Synthesis and Molecular Structure of Two Six-Membered Ru_3C_3 Rings Existing in Boat- and Chairlike Configurations Formed by Insertion of C_9H_6 Units into Metal−Metal Bonds of $[Ru_3(CO)_{12}]$

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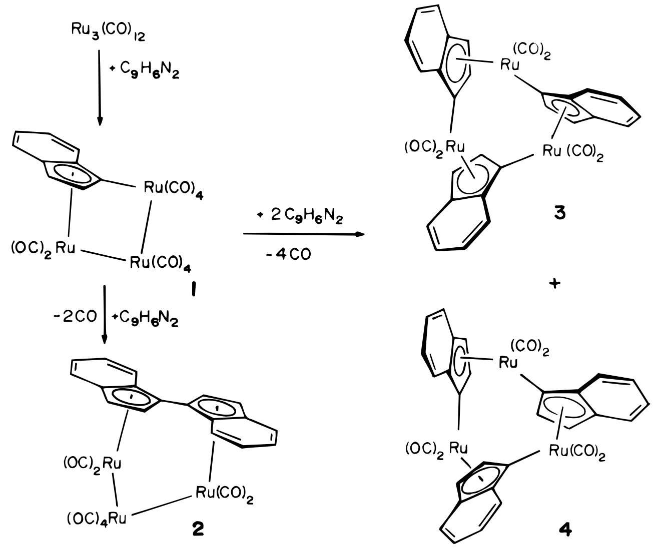
The reaction of diazoindene ($C_9H_6N_2$) with $[Ru_3(CO)_{12}]$ in THF leads to the formation of the clusters $[Ru_3(CO)_{10}(\eta^5{:}\eta^1\text{-}C_9H_6)]$ (**1**), by the insertion of a C_9H_6 moiety into a Ru−Ru bond, $[Ru_3(CO)_8(\eta^5\text{-}C_9H_6)_2]$ (**2**), a trinuclear complex with an open Ru_3 unit containing the 1,1′-bis(indenylidene) ligand, and two metallacyclic ruthenium trimers of formula $[Ru_3(CO)_6(\eta^5{:}\eta^1\text{-}C_9H_6)_3]$ (**3** and **4**). The cyclic trimers have stable chair- and twist-boat-like configurations similar to the boat−chair isomerism of cyclohexane. Both complexes are configurational rather than conformational isomers, because the boat-to-chair ring flip is hampered by the rigid nature of the Ru_3C_3 metallacycle. The structures of **2**−**4** have been established by X-ray crystallography.

Introduction

More than 40 years have elapsed since the discovery of bis(η^5-cyclopentadienyl)iron or ferrocene.[1] Since then the cyclopentadienyl (C_5H_5) ligand has been used extensively throughout organometallic chemistry. The introduction of the cyclopentadienyl ligand as a novel type of ancillary ligand in coordination chemistry[2] ushered in a period of explosive growth of organotransition-metal chemistry, and this development does not yet appear to have come to a halt. On the contrary, cyclopentadienyl transition-metal complexes are increasingly finding applications in catalysis and organic synthesis.[3]

We recently reported a convenient stepwise synthetic route to a cyclic ruthenium trimer without metal−metal bonding.[4] This route involves the use of diazocyclopentadiene as the precursor of cyclopentadienyl units to be inserted in metal−metal bonds of clusters. Increasing attention has recently been given to the indenyl ligand, as for example ansa-bridge metallocene compounds of some reactive transition-metal centers, which are an important class of compounds for stoichiometric and catalytic asymmetric induction.[5] Mono- and binuclear indenyl derivatives have been developed, which may exhibit new types of reactivity in the search for new Ziegler−Natta and Fischer−Tropsch catalysts. Indenyl (C_9H_7) and indenylidene (C_9H_6) bridges in polynuclear compounds are rare and have attracted little attention so far.

Scheme 1



The direct reaction of indene with $[Ru_3(CO)_{12}]$ was reported to give the (η^5-indenyl)ruthenium carbonyl dimers $[Ru(CO)_2(\eta^5\text{-}C_9H_7)]_2$ as well as the tetranuclear cluster $[Ru_4(CO)_7(\mu\text{-}CO)_2(\eta^2{:}\eta^5{:}\eta^2\text{-}C_9H_7)(\eta^5\text{-}C_9H_9)]$.[6] Here we report the reaction of diazoindene ($C_9H_6N_2$) with $[Ru_3(CO)_{12}]$, which affords new compounds derived from the cleavage of metal−metal bonds.

Results and Discussion

The reaction detailed in Scheme 1 was carried out in THF under reflux and gave the new complexes **1**−**4**. All

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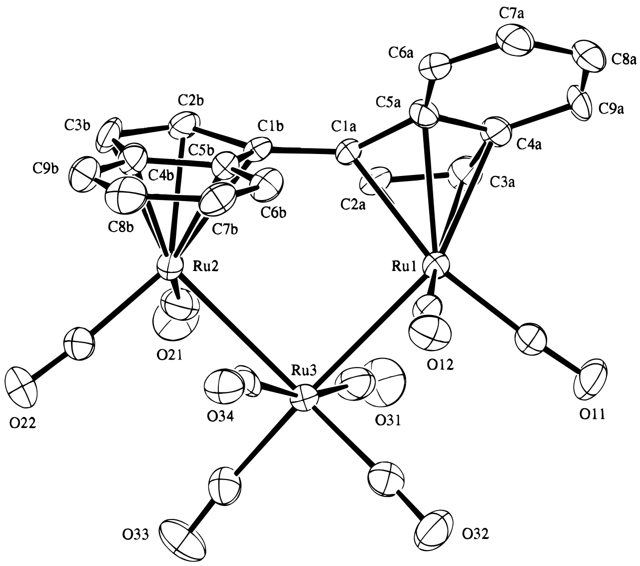

Figure 1. Molecular structure of **2** (ORTEP plot with displacement ellipsoids drawn at 30% probability). In each CO group both atoms are identically numbered; only O atoms are labeled.

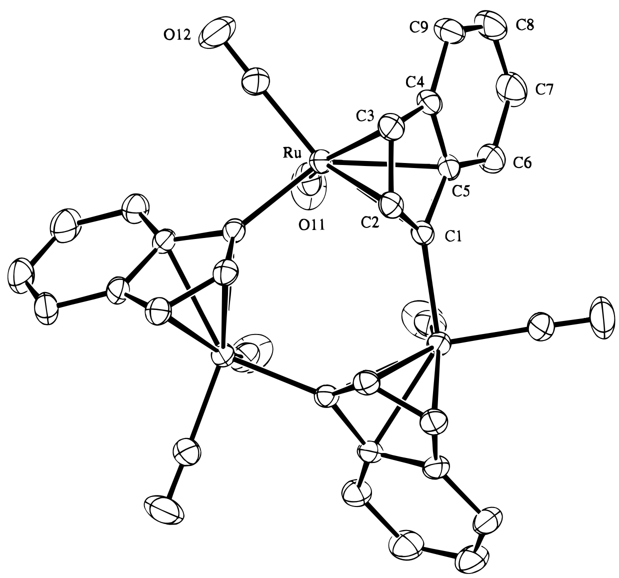

Figure 2. Molecular structure of **3** (ORTEP plot with displacement ellipsoids drawn at 30% probability). In each CO group both atoms are identically numbered; only O atoms are labeled.

compounds are formed with concomitant elimination of N_2 and CO and are thermally stable. All the products were characterized by ^{1}H NMR and IR spectroscopy (see Experimental Section), and for **2**−**4** their X-ray structures (Figures 1−3 and Table 1) were determined. The organic compound 1,1′-bis(indenylidene) ($(C_9H_6)_2$) is also formed during the reaction, whose structure will be reported separately.[7] To account for the formation of **2**, we tried the direct reaction of 1,1′-bis(indenylidene) with $[Ru_3(CO)_{12}]$ in refluxing THF but no products were obtained after 24 h of reaction; also, thermal treatment of compound **2** in the presence of diazoindene did not give **3** or **4**.

Compound **1** was obtained in very low yield and was characterized only by its IR spectrum, being identical

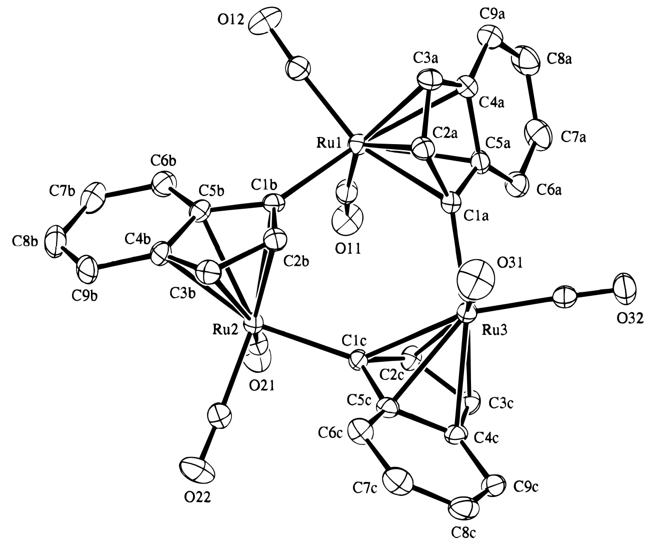

Figure 3. Molecular structure of **4** (ORTEP plot with displacement ellipsoids drawn at 30% probability). In each CO group both atoms are identically numbered; only O atoms are labeled.

with that of the Cp analogue $[Ru_3(CO)_{10}(C_5H_4)]$, obtained from the reaction between $[Ru_3(CO)_{12}]$ and diazocyclopentadiene, whose X-ray structure was determined.[4] We postulate that, in the presence of diazoindene **1** readily converts into **2** and into the cyclotrimers **3** and **4**.

The structural analyses revealed that **2** is a trinuclear complex with an open Ru_3 unit, while isomers **3** and **4** are cyclotrimers with no metal−metal bonds. In the crystal structure of **3** the molecules lay on 3-fold axes (Wyckoff sites *d*) and, therefore, they display C_3 point symmetry and the asymmetric unit consists of only one-third of a molecule.

Compound **2** is the first metal complex containing the 1,1′-bis(indenylidene) ligand to be described. It contains an open $Ru_3(CO)_8$ unit, with both ends of the metal cluster η^5-bonded to the five-membered rings of the $(C_9H_6)_2$ ligand. The resulting Ru_3C_2 metallacycle has an envelope configuration, with C(1a) 0.37 Å out of the mean plane of the other four atoms. Both halves of the organic ligand are planar (maximum deviations from the mean planes 0.077(8) Å for **a** and 0.049(8) Å for **b**), but they are twisted with respect to each other (dihedral angle between mean planes 43.2°). This twist allows for the η^5 interactions, since the Ru(1)···Ru(2) distance, 4.115(6) Å, is longer than the distance between the centroids of the five-membered rings, 3.926(5) Å.[8] In contrast, the organic derivative $(C_9H_6)_2$ is quite planar.[7] The twist is not symmetrical with respect to the plane of the metal atoms (dihedral angles between the Ru_3 plane and the C_9 planes 58.6° for **a** and 99.4° for **b**); *i.e.*, the molecule departs from an ideal propeller-like shape with C_2 point symmetry. However, the ^{1}H NMR spectrum of **2** shows a single set of signals for both

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(8) The relationship between the twist angle and the interatomic distances is: $\cos\tau = 1 - 0.5(d_3^2 - d_2^2)/d_1^2$, where τ = dihedral angle between C_5 planes, d_1 = Ru···centroid distance (or d_1' = Ru···C_5 plane distance), d_2 = centroid···centroid distance, and d_3 = Ru(1)···R(2) distance. This gives $\tau = 37.2°$, which is reasonably close to the observed value of 41.8°. (In **2** $d_1 \neq d_1'$, since the Ru···centroid vector is not exactly perpendicular to the C_5 plane. The observed distances are d_1 = 1.929 and 1.944 Å and d_1' = 1.926 and 1.937 Å; the mean value 1.934 Å was used in the calculation.)

Table 1. Crystal Data, Intensity Data Collection Parameters, and Final Refinement Results for Compounds 2−4

	2	3	4
		Crystal Data	
formula	$C_{26}H_{12}O_8Ru_3$	$C_{33}H_{18}O_6Ru_3$	$C_{33}H_{18}O_6Ru_3$
MW	755.59	813.71	813.71
color	orange	yellow	yellow
morphology	prism	prism	prism
specimen size, mm	0.22 × 0.14 × 0.12	0.42 × 0.25 × 0.24	0.34 × 0.26 × 0.12
T, K	295(1)	295(1)	295(1)
a, Å	7.95(2)	12.973(2)	8.518(5)
b, Å	16.01(2)		18.832(5)
c, Å	19.18(4)	11.554(5)	17.913(5)
β, deg	93.4(3)		103.12(3)
V, Å^3	2437(7)	1683.9(5)	2798(1)
cryst syst	monoclinic	trigonal	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{3}$ (No. 147)	$P2_1/n$ (No. 14)
Z	4	2	4
D_c, g cm^{-3}	2.058	1.605	1.931
F(000)	1456	792	1584
μ(Mo Kα), cm^{-1}	18.85	13.67	16.45
2θ range for cell, deg	20.7−29.6	30.9−38.2	33.2−41.0
		Data Collection	
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	1.10 + 0.35 tan θ	1.26 + 0.35 tan θ	1.40 + 0.35 tan θ
ω-scan speed, deg min^{-1}	2.0	2.0	4.0
2θ range, deg	4.0−55.0	4.0−55.0	4.0−55.0
$h/k/l$ range	0−10/0−20/−24 to +24	−14 to +14/0−16/0−15	0−11/0−24/−23 to +22
check rflns	−2,0,6; −2,−3,−3; −1,−5,4	−4,4,−2; −4,3,−2; −3,2,−3	−3,2,0; 2,0,4; 3,1,−3
mean ΔI for checks, %	−0.7	−11.4	−1.1
no. of reflns, measd	6220	2883	7060
no. reflns, unique	5808	2587	6627
R_{int}	0.0537	0.0134	0.0292
		Refinement (Last Cycle)	
weighting scheme	$\omega = \sigma^{-2}$	$\omega = \sigma^{-2}$	$\omega = \sigma^{-2}$
abs cor		ψ-scan	ψ-scan
transmissn coeff		0.956−1.000	0.840−1.000
no. of reflns obsd, ($I > 2\sigma(I)$)	2409	2127	4856
no. of params refined	334	133	451
R	0.0373	0.0267	0.0241
R_{WGO}	0.0363	0.0342	0.0284
S (GOF)	1.265	3.057	1.383
Δ/σ(max)	0.0004	0.0003	0.0007
Δρ_r (min/max), eÅ^{-3}	−0.52/+0.52	−0.39/+0.44	−0.63/+0.59

halves, even at low temperature, indicating their equivalence in solution.

Isomers **3** and **4** have quite similar IR spectra but completely different ^{1}H NMR spectra (Figure 4). Both are remarkably thermally stable, surviving prolonged heating at 120 °C (d_8-toluene) and no interconversion was observed in their NMR spectra. The novelty of the Ru_3C_3 framework for **3** and **4** prompted the determination of their X-ray structures.

Isomers **3** and **4** are structurally analogous to the cyclopentadienyl cyclotrimer recently reported by us.[4] The bond length patterns for both compounds are quite similar (Tables 3 and 4), including a significant shortening of the C(6)−C(7) and C(8)−C(9) distances. This shortening, which reveals a loss of aromaticity in the six-membered ring, is produced by the coordination of the metal atom and is also observed in **2** but not in the 1,1′-bis(indenylidene) compound.[7] In both isomers the indenyl ligands are quite planar (maximum deviations from the mean planes 0.065(4) Å in **3**, 0.042(4) Å in **4a**, 0.028(3) Å in **4b**, and 0.046(4) Å in **4c**).

Not all of the five Ru−C(n) (n = 1−5) π-bonds are equivalent: in **2** Ru−C(4) and Ru−C(5) are longer (*ca.* 0.12 Å) than Ru−C(1), Ru−C(2), and Ru−C(3); in **3** and **4** Ru−C(1), Ru−C(4), and Ru−C(5) are longer (*ca.* 0.07 Å in both compounds) than Ru−C(2) and Ru−C(3); in the Cp analogue[4] only Ru−C(1) is longer (*ca.* 0.06 Å)

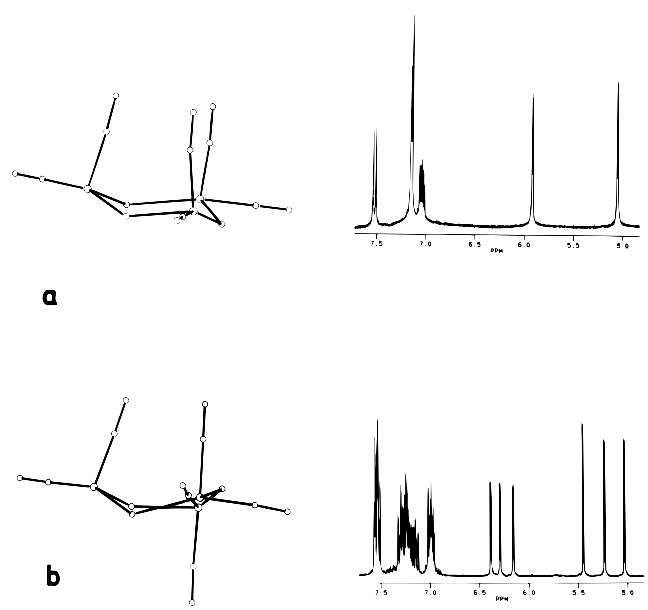

Figure 4. Geometric and spectral differences between (a) compound **3** and (b) compound **4**. Only C(1) atoms of the indenyl rings are shown, for clarity.

than the other four Ru−C π-bonds. These differences are significant and may reflect the presence of electron-withdrawing substituents at given atoms of the five-

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 2

Bond Distances			
Ru(1)−Ru(3)	2.889(4)	Ru(2)−Ru(3)	2.910(2)
Ru(1)−C(1a)	2.231(8)	Ru(2)−C(1b)	2.261(9)
Ru(1)−C(2a)	2.238(9)	Ru(2)−C(2b)	2.224(9)
Ru(1)−C(3a)	2.24(1)	Ru(2)−C(3b)	2.232(9)
Ru(1)−C(4a)	2.312(9)	Ru(2)−C(4b)	2.355(9)
Ru(1)−C(5a)	2.370(9)	Ru(2)−C(5b)	2.388(9)
C(1a)−C(1b)	1.48(1)	Ru(1)···Ru(2)	4.115(6)
Mean Values			
Ru(1)−C(*n*a)	2.236(5) ($n = 1-3$)	Ru(2)−C(*n*b)	2.234(5) ($n = 1-3$)
	2.341(6) ($n = 4, 5$)		2.372(6) ($n = 4, 5$)
Bond Angles			
Ru(1)−Ru(3)−Ru(2)	90.42(7)	Ru(3)−Ru(1)−C(1a)	96.6(2)
Ru(3)−Ru(2)−C(1b)	97.5(2)	Ru(1)−C(1a)−C(1b)	124.0(6)
Ru(2)−C(1b)−C(1a)	120.6(6)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 3[a]

Bond Distances			
Ru−C(1)	2.305(4)	Ru−C(2)	2.257(4)
Ru−C(3)	2.230(4)	Ru−C(4)	2.304(4)
Ru−C(5)	2.332(4)	Ru−C(1)^{i}	2.087(4)
Mean Values			
Ru−C(*n*)		2.244(3) ($n = 2, 3$)	
		2.314(2) ($n = 1, 4, 5$)	
Bond Angles			
C(1)−Ru−C(1)^{ii}	102.8(2)	Ru−C(1)−Ru^{iii}	127.4(2)

[a] Symmetry codes: (i) $1 - y, 1 + x - y, z$; (ii) $y - x, 1 - x, z$; (iii) $1 - y, 1 + x - y, z$.

membered rings, which weaken the corresponding Ru−C π-bonds.

The main difference between the molecular geometries of **3** and **4** lies in the puckering of the Ru_3C_3 metallacycles. In **3** the ring has a chair conformation (Ru and C atoms are at 0.75 and 0.65 Å from the plane of the chair), dictated by the C_3 molecular point symmetry. In **4** it has a boat conformation (Ru(1) and C(1c) are 0.87 and 0.34 Å from the mean plane through Ru(2), Ru(3), C(1a), and C(1b)) and, therefore, is similar to (but more asymmetrical than) that found in the Cp analogue.[4] The calculation of the puckering coordinates (q_2, q_3, ϕ_2;[9] Table 5) provides a more quantitative description of the Ru_3C_3 rings. The values in Table 5 indicate that the metallacycle of **3** has an undistorted chair conformation, while that of **4** has a conformation between twist-boat and screw-boat but is closer to the latter.[10]

The isomerism between **3** and **4** is formally similar to the boat−chair isomerism of cyclohexane. However, in this case both complexes are configurational rather than conformational isomers, because the boat-to-chair ring flip is hampered by the rigid nature of the corners of the Ru_3C_3 metallacycle.[13] To the best of our knowledge this is the first structural characterization of isolated metallacyclic trimers having stable chair- and boatlike configurations.

Experimental Section

A solution of $[Ru_3(CO)_{12}]$ (0.2 g, 0.32 mmol) and 1-diazoindene[14] (0.1 mL, 0.9 mmol) in dried THF (50 mL) was refluxed under nitrogen for 1 h. TLC (SiO_2) of the dark red residue (hexane/methylene chloride 8/1, v/v) gave five bands: $[Ru_3(CO)_{10}(C_9H_6)]$ (**1**), as a yellow solid (6 mg, 11%); $[Ru_3(CO)_8(C_9H_6)_2]$ (**2**), as orange crystals (hexane; 12 mg, 20%); $[Ru_3(CO)_6(C_9H_6)_3]$ (**3**), as yellow crystals (cyclohexane; 20 mg, 30%); $[Ru_3(CO)_6(C_9H_6)_3]$ (**4**), as yellow crystals (hexane; 18 mg, 28%); 1,1′-bis(indenylidene) derivative $(C_9H_6)_2$, as orange crystals (cyclohexane; 38 mg, 38%). IR spectra were recorded in C_6H_{12} and ^1H NMR spectra in $CDCl_3$ (300 MHz, 296 K, J given in Hz). **1**: ν(CO) (cm^{-1}) 2114 w, 2070 s, 2048 w, 2032 vs, 2002 s, 1990 sh, 1947 w. **2**: ν(CO) (cm^{-1}) 2120 s, 2063 vs, 2039 m, 2029 m, 1990 w; ^1H NMR δ 7.77 (m, br, 2H), 7.45 (m, 4H), 7.25 (m, 2H), 6.15 (d, 2H, $J = 3.0$), 5.84 (dd, 2H, $J = 3.0, 0.7$). **3**: ν(CO) (cm^{-1}) 2034 m, 2018 vs, 2011 vs, 1978 m, 1967 vs, 1960 s, 1955 sh; ^1H NMR δ 7.52 (d, br, 3H), 7.14 (d, br, 6H), 7.03 (m, 3H), 5.92 (d, 3H, $J = 2.6$), 5.04 (d, 3H, $J = 2.6$). **4**: ν(CO) (cm^{-1}) 2028 w, 2015 vs, 1971 s, 1961 m, 1957 m; ^1H NMR δ 7.53 (m, 4H), 7.22 (m, 4H), 6.98 (m, 4H), 6.37 (dd, 1H, $J = 2.6, 0.8$), 6.29 (dd, 1H, $J = 2.8, 0.9$), 6.15 (dd, 1H, $J = 2.7, 0.7$), 5.44 (d, 1H, $J = 2.6$), 5.22 (d, 1H, $J = 2.8$), 5.02 (d, 1H, $J = 2.7$).

X-ray Data Collection. Unit cell and intensity measurements were carried out on a Rigaku AFC7S diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 69 Å). Crystal data, intensity data collection parameters, and final refinement results are summarized in Table 1.

The unit-cell parameters were obtained from the least-squares fit of the setting angles of 25 automatically centered reflections. The intensities were recorded using a fixed ω-scan speed. Weak reflections ($I < 15\sigma(I)$) were rescanned up to four times, with accumulated counts. Three standard reflections were monitored every 150 measurements. The data were scaled using the check reflections and corrected by Lorentz and polarization effects. In the latter stages of refinement empirical absorption corrections were applied. These corrections were based on 36 ψ-scan[15] measurements for each of five representative strong reflections.

The space groups of **2** and **4** were uniquely determined by the systematic absences, while for **3** it was chosen on the basis of the Laue symmetry and intensity statistics and confirmed by refinement.

All three structures were solved by direct methods: for **2** the program SAPI-91[16] was used, for **3** SIR-92,[17] and for **4** SHELXS-86.[18] The structures were refined on F by full-matrix least squares with weights $\omega = \sigma(F)^{-2}$. The non-hydrogen atoms were refined anisotropically. The H atoms were treated differently in each structure: in **2** they were placed at calculated positions (C−H = 0.96 Å) with fixed coordinates and fixed displacement parameters ($B_{iso} = 1.2B_{eq}$(C)), in **3** they were placed at calculated positions (C−H = 0.96 Å) with fixed

(9) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.
(10) The set of spherical coordinates Q, Θ, and ϕ ($Q^2 = q_2^2 + q_3^2$, $\Theta = \sin^{-1}(q_2/Q) = \cos^{-1}(q_3/Q)$, $\phi = \phi_2$) defines a sphere of conformations in which the polar points (Θ = 0 or 180°) correspond to chair (C) conformations, while the positions on the equator (Θ = 90°) correspond to boat conformations. For phase angles $\phi = n30°$ (n = integer), the latter have either "pure" boat (B; n = even) or twist-boat (T; n = odd) conformations. Screw-boat (S) conformations are located at $\Theta = 90 \pm 22.5°$, $\phi = n30°$ (n = odd). Therefore, for **3** the closest ideal T and S conformations are located at $\Theta = 90.0°$, $\phi = 150.0°$ and $\Theta = 112.5°$, $\phi = 150.0°$, respectively. For more details see refs 9 and 11.
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(13) To convert **4** into **3**, it would be necessary (a) to break the Ru(2)−C(1c) bond, (b) to rotate about the Ru(3)−C(1a) bond the fragment bonded to Ru(3) (so that C(31) changes from axial to equatorial and C(32) from equatorial to axial), and (c) to make a Ru(2)−C(3c) bond.
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Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 4

Bond Distances					
Ru(1)−C(1a)	2.285(3)	Ru(2)−C(1b)	2.292(3)	Ru(3)−C(1a)	2.106(3)
Ru(1)−C(1b)	2.094(3)	Ru(2)−C(1c)	2.085(3)	Ru(3)−C(1c)	2.343(3)
Ru(1)−C(2a)	2.253(4)	Ru(2)−C(2b)	2.231(3)	Ru(3)−C(2c)	2.256(4)
Ru(1)−C(3a)	2.253(4)	Ru(2)−C(3b)	2.226(4)	Ru(3)−C(3c)	2.234(3)
Ru(1)−C(4a)	2.302(3)	Ru(2)−C(4b)	2.302(3)	Ru(3)−C(4c)	2.290(3)
Ru(1)−C(5a)	2.308(3)	Ru(2)−C(5b)	2.327(3)	Ru(3)−C(5c)	2.324(3)
Mean Values					
Ru(1)−C(*n*a)	2.229(2) ($n = 2, 3$)	Ru(2)−C(*n*b)	2.253(3) ($n = 2, 3$)	Ru(3)−C(*n*c)	2.245(2) ($n = 2, 3$)
	2.307(2) ($n = 1, 4, 5$)		2.298(2) ($n = 1, 4, 5$)		2.319(2) ($n = 1, 4, 5$)
Bond Angles					
C(1a)−Ru(1)−C(1b)	98.8(1)	Ru(1)−C(1a)−Ru(3)	130.3(1)		
C(1b)−Ru(2)−C(1c)	99.2(1)	Ru(1)−C(1b)−Ru(2)	125.8(1)		
C(1a)−Ru(3)−C(1c)	100.7(1)	Ru(2)−C(1c)−Ru(3)	135.2(1)		

Table 5. Puckering Parameters[a] for the Ru_3C_3 Rings of 3 and 4

	3	**4**
q_2 (Å)	0.000(4)	0.744(2)
q_3 (Å)	−0.589(3)	0.227(2)
ϕ_2 (deg)	270.0(2)	157.5(2)
Q (Å)	0.589(3)	0.778(2)
Θ (deg)	180.0(4)	106.9(2)

[a] Calculated with the program PARST-91.[12]

coordinates and refined isotropic displacement parameters, and in **4** their positional and isotropic displacement parameters were refined. The final difference Fourier syntheses were featureless.

The MSC/AFC Diffractometer Control Software[19] was used for data collection and cell refinement. All other calculations and drawings were made using the teXsan software package.[20] Neutral-atom scattering factors were taken from ref 21, anomalous scattering corrections from ref 22, and mass absorption coefficients from ref 23.

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Supporting Information Available: Text giving experimental details for the X-ray structure determinations and tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, and anisotropic displacement parameters for compounds **2**−**4** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(19) *MSC/AFC Diffractometer Control Software*; Molecular Structure Corp., The Woodlands, TX, 1993.

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