18 \le l \le 18$	$0 \le h \le 14$ $0 \le k \le 19$ $-20 \le l \le 20$
rflns collected	4507	6708
unique rflns	4195 (R_{int} = 4.14%)	6174 (R_{int} = 2.08%)
obsd rflns	2993 ($F > 6\sigma$(F))	4493 ($F > 6\sigma(F)$)
abs corr	ψ scans	ψ scans
min/max trans	0.494/0.605	0.593/0.916
	Solution and Refinement	
R_F, %	4.42	4.21
R_{wF}, %	6.53	6.74
GOF	0.83	0.97
largest Δ/σ	0.001	0.010
data/param	10.1	11.8
largest $\Delta(\rho)$, e$^-$ Å^{-3}	1.44	0.88

the phosphine ligand in Cp*Ru(P^{i}Pr$_3$)Cl suggested that a more suitable starting material would be the synthetic precursor to Cp*Ru(P^{i}Pr$_3$)Cl, [Cp*Ru(μ_3-Cl)]$_4$.[5] Indeed, reaction of [Cp*Ru(μ_3-Cl)]$_4$ under 15 psi of acetylene resulted in immediate formation of a green solution that soon became red. This reaction (eq 1) allows preparation of 1 in 79% isolated yield.



(1)

The ^{1}H NMR spectrum of 1 exhibits resonances for the inequivalent Cp* ligands (δ 1.00 and 1.91, benzene-d_6), and protons of the η^2:η^4-μ_2-C_4H_4 portion of the molecule display an AA′XX′ splitting pattern giving rise to multiplets at δ 4.97 and 8.33. The chemical shift of δ 8.33 is assigned to the equivalent α protons of the RuC_4H_4 ring, and the peak at δ 4.97 is attributed to the β protons of the metallacycle. The ruthenacyclopentadiene ring carbons of 1 resonate at δ 164.20 (α-C) and 94.66 (β-C) in the ^{13}C NMR spectrum. In contrast to many other dinuclear metallacyclopentadiene complexes, 1 is stereochemically rigid at room temperature. These ^{1}H and ^{13}C NMR parameters for 1 resemble those recently reported for Cp*(PMe$_3$)Ru(η^2:η^4-μ_2-C_4H_4)RuCp*.[6a]

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 1•CH_2Cl_2

	x	y	z	U(eq)[a]
Ru(1)	4466 (1)	6831 (1)	2956 (1)	27 (1)
Ru(2)	2980 (1)	7238 (1)	1486 (1)	31 (1)
Cl(1)	6860 (2)	7065 (2)	2230 (1)	43 (1)
Cl(2)	4796 (2)	9366 (2)	3273 (1)	42 (1)
Cl(3)	−1135 (3)	1942 (3)	2645 (3)	103 (2)
Cl(4)	−18 (5)	375 (5)	3935 (3)	119 (2)
C(0)	−1202 (13)	337 (13)	3035 (9)	95 (5)
C(1)	3762 (9)	5454 (7)	1891 (5)	35 (2)
C(2)	2130 (10)	5137 (9)	1737 (5)	45 (3)
C(3)	1270 (9)	6125 (9)	2174 (5)	44 (3)
C(4)	2200 (8)	7197 (8)	2680 (5)	35 (2)
C(11)	4924 (9)	4864 (7)	3492 (5)	39 (3)
C(12)	6112 (9)	5883 (9)	3907 (5)	42 (3)
C(13)	5405 (9)	6948 (8)	4354 (5)	37 (2)
C(14)	3759 (9)	6620 (8)	4238 (5)	42 (3)
C(15)	3475 (9)	5310 (8)	3727 (5)	41 (3)
C(16)	5189 (13)	3507 (9)	3008 (6)	66 (4)
C(17)	7802 (9)	5779 (11)	3884 (6)	62 (4)
C(18)	6216 (13)	8179 (10)	4889 (6)	68 (4)
C(19)	2586 (12)	7417 (11)	4689 (6)	64 (4)
C(20)	1957 (10)	4374 (10)	3610 (6)	62 (4)
C(21)	4214 (9)	7804 (8)	373 (5)	41 (3)
C(22)	4256 (9)	9030 (8)	945 (5)	37 (2)
C(23)	2708 (8)	9323 (8)	1083 (5)	36 (2)
C(24)	1689 (9)	8258 (9)	585 (5)	46 (3)
C(25)	2592 (9)	7310 (8)	153 (5)	40 (3)
C(26)	5600 (10)	7175 (10)	22 (6)	57 (3)
C(27)	5704 (10)	9949 (8)	1288 (6)	52 (3)
C(28)	2247 (11)	10579 (9)	1622 (6)	54 (3)
C(29)	−46 (10)	8197 (10)	512 (6)	60 (4)
C(30)	2026 (12)	6120 (10)	−500 (6)	61 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for 1•CH_2Cl_2[a]

	Bond Distances		
Ru(1)–Ru(2)	2.745 (2)	Ru(1)–C(1)	2.075 (7)
Ru(1)–C(4)	2.072 (7)	Ru(2)–C(1)	2.075 (7)
Ru(2)–C(2)	2.171 (8)	Ru(2)–C(3)	2.162 (8)
Ru(2)–C(4)	2.077 (7)	C(1)–C(2)	1.42 (1)
C(2)–C(3)	1.41 (1)	C(3)–C(4)	1.40 (1)
Ru(1)–Cl(1)	2.431 (3)	Ru(1)–Cl(2)	2.421 (3)
Ru(1)–CNT(1)	1.924	Ru(1)–C(11)	2.238 (8)
Ru(1)–C(12)	2.377 (8)	Ru(1)–C(13)	2.356 (7)
Ru(1)–C(14)	2.211 (8)	Ru(1)–C(15)	2.166 (8)
Ru(2)–CNT(2)	1.846		
	Bond Angles		
Ru(2)–Ru(1)–Cl(1)	86.5 (1)	Ru(2)–Ru(1)–Cl(2)	86.6 (1)
Cl(1)–Ru(1)–Cl(2)	87.0 (1)	Ru(2)–Ru(1)–C(1)	48.6 (2)
Cl(1)–Ru(1)–C(1)	81.6 (2)	Cl(2)–Ru(1)–C(1)	134.1 (2)
Ru(2)–Ru(1)–C(4)	48.6 (2)	Cl(1)–Ru(1)–C(4)	134.1 (2)
Cl(2)–Ru(1)–C(4)	81.8 (2)	C(1)–Ru(1)–C(4)	75.1 (3)
Ru(2)–Ru(1)–CNT(1)	154.6	Cl(1)–Ru(1)–CNT(1)	111.2
Cl(2)–Ru(1)–CNT(1)	111.5	C(1)–Ru(1)–CNT(1)	114.1
C(4)–Ru(1)–CNT(1)	114.3	Ru(1)–Ru(2)–C(1)	48.6 (2)
Ru(1)–Ru(2)–C(2)	73.6 (2)	C(1)–Ru(2)–C(2)	39.0 (3)
Ru(1)–Ru(2)–C(3)	73.6 (2)	C(1)–Ru(2)–C(3)	67.9 (3)
C(2)–Ru(2)–C(3)	38.1 (3)	Ru(1)–Ru(2)–C(4)	48.5 (2)
C(1)–Ru(2)–C(4)	75.0 (3)	C(2)–Ru(2)–C(4)	67.2 (3)
C(3)–Ru(2)–C(4)	38.5 (3)	Ru(1)–Ru(2)–CNT(2)	142.6
C(1)–Ru(2)–CNT(2)	143.0	C(2)–Ru(2)–CNT(2)	141.0
C(3)–Ru(2)–CNT(2)	140.1	C(4)–Ru(2)–CNT(2)	141.6
Ru(1)–C(1)–Ru(2)	82.8 (2)	Ru(1)–C(1)–C(2)	115.6 (5)
Ru(2)–C(1)–C(2)	74.1 (5)	Ru(2)–C(2)–C(1)	66.9 (4)
Ru(2)–C(2)–C(3)	70.6 (5)	C(1)–C(2)–C(3)	113.2 (7)
Ru(2)–C(3)–C(2)	71.3 (5)	Ru(2)–C(3)–C(4)	67.5 (4)
C(2)–C(3)–C(4)	113.4 (7)	Ru(1)–C(4)–Ru(2)	82.9 (3)
Ru(1)–C(4)–C(3)	116.7 (6)	Ru(2)–C(4)–C(3)	74.0 (5)

[a] CNT denotes the centroid of a η^5-C_5Me_5 ring.

An X-ray crystal structure determination proved instrumental in defining the coordination geometry for 1.

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(6) (a) Omori, H.; Suzuki, H.; Moro-oka, Y. *Organometallics* **1988**, *8*, 1576. (b) Bruce, M. I.; Matisons, J. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1983**, *251*, 249. (c) Noda, I.; Yasuda, H.; Nakamura, A. *Ibid.* **1983**, *250*, 447. (d) Noda, I.; Yasuda, H.; Nakamura, A. *Organometallics* **1983**, *2*, 1207.

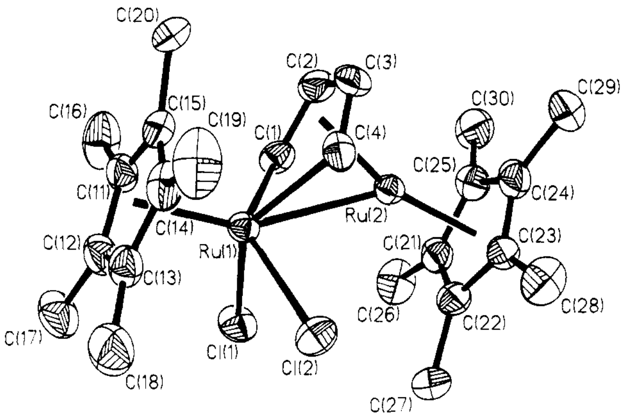
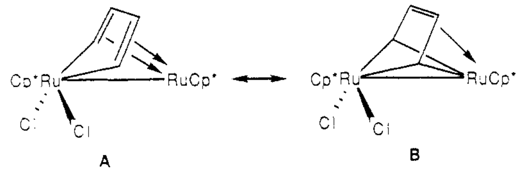


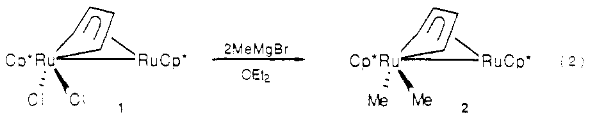
Figure 1. Molecular structure of 1, with atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

The molecular structure is shown in Figure 1, and relevant geometrical parameters are given in Tables II and III. The assymetric unit contains a dichloromethane molecule as solvent of crystallization. There is an approximate (noncrystallographic) mirror plane that bisects 1, containing Ru(1), Ru(2), and the centroids of the two Cp* rings. The intramolecular distance between ruthenium atoms is 2.745 (2) Å, corresponding to a single Ru-Ru bond. The two ruthenium atoms are bridged by a η^2:η^4-μ_2-C_4H_4 fragment, the ends of which are σ-bonded to Ru(1), forming a metallacyclopentadiene ring. The Ru(1)-C bond distances of 2.075 (7) and 2.072 (7) Å are consistent with Ru-C single bonds, as are the Ru(2)-C bond lengths of 2.075 (7) and 2.077 (7) Å. The Ru(1)-C(1)-C(2)-C(3)-C(4) ring may be viewed as being π-bound to Ru(2), but this bonding does not result in the geometry observed for many other related dinuclear complexes with planar metallacyclopentadiene rings.[6b,7,19] Instead, the Ru(1)-C(1)-C(2)-C(3)-C(4) ring is puckered, with Ru(1) lying 0.58 Å out of the least-squares plane defined by carbon atoms C(1)-C(4). For these carbon atoms the mean deviation from planarity is 0.004 Å. These structural features suggest that there are two important valence bond structures (A and B) that contribute to the observed geometry of 1.



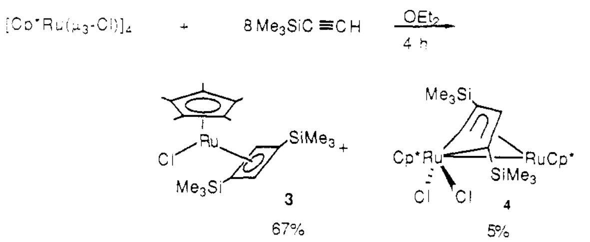
The mean plane of the C_4H_4 fragment is nearly parallel to the least-squares plane defined by the ring carbons of the Cp* group bound to Ru(2), giving Ru(2) a "sandwich" coordination environment. The coordination geometry about Ru(1) describes a distorted octahedron, considering the Cp* ring to occupy one coordination site. The Cp* ring of Ru(1) is bound assymetrically, probably due to steric requirements in the molecule. Carbon atoms C(12) and C(13) are 2.377 (8) and 2.356 (7) Å, respectively, from Ru(1), and the remaining Ru(1)-C(Cp*) distances are 2.238 (8), 2.211 (8), and 2.166 (8) Å. While some ring slippage has occurred, this is not reflected in variations in bond lengths within the Cp* ligand. Structural features for 1 are similar to those of other dinuclear ruthenacyclopentadiene complexes.[6] For $(CO)_3Ru[\eta^2$:η^4-μ_2-$C_4(CO_2Me)_4]Ru(CO)_3$, one ruthenium center is π-bonded to a $RuC_4(CO_2Me)_4$ ring system that is nearly planar.[6b] The metallacycle ring in $Cp^*(PMe_3)Ru(\eta^2$:η^4-μ_2-$C_4H_4)RuCp^*$ is bent with a fold angle of 18.3° (angle between RuC_2 and C_4 least-squares planes).[6a] The corresponding angle in 1 is 20.5°. In contrast to 1, $Cp^*(PMe_3)Ru(\eta^2$:η^4-μ_2-$C_4H_4)$-$RuCp^*$ exhibits two sets of inequivalent Ru-C(α) distances for the ruthenacyclopentadiene ring (av 2.05 Å for Ru in ring; av 2.15 Å for other Ru), and the Cp* ligands have a cis disposition with respect to the Ru-Ru bond.

Heating 1 to 90 °C with excess acetylene (sealed NMR tube) for several hours resulted in no decomposition or reaction to form new products. The $Cp^*Ru(\eta^2$:η^4-μ_2-$C_4H_4)RuCp^*$ dinuclear unit is also stable to alkylation at the ruthenium(V) center. Addition of 2 equiv of MeMgBr to a red diethyl ether slurry of 1 produced an orange solution from which $Cp^*Me_2Ru(\eta^2$:η^4-μ_2-$C_2H_4)RuCp^*$ (2) was isolated as a crystalline orange solid (eq 2). The equivalent methyl ligands for 2 appear as a singlet at δ 0.28 in the ^1H NMR spectrum, and remaining spectroscopic parameters for 2 closely resemble those of 1.



(2)

The process by which 1 is produced (eq 1) obviously involves a number of steps. To obtain more information on this reaction system and perhaps isolate species that correspond to intermediates in the reaction to give 1, the behavior of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ toward other alkynes was examined. Reaction of $Me_3SiC{\equiv}CH$ with a diethyl ether slurry of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ over 4 h results in the pentane-soluble complex 3 as the major product (eq 3). Assignment of the structure of 3 as the 18-electron cyclobutadiene complex $Cp^*Ru[\eta^4$-$C_4H_2(SiMe_3)_2]Cl$ is based on combustion analyses and on NMR and mass spectroscopy. The ^1H NMR spectrum consists of three singlets at δ 0.29, 1.48, and 3.60 in an 18:15:2 ratio. The gated ^{13}C NMR spectrum shows that there are two sets of equivalent cyclobutadienyl ring carbons with similar chemical shifts, at δ 77.59 (s) and 84.26 (dd, J_{CH} = 179 Hz, 4 Hz). These chemical shifts are consistent with values obtained for related $CpRu(\eta^4$-$C_4Ph_4)(X)$ complexes.[8] The similarity of ^{13}C chemical shifts for the cyclobutadiene ring carbons rules out an alternative (isomeric) metallacyclopentadiene structure. For comparison, the metallacycle ring carbons of $CpRu(\sigma,\sigma'$-$CPhCHCHCPh)Br$ give rise to ^{13}C NMR chemical shifts of δ 156.0 and 271.1.[9] The J_{CH} coupling constants for the $C_4H_2(SiMe_3)_2$ ring carbons suggest that head-to-tail coupling of the alkynes has occurred to produce a 1,3-disubstituted ring.[10]



(3)

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(7) See, for example: (a) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806. (b) Felhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4; p 548.

(8) (a) Crocker, M.; Green, M.; Orpen, A. G.; Thomas, D. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1141. (b) Crocker, M.; Froom, S. F. T.; Green, M.; Nagle, K. R.; Orpen, A. G.; Thomas, D. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2803.

(9) Albers, M. O.; de Wall, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680.

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 5

	x	y	z	U(eq)[a]
Ru(1)	1374 (1)	7178 (1)	9779 (1)	37 (1)
Ru(2)	2971 (1)	8343 (1)	10843 (1)	39 (1)
Ru(3)	476 (1)	7609 (1)	11678 (1)	43 (1)
Cl(1)	777 (2)	6505 (1)	10840 (1)	51 (1)
Cl(2)	2452 (2)	7757 (1)	11968 (1)	52 (1)
Cl(3)	930 (1)	8354 (1)	10543 (1)	45 (1)
Si(1)	3748 (2)	6277 (1)	10788 (1)	61 (1)
C(1)	2940 (5)	7646 (4)	9868 (4)	39 (2)
C(2)	2991 (5)	7136 (4)	10407 (4)	40 (2)
C(3)	3187 (14)	5358 (8)	10526 (11)	203 (10)
C(4)	5053 (17)	6266 (13)	10429 (18)	327 (22)
C(5)	4032 (26)	6271 (13)	11749 (9)	362 (22)
C(10)	148 (9)	7509 (6)	8853 (4)	69 (3)
C(11)	1192 (8)	7498 (6)	8617 (4)	62 (3)
C(12)	1578 (6)	6722 (6)	8716 (4)	59 (3)
C(13)	799 (7)	6278 (5)	9024 (4)	59 (3)
C(14)	−91 (7)	6768 (7)	9090 (5)	73 (4)
C(15)	−531 (11)	8192 (9)	8814 (7)	127 (6)
C(16)	1688 (12)	8157 (8)	8240 (6)	124 (6)
C(17)	2599 (8)	6433 (9)	8455 (6)	111 (6)
C(18)	786 (11)	5413 (7)	9138 (7)	115 (6)
C(19)	−1082 (9)	6467 (10)	9370 (7)	138 (7)
C(20)	4438 (6)	8832 (5)	10596 (5)	60 (3)
C(21)	3622 (7)	9295 (5)	10274 (4)	61 (3)
C(22)	3087 (7)	9630 (5)	10816 (6)	72 (4)
C(23)	3541 (9)	9371 (6)	11509 (5)	77 (4)
C(24)	4378 (8)	8872 (6)	11367 (5)	70 (3)
C(25)	5347 (8)	8452 (6)	10248 (8)	97 (5)
C(26)	3481 (13)	9514 (7)	9463 (6)	128 (6)
C(27)	2159 (9)	10194 (7)	10695 (10)	143 (8)
C(28)	3250 (11)	9587 (8)	12241 (7)	126 (6)
C(29)	5206 (10)	8525 (9)	11955 (8)	133 (6)
C(30)	−958 (9)	8166 (8)	11814 (6)	90 (5)
C(31)	−152 (10)	8337 (7)	12430 (8)	92 (5)
C(32)	98 (9)	7633 (11)	12761 (6)	100 (6)
C(33)	−449 (9)	7046 (6)	12398 (7)	77 (4)
C(34)	−1120 (7)	7361 (8)	11836 (5)	78 (4)
C(35)	−1474 (13)	8789 (11)	11334 (10)	189 (10)
C(36)	201 (18)	9133 (11)	12646 (14)	288 (17)
C(37)	976 (12)	7526 (17)	13438 (7)	253 (18)
C(38)	−419 (14)	6184 (8)	12584 (9)	171 (10)
C(39)	−1921 (13)	6932 (18)	11324 (11)	320 (19)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

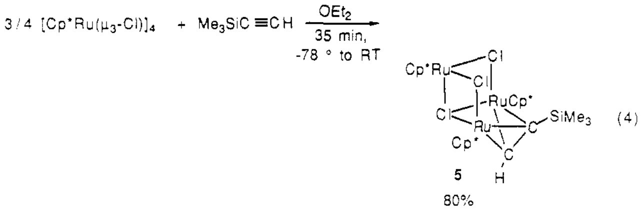
Table V. Selected Bond Distances (Å) and Angles (deg) for 5[a]

Bond Distances			
Ru(1)–C(1)	2.116 (7)	Ru(1)–C(2)	2.220 (6)
Ru(2)–C(1)	2.147 (7)	Ru(2)–C(2)	2.225 (7)
C(1)–C(2)	1.32 (1)	Si(1)–C(2)	1.850 (7)
Si(1)–C(3)	1.77 (2)	Si(1)–C(4)	1.84 (2)
Si(1)–C(5)	1.75 (2)	Ru(1)–Cl(1)	2.449 (2)
Ru(1)–Cl(3)	2.557 (2)	Ru(2)–Cl(2)	2.445 (2)
Ru(2)–Cl(3)	2.562 (2)	Ru(3)–Cl(1)	2.496 (2)
Ru(3)–Cl(2)	2.493 (2)	Ru(3)–Cl(3)	2.558 (2)
Ru(1)–CNT(1)	1.826	Ru(2)–CNT(2)	1.811
Ru(3)–CNT(3)	1.722		
Bond Angles			
Cl(1)–Ru(1)–Cl(3)	80.5 (1)	Cl(1)–Ru(1)–C(1)	118.9 (2)
Cl(3)–Ru(1)–C(1)	85.1 (2)	Cl(1)–Ru(1)–C(2)	85.3 (2)
Cl(3)–Ru(1)–C(2)	89.2 (2)	C(1)–Ru(1)–C(2)	35.2 (3)
Cl(1)–Ru(1)–CNT(1)	119.1	Cl(3)–Ru(1)–CNT(1)	124.6
C(1)–Ru(1)–CNT(1)	117.8	C(2)–Ru(1)–CNT(2)	139.3
Cl(2)–Ru(2)–Cl(3)	80.1 (1)	Cl(2)–Ru(2)–C(1)	119.2 (2)
Cl(3)–Ru(2)–C(1)	84.4 (2)	Cl(2)–Ru(2)–C(2)	86.2 (2)
Cl(3)–Ru(2)–C(2)	88.9 (2)	C(1)–Ru(2)–C(2)	35.0 (3)
Cl(2)–Ru(2)–CNT(2)	119.1	Cl(3)–Ru(2)–CNT(2)	124.9
C(1)–Ru(2)–CNT(2)	117.9	C(2)–Ru(2)–CNT(2)	138.9
Cl(1)–Ru(3)–Cl(2)	89.5 (1)	Cl(1)–Ru(3)–Cl(3)	79.6 (1)
Cl(2)–Ru(3)–Cl(3)	79.3 (1)	Cl(1)–Ru(3)–CNT(3)	89.5
Cl(2)–Ru(3)–CNT(3)	129.2	Cl(3)–Ru(3)–CNT(3)	79.3
Ru(1)–Cl(1)–Ru(3)	102.1 (1)	Ru(2)–Cl(2)–Ru(3)	102.5 (1)
Ru(1)–Cl(3)–Ru(2)	80.6 (1)	Ru(1)–Cl(3)–Ru(3)	97.5 (1)
Ru(2)–Cl(3)–Ru(3)	97.6 (1)	C(2)–Si(1)–C(3)	115.9 (6)
C(2)–Si(1)–C(4)	108.4 (8)	C(3)–Si(1)–C(4)	104 (1)
C(2)–Si(1)–C(5)	114.9 (8)	C(3)–Si(1)–C(5)	107 (1)
C(4)–Si(1)–C(5)	106 (1)	Ru(1)–C(1)–Ru(2)	101.9 (3)
Ru(1)–C(1)–C(2)	76.7 (4)	Ru(2)–C(1)–C(2)	75.7 (4)
Ru(1)–C(2)–Ru(2)	96.3 (3)	Ru(1)–C(2)–Si(1)	128.5 (4)
Ru(2)–C(2)–Si(1)	129.4 (3)	Ru(1)–C(2)–C(1)	68.0 (4)
Ru(2)–C(2)–C(1)	69.3 (4)	Si(1)–C(2)–C(1)	142.6 (6)

[a] CNT denotes the centroid of a η^5-C_5Me_5 ring.

The reaction in eq 3 produces a second complex (**4**) in yields of about 5%. This species could not be isolated in pure form, but its structure was assigned on the basis of ^{1}H and ^{13}C NMR spectra. Complex **4**, Cp*Cl$_2$Ru[η^2:η^4-μ_2-$C_4H_2(SiMe_3)_2$]RuCp*, exhibits spectra similar to those of **1**, but with important differences resulting from the presence of two trimethylsilyl groups. Two sets of doublets at δ 5.77 ($^4J_{HH}$ = 1.5 Hz, β-H) and 8.82 ($^4J_{HH}$ = 1.5 Hz, α-H) in the ^{1}H NMR spectrum are assigned to ruthenacyclopentadiene protons. The small J_{HH} coupling constant of 1.5 Hz and the presence of inequivalent SiMe$_3$ groups are consistent with a 1,3-substitution pattern for the SiMe$_3$ groups. The ^{13}C NMR spectrum revealed four resonances for the metallacycle ring carbons, at δ 101.31, 105.88, 174.52, and 179.18. Although reductive elimination of similar metallacyclopentadiene ligands to give a cyclobutadiene complex has precedence,[1,10b,11,19] such a reaction has not been observed for **4**. Upon heating **4** to 90 °C for 12 h (in benzene-d_6), no decomposition or conversion to **3** was observed. Additionally, compound **4** does not appear to react with Me$_3$SiC≡CH to produce **3** (over 7 h at 90 °C).

If [Cp*Ru(μ_3-Cl)]$_4$ is allowed to react with less Me$_3$SiC≡CH (ca. 1 equiv) at low temperature over only 35 min, a new product is observed (eq 4). Triruthenium cluster Cp*$_3$Ru$_3$(μ_2-Cl)$_2$(μ_3-Cl)(η^2-μ_2-HC≡CSiMe$_3$) (**5**) is stable in the solid state under an inert atmosphere but decomposes in benzene-d_6 to rapidly deposit a brown solid from solution. Among the decomposition products observed by ^{1}H NMR spectroscopy were **3** and **4**. Compound **5** appears to be somewhat more stable in dichloromethane-d_2 and gives a solution in this solvent that persists at −20 °C for several hours. The ^{1}H NMR spectrum of this solution (−20 °C) shows the presence of one alkyne unit per three Cp* ligands. However, the Cp* ligands are represented by two singlets of equal area at δ 1.60 and 1.67, and cooling of the sample to −90 °C results in no broadening or splitting of these peaks. This solution behavior for **5** is therefore not consistent with the observed solid-state structure (vide infra), and we conclude that the compound does not maintain its integrity in solution. We are not yet able to assign a structure to the compound(s) in solution. Addition of excess (6 equiv) Me$_3$SiC≡CH in benzene-d_6 to **5** resulted in immediate conversion to **3** (>95% yield by ^{1}H NMR spectroscopy) and a trace amount of **4**.



A crystal structure determination for **5** (Figure 2) revealed a trinuclear cluster containing a perpendicularly

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(10) (a) Ville, G.; Vollhardt, K. P. C. *J. Magn. Reson.* **1981**, *45*, 525. (b) Ville, G.; Vollhardt, K. P. C.; Winter, M. *Organometallics* **1984**, *3*, 1177.

(11) (a) Gardner, S. A.; Rausch, M. D. *J. Organomet. Chem.* **1974**, *78*, 415. (b) Lee, W.-S.; Brintzinger, H. H. *Ibid.* **1977**, *127*, 93.

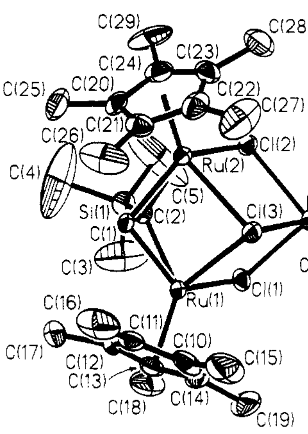


Figure 2. Molecular structure of **5**, with atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

oriented bridging alkyne. Important bond distances and angles are given in Table V. This structure is related to that of the tetramer from which it is derived, $[Cp^*Ru(\mu_3\text{-}Cl)]_4$, in that a Cp*RuCl unit, which donates four electrons to the cluster, has been replaced by a four-electron alkyne ligand. The structure of **5** may be described as a distorted cube with a missing vertex. The seven remaining vertices consist of the three ruthenium atoms, the three bridging chlorides, and the center of the C≡C triple bond of the coordinated alkyne. The three faces of this incomplete cube are very nearly planar (deviations from the least-squares planes are ≤0.06 Å) and form angles of 90 ± 10° with each other. Angles at each vertex are 90 ± 16°. The alkyne ligand is nearly parallel to the Ru(3)–Cl(3) bond and forms an angle of 89.3° with the Ru(1)–Ru(2) vector.

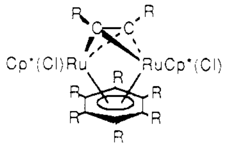
The coordination environment about each Ru center can be described as a three-legged piano stool, if the alkyne ligand is viewed as occupying a single coordination site for Ru(1) and Ru(2). The C(1)–C(2) bond distance of 1.32 (1) Å is close to that of a typical C=C double bond. The Ru–C(alkyne) distances of 2.116 (7), 2.220 (6), 2.225 (7), and 2.147 (7) Å in **5** are slightly shorter than related distances in $Ru_4(CO)_{12}(\mu_4\text{-}PhC{\equiv}CPh)$,[12] for which the average Ru–C(alkyne) bond length is 2.25 (1) Å. The alkyne unit is bound rather asymmetrically to the triruthenium cluster, probably due to steric interactions between the trimethylsilyl and Cp* groups. The C(1) carbon atom is 0.09 Å closer to the Ru atoms than is C(2), the carbon to which the trimethylsilyl group is attached. There are three different Ru–Cl bond distances in **5**, indicating three types of Ru–Cl interactions. The Ru(1)–Cl(1) and Ru(2)–Cl(2) bond distances of 2.449 (2) and 2.445 (2) Å, respectively, represent normal single-bond distances in complexes of this type (cf. the Ru–Cl distance of 2.453 (2) Å in $Cp(PPh_3)_2RuCl$[13]). The longer Ru(3)–Cl(1) and Ru(3)–Cl(2) bond lengths of 2.496 (2) and 2.493 (2) Å represent the Cl-to-Ru dative bond interactions. Finally, the longest Ru–Cl distances, averaging 2.559 (2) Å, are those to triply bridging Cl(3).

The interaction of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with the more electron-poor alkyne dimethyl acetylenedicarboxylate ($MeO_2CC{\equiv}CCO_2Me$ = DMAD) was also investigated. Reaction of an excess (ca. 10 equiv per tetramer) of the alkyne with the ruthenium tetramer gave a single product (67% yield) as red-brown microcrystals from ether (eq 5).

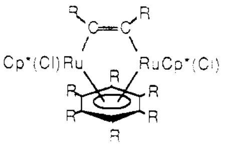
$$[Cp^*Ru(\mu_3\text{-}Cl)]_4 + 8DMAD \xrightarrow{OEt_2} \underset{\mathbf{6}}{2Cp^*_2Ru_2(DMAD)_4Cl_2} \quad (5)$$

An elemental analysis for this product provided the empirical formula $Cp^*Ru(DMAD)_2Cl$, and a molecular weight determination showed that **6** is dimeric in solution. The ^1H NMR spectrum in benzene-d_6 contained a single resonance for the Cp* ligands and two –OMe peaks (at δ 3.42 and 3.52) in a 3:1 ratio. Variable-temperature NMR studies revealed no exchange processes down to −90 °C (dichloromethane-d_2). The presence of 3 equivalent DMAD units in a dimeric structure can be explained by a bridging arene ring that results from cyclotrimerization of DMAD. This proposal is supported by the mass spectrum, which exhibits peaks at m/e 650 $[Cp^*_2Ru_2Cl_2(MeO_2CC{\equiv}CCO)]^+$, 426 $[C_6(CO_2Me)_6]^+$, 395 $[C_6(CO_2Me)_5(CO)]^+$, and 366 $[C_6(CO_2Me)_5]^+$. Loss of methoxy and $-CO_2Me$ groups are expected fragmentation patterns for aromatic esters of this type.[14] A related cyclotrimerization of DMAD at ruthenium occurs when $(\eta^6\text{-}C_6H_6)Ru(1,3\text{-cyclohexadiene})$ is irradiated in the presence of DMAD to produce the bis(arene) complex $Ru(C_6H_6)[C_6(CO_2Me)_6]$.[15] A few other dinuclear complexes with bridging arene ligands have been reported,[16] and in $(CpFe)_2(\eta^6\text{-}\mu_2\text{-}C_6R_6)$ (R = Me, Et) the bridging arene ligand arises from alkyne cyclotrimerization.[16a] Of most relevance is the recently reported dinuclear complex $Cp^*Ru(\mu\text{-}PPh_2)(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)RuCp^*$, which contains a bridging benzene ligand.[16c] In contrast to $(\eta^5\text{-}C_5R_5)Rh$ complexes (R = H, Me), $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ does not catalytically cyclotrimerize DMAD.[17]

Possible structures for the dinuclear complex **6** are shown in C and D, R = CO_2Me. The bridging alkyne



C



D

group could be oriented in either a perpendicular or parallel fashion. Unfortunately, the available data do not distinguish between these two possibilities. In structure C the arene group donates four electrons to the two ruthenium centers, and in D the arene acts as a four- or six-electron donor depending on whether or not a Ru–Ru bond exists. Several attempts were made to grow crystals of **6** suitable for X-ray diffraction, but none proved successful.

Discussion

This preliminary investigation of reactions of coordinatively unsaturated Cp*Ru species with alkynes has revealed the formation of alkyne cluster complex **5** and coupled alkyne complexes **1**, **3**, **4**, and **6**. Reaction of excess acetylene with $Cp^*Ru(P^iPr_3)Cl$ or $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ produces high yields of the dinuclear ruthenacyclopentadiene complex **1**. Compound **1** is analogous to many other di-

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(12) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1977**, 1417.

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

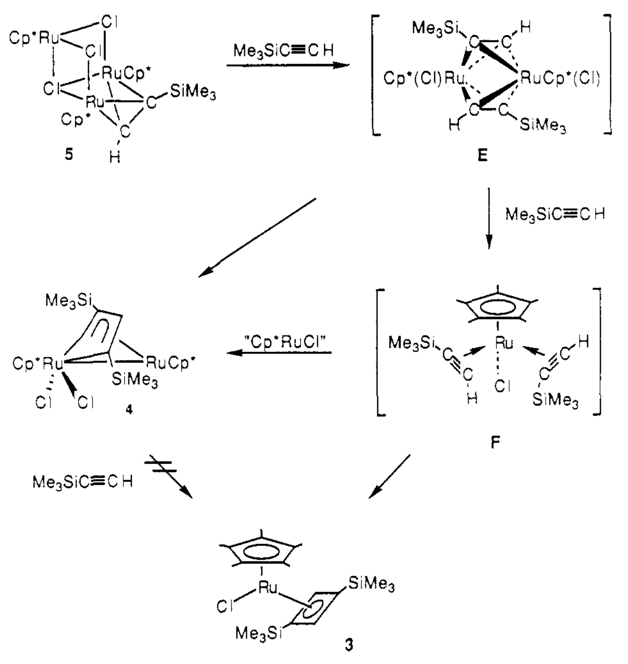
(14) McLafferty, M. F. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980; pp 201–206.

(15) Lucherini, A.; Porri, L. *J. Organomet. Chem.* **1978**, *155*, C45.

(16) (a) Jonas, K.; Koepe, G.; Schieferstein, L.; Mynott, R.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 620. (b) Jonas, K.; Wiskamp, V.; Tsay, Y.-H.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5480. (c) Omori, H.; Suzuki, H.; Take, Y.; Moro-oka, Y. *Organometallics* **1989**, *8*, 2270.

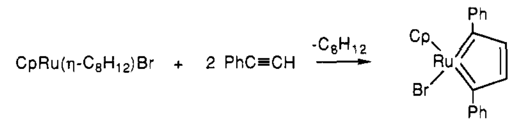
(17) Abdulla, K.; Booth, B. L.; Stacey, C. *J. Organomet. Chem.* **1985**, *293*, 103.

Scheme I



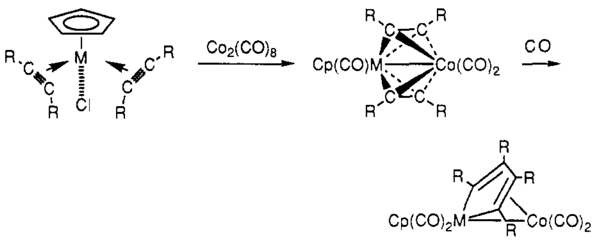
nuclear metallacyclopentadiene complexes but is somewhat unusual in possessing two directly bonded ruthenium centers that are formally in quite different oxidation states, Ru(V) and Ru(I). The crystal structure of **1** suggests, however, that it is also valid to describe the complex in a more oxidized Ru(V)/Ru(III) form.

Much precedent exists for alkyne-coupling reactions of the types reported here.[1] A reaction related to those in eq 1, in which the mononuclear metallacyclopentatriene complex CpRu(σ,σ'-CPhCHCHCPh)Br is formed, was reported by Singleton and co-workers (eq 6, C$_8$H$_{12}$ = cycloocta-1,5-diene).[9] It is interesting to note the difference between substitution patterns in this product and those observed for **3** and **4**. Presumably the greater steric demands of the Cp* ligand prohibit alkyne couplings that would lead to 2,4-substituted ruthenacyclopentadiene rings or 1,2-substituted cyclobutadiene products. It is also interesting that no mononuclear products analogous to CpRu(σ,σ'-CPhCHCHCPh)Br have been observed in the pentamethylcyclopentadienyl ruthenium systems. This suggests that species such as Cp*Ru(σ,σ'-CHCHCHCH)Cl and Cp*Ru[σ,σ'-C(SiMe$_3$)CHC(SiMe$_3$)CH]Cl might be quite reactive under the conditions that we have examined. Note that complex **1** is formally derived from oxidative addition of a Cp*RuCl unit to Cp*Ru(σ,σ'-CHCHCHCH)Cl.



(6)

Possible reaction sequences for the formation of complexes **3** and **4** are shown in Scheme I. Initial displacement of a "Cp*RuCl" fragment from [Cp*Ru(μ_3-Cl)]$_4$ by the alkyne HC≡CSiMe$_3$ is relatively clean and allows isolation of triruthenium cluster **5**. This labile cluster species is a precursor to **3** and **4**, since **5** was observed to thermally decompose to a mixture of **3** and **4**, and reaction of **5** with an excess of HC≡CSiMe$_3$ gives a high yield of cyclobutadiene complex **3**. Note also that the mass spectrum of **5** contains peaks due to the ions [**3**]$^+$, [**4** − Cl]$^+$, and [**4** − 2Cl]$^+$. Displacement of another "Cp*RuCl" unit from **5** could form an intermediate dimeric alkyne complex such as E. A related iron complex, [(Me$_3$SiC≡CSiMe$_3$)Fe]$_2$(η^2-μ_2-Me$_3$SiC≡CSiMe$_3$)$_2$, has recently been reported.[18] Small quantities of **4** that are observed in the reactions of [Cp*Ru(μ_3-Cl)]$_4$ and **5** could arise from rearrangement of E via alkyne coupling and chloride migration. A related cyclization process for a heterobimetallic system has been reported (eq 7, M = Mo, W; R = CF$_3$).[19] Alternatively, reaction of E with alkyne could proceed to a mononuclear species F, which then takes up an equivalent of "Cp*RuCl" to give **4**. It is also concievable that intermediate F rearranges directly to **3**, and this process could possibly proceed via the metallacyclopentatriene complex Cp*Ru[σ,σ'-C(SiMe$_3$)CHC(SiMe$_3$)CH]Cl.[8b] Apparently **4** is not a precursor to **3**, since heating **4** with trimethylsilylacetylene (90 °C for 7 h) results in no reaction.



(7)

Experimental Section

Manipulations were performed under an inert atmosphere of nitrogen or argon by using standard Schlenk techniques and/or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Mikroanalytisches Labor Pascher. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. ^{1}H NMR were recorded at 300 MHz with a GE QE-300 spectrometer or at 90 MHz with a Varian EM-390 instrument. ^{13}C NMR spectra were recorded at 75.5 MHz on the GE QE-300. Acetylene (Liquid Carbonics), trimethylsilylacetylene (Aldrich), and dimethyl acetylenedicarboxylate (Lancaster Synthesis) were used as received.

Cp*Cl$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)RuCp* (1). (a) Benzene (25 mL) was added to [Cp*Ru(μ_3-Cl)]$_4$ (0.275 g, 0.25 mmol) in a pressure bottle. Acetylene (15 psi) was admitted to immediately give a green solution that soon turned red. After this stirred for 2 h, the volatiles were removed, and dichloromethane (20 mL) was added. Concentration and cooling (−40 °C) gave the product as red crystalline rectangles (mp 309–310 °C) in 79% yield (0.237 g); IR (Nujol, CsI, cm^{-1}) 1221 s, 1168 m, 1070 w, 1030 m, 1013 m, 1000 m, 839 m, 489 s, 430 w; ^{1}H NMR (300 MHz, benzene-d_6, 23 °C) δ 1.00 (s, 15 H, Cp*), 1.91 (s, 15 H, Cp*), 4.97 (m, 2 H, CH*H*=CHCH), 8.33 (m, 2 H, *C*HCH=CHC*H*); ^{13}C{^{1}H} NMR (75.5 MHz, dichloromethane-d_2, 23 °C) δ 9.77 (C$_5$*Me*$_5$), 10.86 (C$_5$*Me*$_5$), 94.26 (C$_5$Me$_5$), 94.66 (RuCHCH), 104.81 (C$_5$Me$_5$), 164.20 (RuCHCH). Anal. Calcd for C$_{24}$H$_{34}$Cl$_2$Ru$_2$: C, 48.4; H, 5.75; Cl, 11.9. Found: C, 48.6; H, 6.15; Cl, 11.5.

(b) Cp*Ru(P^{i}Pr$_3$)Cl (0.20 g, 0.46 mmol) was dissolved in toluene (20 mL), and the resulting solution pressurized with acetylene (15 psi). After stirring for 30 min, the solution was degassed, concentrated, and cooled (−40 °C) to give **1** in 55% yield (0.075 g). Crystallization of this material from dichloromethane (in the presence of P^{i}Pr$_3$, from starting material) results in isolation of a dichloromethane solvate, **1**·CH$_2$Cl$_2$.

Cp*Me$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)RuCp* (2). To a red slurry of **1** (0.17 g, 0.28 mmol) in diethyl ether (25 mL) was added MeMgBr (0.25 mL of a 2.8 M diethyl ether solution, 0.70 mmol) via syringe at room temperature. The resulting orange solution was stirred for 1 h. Volatiles were evacuated, and the crude orange residue was extracted with diethyl ether (20 mL). Concentration and cooling of the diethyl ether extract gave orange crystals (mp 230–231 °C) in 58% yield (0.090 g). The product may be recrystallized with

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(18) Schäufele, H.; Pritzkow, H.; Zenneck, U. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 1519.

(19) Davidson, J. L.; Manojilovic-Muir, L.; Muir, K. W.; Keith, A. N. *J. Chem. Soc., Chem. Commun.* **1980**, 749.

pentane; IR (Nujol, CsI, cm^{-1}) 1260 m, 1229 m, 1185 w, 1070 w, 1022 s, 1008 m sh, 895 m, 826 m, 798 m br, 490 s, 425 w; ^1H NMR (300 MHz, benzene-d_6, 23 °C) δ 0.28 (s, 6 H, RuMe), 1.19 (s, 15 H, Cp*), 1.74 (s, 15 H, Cp*), 4.88 (m, 2 H, $CHCH{=}CHCH$), 7.37 (m, 2 H, $CHCH{=}CHCH$); $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 23 °C) δ 3.39 ($RuCH_3$), 8.55 (C_5Me_5), 10.81 (C_5Me_5), 89.47 (C_5Me_5), 94.26 (RuCHCH), 95.91 (C_5Me_5), 163.19 (RuCHCH). Anal. Calcd for $C_{26}H_{40}Ru_2$: C, 56.3; H, 7.27. Found: C, 56.2; H, 7.25.

Cp*Ru[η^4-$C_4H_2(SiMe_3)_2$]Cl (3). A cold (−78 °C) solution of $Me_3SiC{\equiv}CH$ (0.153 g, 1.56 mmol) in diethyl ether (40 mL) was added to a flask containing $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (0.20 g, 0.18 mmol), immediately producing a maroon solution. The resulting reaction mixture was allowed to stir for 4 h at room temperature, and then all volatile material was removed in vacuo. The red solid was extracted with pentane (40 mL), and the pentane extract was concentrated and cooled (−30 °C) to give two crops of product as red crystals (mp 285–287 °C) in a combined yield of 67% (0.23 g). The first crop also contained compound **4** (5%, 0.020 g, by ^1H NMR spectroscopy). IR (Nujol, CsI, cm^{-1}) 1327 w, 1272 m, 1243 s, 1087 m, 1023 w, 986 m, 968 w, 862 sh s, 852 sh s, 839 s, 760 m, 690 w, 634 w, 417 vw, 387 vw, 356 vw; ^1H NMR (300 MHz, benzene-d_6, 23 °C) δ 0.29 (s, 18 H, $SiMe_3$), 1.48 (s, 15 H, Cp*), 3.60 (s, 2 H, $C_2H_2(SiMe_3)_2$); ^{13}C NMR (75.5 MHz, benzene-d_6, 23 °C) δ 1.14 (q, $^1J_{CH}$ = 119 Hz, $SiCH_3$), 10.75 (q, $^1J_{CH}$ = 127, C_5Me_5), 77.59 (s, η^4-$CH_2(CSiMe_3)_2$), 84.26 (dd, $^1J_{CH}$ = 179 Hz, $^3J_{CH}$ = 4 Hz, η^4-$CH_2(CSiMe_3)_2$), 98.60 (s, C_5Me_5); MS, exact mass calcd for $C_{20}H_{35}ClSi_2Ru$ 468.1009, found 468.1035, *m/e* 468 $[M]^+$, 432 $[M - Cl]^+$, 345 $[Cp^*RuCl(SiMe_3)]^+$, 272 $[Cp^*RuCl]^+$, 73 $[SiMe_3]^+$. Anal. Calcd for $C_{20}H_{35}ClSi_2Ru$: C, 51.3; H, 7.54. Found: C, 51.5; H, 7.59.

$Cp^*Cl_2Ru[\eta^2{:}\eta^4\text{-}\mu_2\text{-}C_4H_2(SiMe_3)_2]RuCp^*$ (4). Because of difficulty in separating small amounts (≤5% total yield, by ^1H NMR spectroscopy with crude reaction mixtures) of **4** formed during the synthesis of **3**, no attempts were made to isolate it in pure form. However, its structure was deduced from spectroscopic properties, which are similar to those for **1**; ^1H NMR (300 MHz, benzene-d_6, 23 °C) δ 0.23 (s, 9 H, $SiMe_3$), 0.68 (s, 9 H, $SiMe_3$), 1.09 (s, 15 H, Cp*), 1.87 (s, 15 H, Cp*), 5.77 (d, $^4J_{CH}$ = 1.5 Hz, 1 H, $CHCSiMe_3CHCSiMe_3$), 8.82 (d, $^4J_{CH}$ = 1.2 Hz, 1 H, $CHCSiMe_3CHCSiMe_3$); $^{13}C\{^1H\}$ NMR (75.5 Hz, benzene-d_6, 23 °C) δ 0.52 ($SiMe_3$), 1.15 ($SiMe_3$), 10.32 (C_5Me_5), 12.21 (C_5Me_5), 95.34 (C_5Me_5), 101.31 ($RuCHCSiMe_3$), 104.52 (C_5Me_5), 105.91 ($RuCSiMe_3CH$), 174.42 ($RuCSiMe_3CH$), 179.18 ($RuCHCSiMe_3$).

Reaction of 4 with $HC{\equiv}CSiMe_3$. Since **4** is somewhat less soluble in pentane than **3**, it is possible to obtain small samples that are enriched in **4** by careful crystallization from solutions containing both **3** and **4**. In this way a 30-mg mixture of **4** and **3** (molar ratio 4:1, by ^1H NMR integration) was obtained and dissolved in 0.4 mL of benzene-d_6 in an NMR tube. Trimethylsilylacetylene (ca. 2 equiv based on **4**) was added by syringe, and the tube was flame-sealed. Heating this mixture to 90 °C for 7 h produced no evidence for reaction (by ^1H NMR spectroscopy).

$Cp^*_3Ru_3(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)(\eta^2\text{-}\mu_2\text{-}HC{\equiv}CSiMe_3)$ (5). At −78 °C, $Me_3SiC{\equiv}CH$ (52 μL, 0.37 mmol) in diethyl ether (15 mL) was added to a cooled (−78 °C) suspension of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (0.30 g, 0.27 mmol) in diethyl ether (30 mL). This mixture was allowed to stir at −78 °C for 5 min, and then the −78 °C bath was replaced with an ice bath (0 °C) for 15 min. The ice bath was then removed and the solution was stirred for an additional 15 min. The resulting dark maroon solution was then filtered, concentrated, and cooled (−30 °C) to give the product as dark red crystals (mp > 300 °C) in 80% yield (0.20 g); IR (Nujol, CsI, cm^{-1}) 3055 m, 1251 w, 1238 m, 1074 w, 1021 s, 852 s, 840 s, 760 w, 750 w, 635 w, 622 w; ^1H NMR (300 MHz, dichloromethane-d_2, 23 °C) δ 0.24 (s, 9 H), 1.63 and 1.70 (both s, total 45 H, Cp^*_3), 8.07 (s, 1 H, $HC{\equiv}CSiMe_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, dichloromethane-d_2, −20 °C) δ 4.01 ($SiMe_3$), 10.60 (C_5Me_5), 11.46 (C_5Me_5), 88.07 (C_5Me_5), 88.95 (C_5Me_5), 115.99 ($HC{\equiv}CSiMe_3$), 138.98 ($HC{\equiv}CSiMe_3$); MS, *m/e* 708 $[\mathbf{4} - Cl]^+$, 607 $[Cp^*_2Ru_2(HC{\equiv}CSiMe_3)_2]^+$, 544 $[Cp^*_2Ru_2Cl_2]^+$, 468 $[\mathbf{3}]^+$, 372 $[Cp^*RuCl(HC{\equiv}CSiMe_3)]^+$, 272 $[Cp^*RuCl]^+$, 236 $[Cp^*Ru]^+$. Anal. Calcd for $C_{35}H_{55}Cl_3Ru_3Si$: C, 46.0; H, 6.07; Cl, 11.6. Found: C, 46.5; H, 6.21; Cl, 11.9.

Reaction of 5 with $HC{\equiv}CSiMe_3$. Trimethylsilylacetylene ($HC{\equiv}CSiMe_3$, 0.020 g, 0.20 mmol) in benzene-d_6 (0.4 mL) was added to solid **5** (0.037 g, 0.034 mmol) in an NMR tube. The reaction mixture immediately turned purple and then red as the solution was shaken. ^1H NMR spectroscopy revealed the presence of **3** (>95%) and a trace amount of **4**.

$Cp^*_2Ru_2Cl_2(MeO_2CC{\equiv}CCO_2Me)[C_6(CO_2Me)_6]$ (6). A solution of dimethyl acetylenedicarboxylate (0.35 g, 2.45 mmol) in diethyl ether (40 mL) was added to $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (0.27 g, 0.25 mmol) at room temperature. This led to rapid formation of a clear, dark orange–brown solution. After this stirred for 25 min, the volatiles were removed in vacuo, and the resulting crude solid extracted with diethyl ether (1 × 25 mL, 2 × 40 mL). Cooling the combined extracts to −40 °C resulted in formation of dark red–brown crystals (mp 147–148 °C) in 67% yield (0.37 g); IR (Nujol, CsI, cm^{-1}) 1742 s, 1700 m, 1684 m, 1578 w, 1329 w, 1250 m sh, 1230 s, 1183 m sh, 1165 m sh, 1115 w, 1050 w, 1030 w, 989 m, 968 w, 870 w, 853 m, 621 w; ^1H NMR (300 MHz, benzene-d_6, 23 °C) δ 1.46 (s, 30 H, Cp*), 3.42 (s, 18 H, $C_6(CO_2Me)_6$), 3.52 (s, 6 H, $MeO_2CC{\equiv}CCO_2Me$); $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 23 °C) δ 9.16 (q, $^1J_{CH}$ = 127 Hz, C_5Me_5), 51.03 (q, $^1J_{CH}$ = 145 Hz, OMe), 52.93 (q, $^1J_{CH}$ = 147 Hz, OMe), 96.49 (s, C_5Me_5), 129.34 (MeO_2CCCCO_2Me), 134.46 ($(MeO_2C)_6C_6$), 165.38 (q, $^3J_{CH}$ = 4.7 Hz, MeO_2CC), 168.67 (q, $^3J_{CH}$ = 4 Hz (poorly resolved coupling), MeO_2CC); MS, *m/e* 650 $[Cp^*_2Ru_2Cl_2(MeO_2CC{\equiv}CCO)]^+$, 543 $[Cp^*_2Ru_2Cl_2]^+$, 426 $[C_6(CO_2Me)_6]^+$, 395 $[C_6(CO_2Me)_5C{\equiv}O]^+$, 366 $[C_6(CO_2Me)_5]^+$, 236 $[Cp^*Ru]^+$, 59 $[MeOC{\equiv}O]^+$. Anal. Calcd for $C_{22}H_{27}ClO_8Ru$: C, 47.5; H, 4.89; Cl, 6.29. Found: C, 47.6; H, 5.00; Cl, 6.31. Molecular weight (isothermal distillation in methylene chloride): 990; calcd 1112 (11% error).

Collection and Solution of Diffraction Data. Parameters summarizing the collection and solution of diffraction data for $\mathbf{1}\cdot CH_2Cl_2$ and **5** are given in Table I. Crystals were mounted in glass capillary tubes in an inert-atmosphere glovebox and flame-sealed. Data were collected at 296 K on a Nicolet R3m/V automated diffractometer equipped with a highly ordered graphite monochrometer, using Mo Kα radiation (λ = 0.71073 Å). Both data sets were corrected for Lorentz and polarization effects and slight crystal decay (≈2%). Each structure was solved by direct methods and refined by full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI).

For $\mathbf{1}\cdot CH_2Cl_2$, satisfactory refinement was obtained for $P\bar{1}$. One reflection had $\delta/\sigma > 10$ and was omitted from the final refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the metallocyclopentadiene fragment, H(1), H(2), H(3), and H(4), were located from Fourier difference maps and then fixed (d(C–H) = 0.96 Å) with independent isotropic thermal parameters. The remaining hydrogen atoms (including those of the solvent of crystallization) were refined in fixed, idealized positions with fixed isotropic thermal parameters.

The space group for **5** was uniquely determined from systematic absences. One reflection had $\delta/\sigma > 10$ and was removed prior to the final refinement. All non-hydrogen atoms were refined anisotropically. The acetylenic hydrogen, H(1), was located via Fourier difference maps and given a fixed, isotropic thermal parameter. The remaining hydrogen atoms were fixed in idealized positions (d(C–H) = 0.96 Å, fixed isotropic thermal parameters approximately 1.2 times the isotropic thermal parameter of the attached carbon atom). Unusually short SiC bonds probably result from the large thermal parameters for C(3), C(4), and C(5).

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Registry No. 1, 125518-35-6; $\mathbf{1}\cdot CH_2Cl_2$, 125518-40-3; **2**, 125518-36-7; **3**, 125518-37-8; **4**, 125518-38-9; **5**, 125518-39-0; DMAD, 762-42-5; $[Cp^*Ru(\mu_3\text{-}Cl)]_4$, 113860-07-4; $Cp^*Ru(P^iPr_3)Cl$, 117340-72-4; $HC{\equiv}CH$, 74-86-2; $MeSiC{\equiv}CH$, 1066-54-2.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1** and **5** (9 pages); a listing of observed and calculated structure factors for **1** and **5** (38 pages). Ordering information is given on any current masthead page.