Steric Congestion in a Cyclopentadienyl Ligand Bearing *tert*-Butyl Groups on Three Contiguous Carbon Atoms: Crystal and Molecular Structure of (η^5-1,2,3-Tri-*tert*-butylcyclopentadienyl)(η^5-indenyl)rhodium(III) Hexafluorophosphate

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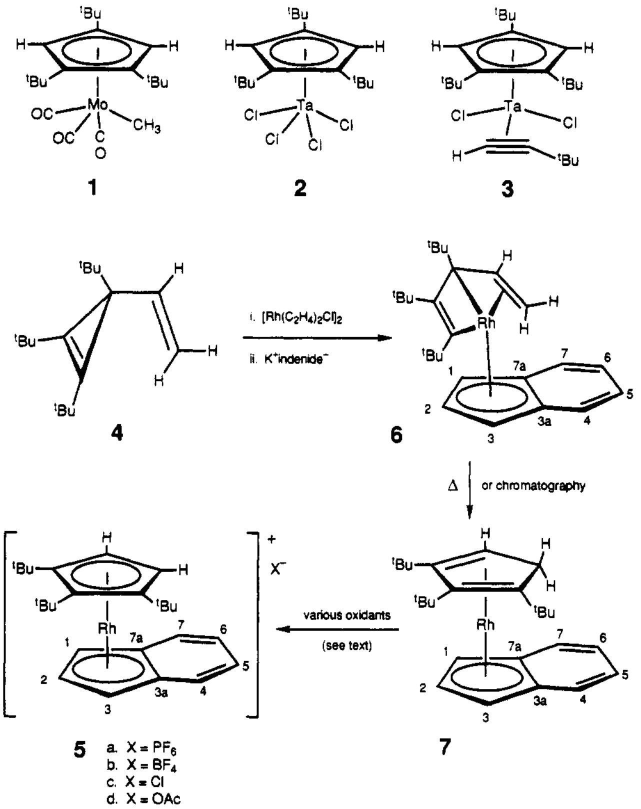
Received June 7, 1991

The (η^5-1,2,3-tri-*tert*-butylcyclopentadienyl)(η^5-indenyl)rhodium(III) cation is produced from (η^5-indenyl)(η^4-1,2,3-tri-*tert*-butylcyclopentadiene)rhodium(I) by formal hydride removal using trityl fluoroborate, oxidation using either *N*-bromosuccinimide or deuteriochloroform, or reaction with acetic acid. This cation contains the first example of a cyclopentadienyl ligand bearing three *tert*-butyl groups on contiguous carbon atoms. The structure of the hexafluorophosphate salt has been determined by a single-crystal X-ray diffraction study; this salt crystallizes in the monoclinic $P2_1/c$ space group, with a = 16.363 (3) Å, b = 9.965 (2) Å, c = 17.710 (2) Å, and β = 117.404 (16)°. The structure shows the expected sandwich arrangement, with almost parallel and eclipsed rings. Steric congestion between adjacent *tert*-butyl groups causes some in-plane deformations of the cyclopentadienyl ligand and its substituents but does not cause significant puckering or ring slippage of either the cyclopentadienyl or indenyl rings from η^5-coordination. The solution structure is shown to be unslipped using NMR spectroscopy, and counterion effects on proton and carbon chemical shifts are discussed.

Introduction

Scheme I



5 a. $X = PF_6$
b. $X = BF_4$
c. $X = Cl$
d. $X = OAc$

The cyclopentadienyl ligand is perhaps the most ubiquitous in organometallic chemistry, and thousands of compounds containing the parent ligand and its substituted analogues grace the pages of the chemical literature. There has been considerable recent interest in compounds containing sterically bulky cyclopentadienyl ligands as a means of imparting kinetic stability to otherwise reactive complexes of main-group elements, transition metals, lanthanoids, and actinoids. To this end, numerous examples of cyclopentadienyl ligands containing 1,3-bis(trimethylsilyl),[2] 1,2,4-tris(trimethylsilyl),[3] or 1,3-di-*tert*-butyl[4] groups have been reported. Neither the 1,2-di-*tert*-butyl- nor 1,2,3-tri-*tert*-butylcyclopentadienyl anions nor their parent dienes appear to have been reported, and while tetra-*tert*-butylcyclopentadiene has been synthesized,[5] its

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[2] For examples, see: (a) Jutzi, P.; Leffers, W.; Pohl, S.; Saak, W. *Chem. Ber.* **1989**, *122*, 1449–1456. (b) Jutzi, P.; Leffers, W.; Müller, G.; Huber, B. *Ibid.* **1989**, *122*, 879–884. (c) Okuda, J. *J. Organomet. Chem.* **1989**, *369*, C1–C4. (d) Okuda, J.; Herdtweck, E. *Ibid.* **1989**, *373*, 99–105. (e) Engelhardt, L. M.; Junk, P. C.; Raston, C. L.; White, A. W. *J. Chem. Soc., Chem. Commun.* **1988**, 1500–1501.

[3] For examples, see: (a) Jutzi, P.; Schlüter, E.; Pohl, S.; Saak, W. *Chem. Ber.* **1985**, *118*, 1959–1967. (b) Okuda, J. *J. Organomet. Chem.* **1989**, *375*, C13–C16. (c) Okuda, J. *Ibid.* **1988**, *353*, C1–C4. (d) Okuda, J. *Chem. Ber.* **1989**, *122*, 1259–1260. (e) Okuda, J. *Ibid.* **1988**, *121*, 1899–1905. (f) Okuda, J. *Ibid.* **1990**, *123*, 87–88.

[4] For examples, see: (a) Jutzi, P.; Dickbreder, R. *J. Organomet. Chem.* **1989**, *373*, 301–306. (b) Jutzi, P.; Schnittinger, J. *Chem. Ber.* **1989**, *122*, 629–632. (c) Okuda, J. *J. Organomet. Chem.* **1990**, *385*, C39–C42. (d) El-Hinnawi, M. A.; El-Khateeb, M. Y.; Jibril, I.; Abu-Orabi, S. T. *Synth. React. Inorg. Met-Org. Chem.* **1989**, *19*, 809–826; *Chem. Abstr.* **1990**, *112*, 198716k. (e) Bel'skii, V. K.; Knyazhanskii, S. Ya.; Bulychev, B. M.; Soloveichik, G. L. *Metalloorg. Khim.* **1989**, *2*, 567–569; *Chem. Abstr.* **1990**, *112*, 139272q. (f) Knyazhanskii, S. Ya.; Bel'skii, V. K.; Bulychev, B. M.; Soloveichik, G. L. *Ibid.* **1989**, *2*, 569–574; *Chem. Abstr.* **1990**, *112*, 139273r. (g) Bel'skii, V. K.; Knyazhanskii, S. Ya.; Bulychev, B. M.; Soloveichik, G. L. *Ibid.* **1989**, *2*, 1125–1128; *Chem. Abstr.* **1990**, *112*, 217134n. (h) Bel'skii, V. K.; Knyazhanskii, S. Ya.; Bulychev, B. M.; Soloveichik, G. L. *Ibid.* **1989**, *2*, 754–756; *Chem. Abstr.* **1990**, *112*, 198633f. (i) Kaluski, Z. I.; Gusey, A. I.; Kalinin, A. E.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1972**, *13*, 950–953; *Chem. Abstr.* **1973**, *78*, 34920a. (j) Hofmann, W.; Buchner, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 795–797. (k) Werner, H.; Hofmann, W. *Chem. Ber.* **1981**, *114*, 2681–2699. (l) Krimmer, H. P.; Stowasser, B.; Hafner, K. *Tetrahedron Lett.* **1982**, *23*, 5135–5138.

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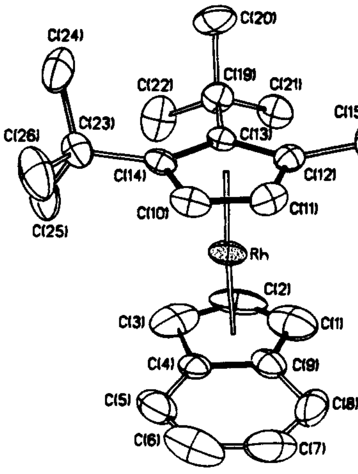

Figure 1. ORTEP plot of the cationic portion of complex **5a**.

preparation may be daunting enough to make it an unlikely ligand precursor for organometallic chemistry. Some compounds containing the mixed 1,2-bis(trimethylsilyl)-4-*tert*-butylcyclopentadienyl ligand have been prepared,[6] and the recently reported syntheses of 1,3,5-tri-*tert*-butylcyclopentadiene[7] have spawned some complexes (e.g. **1**), of the corresponding 1,2,4-tri-*tert*-butylcyclopentadienyl anion.[8,9] In addition, complexes **2** and **3** each contain a 1,2,4-tri-*tert*-butylcyclopentadienyl ligand assembled from smaller carbon subunits within the coordination sphere of tantalum.[10]

Complexes containing *tert*-butyl groups on adjacent carbon atoms might be expected to show severe steric repulsion between these substituents, considerably more so than for analogous trimethylsilyl compounds which have a significantly longer C–Si bond. However, no X-ray structural information is available on any cyclopentadienyl complexes containing adjacent *tert*-butyl groups, which might allow evaluation of such repulsion effects. We have discovered an indirect route to the first example of a cyclopentadienyl ring bearing three adjacent *tert*-butyl groups, via the ring expansion of 1,2,3-tri-*tert*-butyl-3-vinyl-1-cyclopropene (**4**) to give the rhodocenium cation **5**, as shown in Scheme I.[11,12] Here we report full details of the synthetic routes to **5** and the crystal structure of its hexafluorophosphate salt, which demonstrates that significant in-plane distortion of the cyclopentadienyl ligand does indeed occur.

Results and Discussion

As previously described,[11,12] the cyclopentadiene complex **7** can easily be prepared by sequential treatment of tri-*tert*-butylvinylcyclopropene (**4**) with $[Rh(C_2H_4)_2Cl]_2$, followed by potassium indenide, to give **6**, which rearranges to **7** on heating or during chromatographic purification.[12]

Table I. Crystallographic Data for 5a

	(a) Crystal Parameters		
formula	$C_{26}H_{36}F_6PRh$	Z	4
space group	$P2_1/c$	cryst dimens, mm	0.38 × 0.40 × 0.41
cryst syst	monoclinic	cryst color	golden yellow
a, Å	16.363 (3)	D(calc), g/cm^3	1.545
b, Å	9.965 (2)	μ(Mo Kα), cm^{-1}	7.59
c, Å	17.710 (2)	temp, °C	23
β, deg	117.404 (16)		
V, Å^3	2563.7 (9)		
	(b) Data Collection		
diffractometer	Nicolet R3m	rflns collcd	4959
monochromator	graphite	indpt rflns	4508
scan technique	Wyckoff	R(merg), %	2.08
radiation (λ, Å)	Mo Kα (0.71073)	indpt rflns obsd $F_o > 5\sigma(F_c)$	3288
2θ scan range, deg	4–50	std refns	3 std/197 rflns
data collcd (h,k,l)	±20,+12,+22	var in stds, %	<1
	(c) Refinement		
$R(F)$, %	5.42	$\Delta(\rho)$, e Å^{-3}	0.782
$R_w(F)$,[a] %	5.88	N_c/N_v	10.71
Δ/σ(max)	0.015	GOF	1.494

[a] Weighting scheme: $w^{-1} = R^2(F_o) + g(F_o)^2$, where $g = 0.001$.

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 5a

	x	y	z	U[a]
Rh	2117.7 (3)	6867.7 (5)	5568.2 (3)	47.2 (2)
P	1707 (2)	3467 (2)	2536 (1)	70 (1)
F(1)	2478 (6)	4467 (8)	2642 (4)	181 (5)
F(2)	2079 (5)	3362 (8)	3504 (4)	164 (4)
F(3)	954 (5)	2443 (8)	2426 (4)	144 (4)
F(4)	1282 (6)	3632 (12)	1594 (4)	248 (7)
F(5)	1130 (7)	4591 (9)	2597 (7)	236 (8)
F(6)	2292 (7)	2325 (9)	2535 (9)	253 (9)
C(1)	1442 (6)	4892 (10)	5443 (8)	102 (6)
C(2)	1266 (5)	5371 (11)	4671 (7)	99 (5)
C(3)	797 (5)	6646 (11)	4468 (5)	105 (4)
C(4)	624 (4)	6872 (7)	5232 (4)	50 (2)
C(5)	200 (5)	7865 (8)	5465 (6)	83 (4)
C(6)	194 (6)	7747 (12)	6203 (7)	110 (6)
C(7)	571 (6)	6716 (13)	6734 (6)	97 (5)
C(8)	986 (5)	5681 (11)	6588 (6)	92 (4)
C(9)	1036 (4)	5758 (6)	5756 (5)	60 (3)
C(10)	2783 (4)	8651 (7)	6255 (4)	50 (3)
C(11)	3188 (4)	7528 (7)	6754 (4)	52 (3)
C(12)	3612 (4)	6716 (6)	6384 (3)	43 (2)
C(13)	3403 (3)	7368 (6)	5561 (3)	37 (2)
C(14)	2925 (3)	8636 (6)	5520 (3)	41 (2)
C(15)	4190 (5)	5506 (7)	6901 (4)	68 (3)
C(16)	5195 (5)	5611 (8)	7003 (5)	88 (4)
C(17)	3772 (6)	4100 (7)	6550 (5)	97 (5)
C(18)	4311 (7)	5542 (10)	7806 (5)	110 (5)
C(19)	3724 (4)	6884 (7)	4912 (4)	52 (3)
C(20)	4670 (5)	7495 (8)	5168 (5)	80 (4)
C(21)	3787 (5)	5354 (7)	4883 (4)	64 (3)
C(22)	3045 (6)	7246 (8)	3991 (4)	82 (4)
C(23)	2626 (4)	9882 (7)	4924 (4)	56 (3)
C(24)	3416 (6)	10438 (8)	4803 (5)	83 (4)
C(25)	1757 (5)	9678 (8)	4092 (4)	87 (4)
C(26)	2378 (6)	11032 (8)	5373 (6)	97 (5)

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

Cyclopentadiene complex **7** can be converted to the rhodocenium cation **5** by four routes. Formal hydride abstraction from **7**, using trityl fluoroborate, generates the fluoroborate salt **5b** conveniently and in the highest yield. Oxidation of cyclopentadiene complexes with *N*-bromosuccinimide (NBS) is known to give cyclopentadienyl

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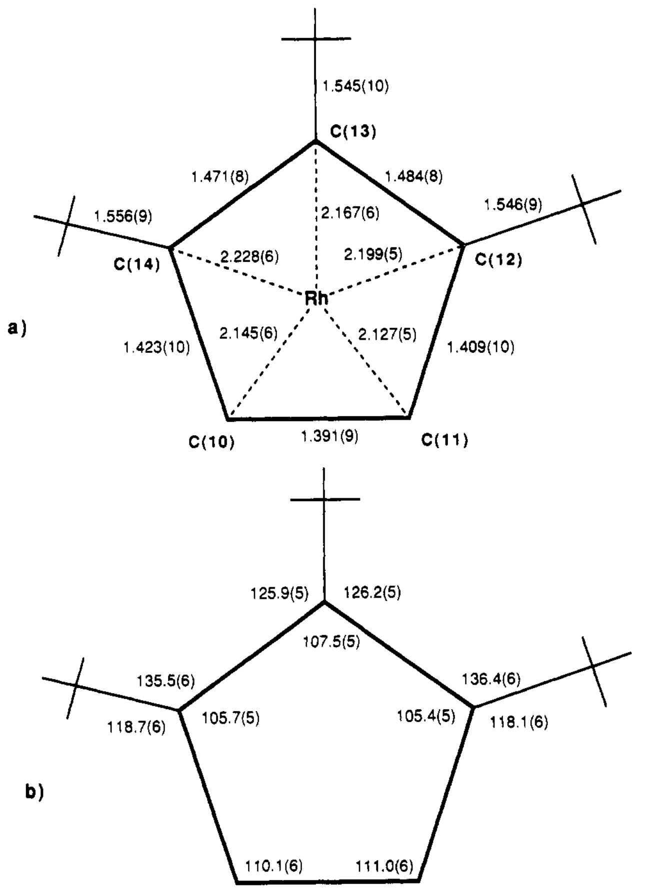

Figure 2. (a) Selected bond lengths (Å) and (b) selected bond angles (deg) for the cyclopentadienyl ring of complex **5a**.

compounds.[13-15] In analogous fashion, oxidation of **7** with NBS gives **5**, which is best isolated as the PF_6^- salt **5a**. Similar to Maitlis's observation that endo-methyl [Rh(η^5-C_5H_5)(η^4-C_5Me_5H)] is oxidized by chloroform,[16] **7** slowly converts to the chloride salt **5c** in chloroform solution. Finally, treatment of **7** with acetic acid generates the acetate salt **5d**, presumably by hydride loss to form hydrogen gas. In the course of a recent deuterium labeling study,[12] these reactions were all found to occur with exclusive loss of the exo hydride.

The molecular structure of the hexafluorophosphate salt **5a** was determined by a single-crystal X-ray diffraction study. Table I lists the crystallographic and refinement parameters, and Table II the fractional coordinates for compound **5a**. An ORTEP plot of the cationic part of the structure is presented in Figure 1, and selected bond lengths and angles relevant to the Rh–cyclopentadienyl and Rh–indenyl interactions are shown in Figures 2 and 3, respectively. Overall the structure adopts the expected sandwich arrangement with the two rings almost parallel and almost eclipsed; the angle between the Rh–ring centroid vectors is 175.2 (3)°, and the average deviation from an eclipsed structure is ~6°.[17] Both rings are bound in

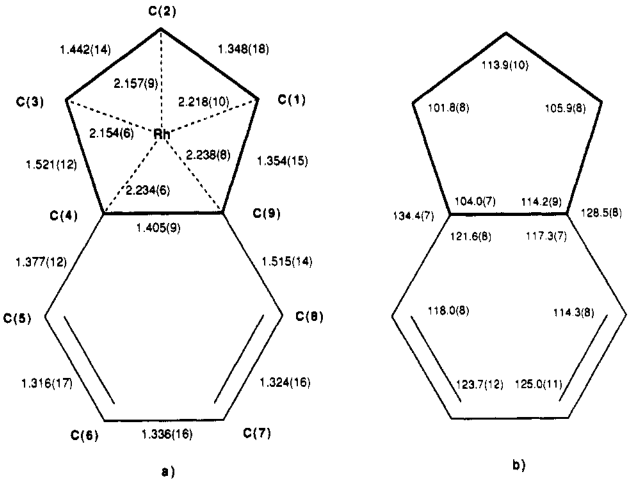

Figure 3. (a) Selected bond lengths (Å) and (b) selected bond angles (deg) for the indenyl ring of complex **5a**.

an η^5-fashion to rhodium, as expected for an 18-electron complex, although the Rh–cyclopentadienyl centroid distance [1.798 (6) Å] is slightly shorter than the corresponding Rh–indenyl centroid distance of 1.855 (6) Å. Not unexpectedly, the complex adopts a conformation such that the arene portion of the indenyl ligand eclipses the less sterically hindered bay area between C(10) and C(11) of the cyclopentadienyl ligand.

Given the steric bulk of the *tert*-butyl groups, the cyclopentadienyl ring of **5a** was expected to exhibit pronounced torsional deformation due to steric repulsion between adjacent *tert*-butyl groups. The structure, however, shows only a slight deviation from planarity, the mean distance from the ring carbons to the least-squares plane being 0.035 Å; the lateral *tert*-butyl-bearing carbons C(12) and C(14) tip away from the rhodium and the other three carbons tip toward it. Instead of deforming torsionally, the steric strain of the *tert*-butyl groups is relieved by in-plane deformation of the bond angles and lengths. The bond angles vary considerably from the ideal 108.0° expected for a pentagon, and the bond lengths between the *tert*-butyl-bearing carbons C(12)–C(13)–C(14) are significantly longer than the typical value of ~1.40 Å for cyclopentadienylrhodium complexes.[18] These deformations presumably allow the *tert*-butyl groups to protrude away from each other, from the ring centroid, and from the metal while still permitting the ring π orbitals to maintain healthy overlap with the metal orbitals. In keeping with the slight ring puckering, the *tert*-butyl groups splay away from the metal to different extents, the lateral groups attached to C(12) and C(14) bending roughly 10° away from the least-squared plane of the ring and the central group attached to C(13) by 2.6°. For comparison, the trimethylsilyl groups of tetrakis- and hexakis(trimethylsilyl)ferrocene bend ~8° out of the plane of the rings.[2d,3c] The effect of the steric congestion can be seen in contraction of the endocyclic angles at C(12), C(13), and C(14), expansion of the endocyclic angles at C(10) and C(11), and the large exocyclic angles of ~136° at C(13)–C(12)–C(15) and C(13)–C(14)–C(23). Similar steric re-

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[17] This value is the average of the dihedral angles between eclipsed carbons (e.g. dihedral angle C(13)–cyclopentadienyl centroid–indenyl centroid–C(2) = 8.3 (8)°). The computations were carried out using the ChemX suite of programs (Chemical Design Ltd.).

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Table III. Spectroscopic and Crystallographic Data Indicating Indenyl Hapticity[a]

compd[b]	$\Delta\delta$(C), ppm	Δ (slip), Å	fold, deg	hinge, deg
5a[c]	−22.4	0.05	3.47	4.76
Undistorted η^5-Indenyl Complexes				
$[Fe(ind)_2]$[d]	−40.7	0.03		
$[Co(ind)_2{}^+]$[d]	−30.7			
$[Rh(ind)(Cp^*)]^+$[d]	−34.2			
$[Rh(ind)(dq)]^+$[d,e]	−23	0.05	2.55	2.35
Distorted η^5-Indenyl Complexes				
$[Rh(ind)(C_2H_4)_2]$[d,e]	−16.2	0.16	7.40	8.08
$[Ir(ind)(H)(PPh_3)_2]^+$[d]	−13.2	0.19		
$[Rh(ind)(Me)(PPh_3)_2]^+$[d]	−13.6			
$[\{Cp_2Zr(\mu\text{-}PEt_2)_2\}Rh(ind)(Me)]$[d]	−8.8			
$[Cr(CO)_3(\mu\text{-}\eta^6{:}\eta^5\text{-ind})Rh(cod)]$[f]		0.15		8.2
$[Rh(ind^*)(cod)]$[d]		0.15	7.83	8.90
η^3-Indenyl Complexes				
$[Ni(ind)_2]$[d]	5.7			
$[Pd(ind)Cl]_2$[d]	7.9			
$[Ir(ind)(PMe_2Ph)_3]$[d,e]	28.1	0.80	28	
$[Fe(ind)(CO)_3]^-$[f,g]	28.8	0.69	22	
$[W(\eta^3\text{-ind})(\eta^5\text{-ind})(CO)_4]$[f]				
η^3		0.72		26
η^5		0.08		

[a] $\Delta\delta(C) = \delta\{C_{3a/7a}(\eta\text{-indenyl})\} - \delta\{C_{3a/7a}(\text{indenyl sodium})\}$.[20,21] $\Delta = \{[d(Rh\text{–}C_{3a}) + d(Rh\text{–}C_{7a})]/2\} - \{[d(Rh\text{–}C_3) + d(Rh\text{–}C_7)]/2\}$.[19] Fold angle = angle between the normals to the planes defined by (C_1, C_2,C_3) and (C_1,C_{7a}, C_{3a},C_3).[19] Hinge angle = angle between the normals to the planes defined by (C_1,C_2,C_3) and (C_{7a},C_{3a},C_4,C_5,C_6,C_7).[19] [b] Ligand abbreviations: Cp, η^5-C_5H_5; Cp*, η^5-C_5Me_5; cod, η^4-1,5-cyclooctadiene; dq, η^4-duroquinone; ind, indenyl; ind*, 4,5,6,7-tetramethylindenyl. [c] This work, PF_6 salt, CD_3CN. [d] Reference 20. [e] Reference 19a. [f] Reference 19b. [g] Reference 23.

pulsion effects on endo- and exocyclic bond lengths and angles can be found in complexes containing the 1,2,4-tris(trimethylsilyl)cyclopentadienyl ligand.[3]

There is considerable interest in the nature of bonding in indenyl complexes of the transition metals, and it was of interest to see whether the steric bulk of the cyclopentadienyl ligand would influence the nature of the rhodium–indenyl interaction. Various methods have been used to quantify the metal–indenyl bonding in terms of slippage, hinging, and folding of the indenyl ring.[19] In order to be consistent with other papers on this subject, the common numbering system for indenyl carbon atoms shown in the line drawing for complexes **5** is used for further discussion. The structural parameters of the indenyl ligand in **5a** all indicate that an undistorted η^5-structure exists in the solid state, with slip, fold, and hinge values typical of η^5 species. The small slippage parameter, $\Delta = \{[d(Rh\text{–}C_{3a}) + d(Rh\text{–}C_{7a})]/2\} - \{[d(Rh\text{–}C_3) + d(Rh\text{–}C_7)]/2\} = 0.05$ Å, fold angle = angle between planes (C_1, C_2,C_3) and (C_{3a},C_4,C_5,C_6,C_7,C_{7a}) = 35°, and hinge angle = angle between planes (C_1,C_2,C_3) and (C_1,C_{7a},C_{3a},C_3) = 4.8° indicate that the fusion carbons of the indenyl ring are bound to the metal and that the indenyl ligand is essentially planar. Comparison data with other indenyl complexes are presented in Table III.

Solution methods have also been developed for ascertaining the nature of indenyl ligand bonding. Baker and Tulip[20] have found that the difference in the ^{13}C chemical shifts of the ring-fusion carbons in the complexed indenyl ligand and in free sodium indenide[22] provides an indication of indenyl hapticity. Some examples including **5** are listed in Table III. Values of $\Delta\delta$(C) between −40 and −20 ppm indicate undistorted η^5 coordination, values between −20 and 0 ppm, distorted η^5 coordination, and values between 5 and 30 ppm, η^3 coordination. Using Baker and Tulip's $\Delta\delta$(C) criterion, compounds **5** clearly contain undistorted η^5-indenyl ligands in solution (Table III), but it should be noted that a counterion dependence is evident by both proton and carbon NMR spectroscopy (Tables IV and V). That the chemical shifts of cation **5** in deuteriochloroform are dependent on the counterion presumably indicates tight ion-pairing in this solvent. When spectra are taken in deuterioacetonitrile, however, the counterion dependance vanishes, suggesting ion separation in the more polar solvent.

Conclusions

In conclusion, the crystal structure of the rhodocenium cation in **5a** shows a remarkably undistorted structure for a complex containing a cyclopentadienyl ring bearing three contiguous *tert*-butyl groups. There is indeed evidence of structural deformations of the cyclopentadienyl ring and its substituents due to steric repulsion between adjacent *tert*-butyl groups, but these deformations are principally in-plane rather than torsional in nature. The presence of the very bulky cyclopentadienyl ligand has no significant effect on the bonding between the η^5-indenyl ligand and the rhodium.

Experimental Section

All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried using Aquasorb. Benzene, 35–60 °C petroleum ether, and ethers were distilled under nitrogen from sodium or potassium benzophenone ketyl; chlorinated solvents, from P_4O_{10}, 10% Na/Pb alloy, or CaH_2; and methanol, from CaH_2. ^1H (300 MHz), $^2H\{^1H\}$ (46 MHz) and ^{13}C and $^{13}C\{^1H\}$ (75 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer in the solvent indicated. Chemical shifts are reported as ppm downfield of internal TMS. Coupling constants are in hertz. Numbered carbons and protons refer to indenyl positions as shown in the line drawings. IR spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectrophotometer. Melting points of samples in capillaries sealed under vacuum were obtained using an Electrothermal device and are uncorrected. Sodium borodeuteride, *N*-bromosuccinimide, and ammonium hexafluorophosphate were obtained from Aldrich. Sodium borohydride and potassium metal were obtained from Alpha. Florisil was obtained from Fisher and activated overnight under vacuum at 200 °C before use. Indene was purchased from Aldrich and distilled before use.

(η^5-Indenyl)((1–3,5-η)-3,4,5-tri-*tert*-butyl-2,4-pentadienediyl)rhodium(III) (6). Indene (190 μL, 1.63 mmol) was refluxed over potassium metal (50 mg, 1.27 mmol) in THF (4.8 mL) until all the potassium had been consumed (1.5 h). Bis(μ-chloro)bis(1–3,5-η-3,4,5-tri-*tert*-butyl-2,4-pentadienediyl)dirhodium(III)[11] (200 mg, 0.53 mmol Rh) was added to half the cooled amber solution (2.5 mL, 0.64 mmol of potassium indenide, 1.2 equiv) to give a deep red solution, which was stirred 4.5 h at room temperature and then evaporated to dryness. Extraction of the residue with petroleum ether, filtration through Celite, and evaporation gave **6** as a red oil (220 mg, 92%). The ^1H NMR spectrum was as reported.[12]

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Table IV. Solvent and Counterion Dependence of Proton Chemical Shifts[a] of Rhodocenium Cation 5

solvent	X⁻	indenyl H(4)–H(7)	indenyl H(1), H(3)	indenyl H(2)	Cp ═CH	lateral *t*-Bu	central *t*-Bu	OAc
CD_3CN	all	7.65, 7.44	6.45	5.81	5.50	1.43	1.40	(1.88)
$CDCl_3$	PF_6	7.59, 7.41	6.34	5.88	5.88	1.43	1.30	
$CDCl_3$	Cl	7.61, 7.37	6.51	6.30	6.19	1.16	1.26	
$CDCl_3$	OAc	7.57, 7.36	6.46	6.11	6.00	1.41	1.24	2.05

[a] In ppm, referenced to internal TMS.

Table V. Solvent and Counterion Dependence of Carbon Chemical Shifts[c] of Rhodocenium Cation 5

solvent	X⁻	indenyl C(4)–C(7)	indenyl C(3a), C(7a)	indenyl C(1), C(3)	indenyl C(2)	Cp ═CH
CD_3CN	PF_6	131.6, 125.4	106.1	81.3	87.2	87.1
$CDCl_3$	PF_6[a]	130.5, 124.5	105.0	79.3	86.4	85.0
$CDCl_3$	Cl	130.3, 124.9	105.6	80.2	88.2	86.5
J_{RhC}[b]			5.6	7.2	7.3	8.2

solvent	X⁻	lateral C(*t*-Bu)	central C(*t*-Bu)	lateral Me_3C	central Me_3C	lateral Me_3C	central Me_3C
CD_3CN	PF_6	122.3	117.3	35.1	34.2	35.2	35.0
$CDCl_3$	PF_6[a]	120.7	117.4	33.3	33.9	34.7	34.2
$CDCl_3$	Cl	121.7	117.3	34.6	33.7	35.1	34.1
J_{RhC}[b]		7.8	7.0				

[a] −50 °C. [b] In Hz. [c] In ppm, referenced to internal TMS.

(η^5-Indenyl)(η^4-1,2,3-tri-*tert*-butylcyclopentadiene)rhodium(III) (7). By Chromatography. Complex **6** (220 mg) was applied to a Florisil column (1 × 55 cm, −55 °C, under N_2) with petroleum ether and eluted with methylene chloride/petroleum ether (400 mL, 1:9). Evaporation gave **7** as a yellow oil (190 mg, 80%). ^1H NMR (C_6D_6): δ 7.11 (m, 2 H, $H_{4,7}$), 6.85 (m, 2 H, $H_{5,6}$), 6.13 (dt, $J_{HH} = J_{RhH} = 2.6$, H_2), 5.76 (br, 1 H, $H_{1/3}$), 5.63 (br, H, $H_{1/3}$), 3.69 (ddd, 1 H, $J_{HH} = 2.7, 1.4$, $J_{RhH} = 1.5$, $H_{olefinic}$), 2.49 (ddd, 1 H, $J_{HH} = 12.4, 1.3$, $J_{RhH} = 4.6$, H_{exo}), 2.38 (ddd, 1 H, $J_{HH} = 12.4, 2.6$, $J_{RhH} = 2.6$, H_{endo}), 1.35 (s, 9 H, ^tBu), 1.32 (s, 9 H, ^tBu), 1.14 (s, 9 H, ^tBu). ^{13}C NMR (C_6D_6): δ 122.4 (d, $J_{CH} = 153$, $C_{5/6}$), 122.3 (d, $J_{CH} = 157$, $C_{5/6}$), 120.9 (d, $J_{CH} = 167$, $C_{4/7}$), 120.4 (d, $J_{CH} = 158$, $C_{4/7}$), 113.1 (d, $J_{RhC} = 1.9$, $C_{3a/7a}$), 112.2 (d, $J_{RhC} = 1.9$, $C_{3a/7a}$), 107.8 (d, $J_{RhC} = 6.8$, C^tBu), 107.7 (d, $J_{RhC} = 7.3$, C^tBu), 92.0 (dd, $J_{RhC} = 7.0$, $J_{CH} = 172$, $C_{1/2/3}$), 76.4 (dd, $J_{RhC} = 6.0$, $J_{CH} = 173$, $C_{1/2/3}$), 75.7 (d, $J_{RhC} = 12$, C^tBu), 74.1 (dd, $J_{RhC} = 5.4$, $J_{CH} = 174$, $C_{1/2/3}$), 45.5 (dd, $J_{RhC} = 13.4$, $J_{CH} = 169$, $CHCH_2$), 42.1 (dt, $J_{RhC} = 5.1$, $J_{CH} = 130$, CH_2), 36.1 (q, $J_{CH} = 125$, CH_3), 35.0 (s, Me_3C), 34.8 (s, Me_3C), 33.4 (q, $J_{CH} = 125$, CH_3), 33.3 (q, $J_{CH} = 125$, CH_3), 32.7 (s, Me_3C).

By Reduction of 5. Complex **7**-*exo-D* was prepared from **5a** by a modification of two literature reductions.[13,24] Sodium borodeuteride (1.6 mg, 0.037 mmol, 6 equiv) was added to an ethanolic (95%, 3 mL) solution of **5a** (X = PF_6) (15 mg, 0.024 mmol). The resultant burgundy solution was stirred 10 min and evaporated, and the residue was extracted with water/benzene. Passage of the benzene extracts through a 10-mm column of magnesium sulfate and evaporation of the orange eluate gave **7** as a yellow oil which slowly solified on standing: 3.8 mg (34%), mp 109–110 °C. ^1H NMR (C_6D_6): δ 7.11 (m, 2 H, $H_{4,7}$), 6.85 (m, 2 H, $H_{5,6}$), 6.20 (m, 1 H, H_2), 5.77 (dd, 1 H, $J_{HH} = 3.5$, $J_{RhH} = 1.4$, $H_{1/3}$), 5.67 (dd, 1 H, $J_{HH} = 3.5$, $J_{RhH} = 1.4$, $H_{1/3}$), 3.68 (dd, 1 H, $J_{HH} = 2.9$, $J_{RhH} = 1.8$, $H_{olefinic}$), 2.36 (ddt, 1 H, $J_{HH} = J_{RhH} = J_{HD} = 2.4$, H_{endo}), 1.35 (s, 9 H, ^tBu), 1.32 (s, 9 H, ^tBu), 1.13 (s, 9 H, ^tBu). $^2H\{^1H\}$ NMR (C_6H_6): δ 2.50 (s, 1 D, D_{exo}). IR (KBr): 2961 (s), 2922 (m), 2059 cm^{-1} (br, w).

(η^5-Indenyl)(η^5-1,2,3-tri-*tert*-butylcyclopentadienyl)rhodium(III) Cation (5). Complex **7** was converted to rhodocenium cation **5** by four routes:

Oxidation by NBS.[14,16] Solid ammonium hexafluorophosphate (288 mg, 1.39 mmol) and NBS (220 mg, 1.24 mmol) were added to a solution of **7** (222 mg, 0.490 mmol) in methanol/petroleum ether (2:1, 15 mL) under nitrogen. The resulting yellow precipitate was filtered out, washed with water, methanol, and petroleum ether, and dried, giving **5a** (X = PF_6), 128 mg (43%), mp 234–235 °C. ^1H NMR (CD_3CN): δ 7.65 (m, 2 H, $H_{4,7}$), 7.44 (m, 2 H, $H_{5,6}$), 6.45 (dd, 2 H, $J_{HH} = 2.7$, $J_{RhH} = 0.7$, $H_{1,3}$), 5.81 (dt, 1 H, $J_{HH} = 2.7$, $J_{RhH} = 1.3$, H_2), 5.50 (d, 2 H, $J_{RhH} = 0.9$, CHC^tBu), 1.43 (s, 18 H, ^tBu), 1.40 (s, 9 H, ^tBu). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 131.6 (s, $C_{5,6}$), 125.4 (s, $C_{4,7}$), 122.3 (d, $J_{RhC} = 7.8$, lateral C^tBu), 117.3 (d, $J_{RhC} = 7.0$, central C^tBu), 106.1 (d, $J_{RhC} = 5.6$, $C_{3a,7a}$), 87.7 (d, $J_{RhC} = 7.3$, C_2), 87.1 (d, $J_{RhC} = 8.2$, CHC^tBu), 81.3 (d, $J_{RhC} = 7.2$, $C_{1,3}$), 35.2 (s, lateral $C(Me)_3$), 35.1 (s, central $C(Me)_3$), 35.0 (s, lateral $C(Me)_3$), 34.2 (s, central $C(Me)_3$). See Tables IV and V for NMR data in other solvents.

A crystal suitable for diffraction was prepared by diffusion of ether into a methanolic solution of **5a**, followed by a slow cooling to −78 °C.

"Hydride Abstraction" by Trityl Fluoroborate.[13,15,25] A solution of **7** (8.9 mg, 0.019 mmol) in methylene chloride (1 mL) was added to trityl fluoroborate[26] (6.4 mg, 0.019 mmol). The mixture was allowed to stir 3 min, concentrated, and precipitated with ether (3 mL) at 0 °C. The supernatant was removed and the yellow precipitate washed with ether, leaving **5b** (X = BF_4): 7.3 mg (70%). The ^1H NMR (CD_3CN) spectrum was identical to that from the NBS reaction above.

Oxidation by $CDCl_3$.[16,24] An NMR sample of **7** in deuteriochloroform was allowed to stand at 25 °C. Complex **5c** (X = Cl) slowly formed quantitatively over 6 days. Evaporation and dissolution in deuterioacetonitrile gave a ^1H NMR spectrum identical to that from the NBS reaction above.

Reaction with Acetic Acid. A drop of acetic acid was added to an NMR sample of **7** in chloroform under N_2. Conversion to **5d** (X = OAc) was complete in 24 h at 25 °C. Evaporation and dissolution in deuterioacetonitrile gave a ^1H NMR spectrum identical to that from the NBS reaction above, with the addition of a singlet at δ 1.88 (OAc).

Crystal Structure Determination of 5a. Crystal, data collection, and refinement parameters are collected in Table I. Golden yellow crystals of **5a** were mounted on glass fibers with epoxy cement. The unit cell parameters for **5a** were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterizations showed 2/*m* Laue symmetry. Systematic absences in the diffraction data uniquely established the space group as $P2_1/c$. No absorption correction was applied to the data (regular-shaped crystal, low μ).

The structure was solved by a Patterson map, which located the Rh atom. The remaining non-hydrogen atoms were located from subsequent difference Fourier synthesis. All hydrogen atoms were included as idealized isotropic contributions. All non-hydrogen atoms were refined with anisotropic thermal parameters. All computer programs and the sources of the scattering factors

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are contained in the SHELXTL program library (5.1) (Nicolet Corp., Madison, WI).

Acknowledgment. We are grateful to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of our research. A generous loan of rhodium salts from Matthey-Bishop Inc. is also gratefully acknowledged.

Registry No. **5a**, 129849-96-3; **5b**, 137394-56-0; **5c**, 137394-57-1; **5d**, 137394-58-2; **6**, 137394-55-9; **7**, 129849-93-0; **7**-*exo-D*, 137394-59-3; NBS, 128-08-5; CCl_3D, 865-49-6; HOAc, 64-19-7; indene, 95-13-6; bis(μ-chloro)bis(1–3,5-η-3,4,5-tri-*tert*-butyl-2,4-pentadienediyl)dirhodium(III), 134342-32-8; trityl tetrafluoroborate, 341-02-6.

Supplementary Material Available: For complex **5a**, tables of atomic coordinates and isotropic thermal parameters (Table 1S), bond lengths (Table 2S), bond angles (Table 3S), anisotropic thermal parameters (Table 4S), and H atom coordinates and isotropic thermal parameters (Table 5S) (6 pages); a table of observed and calculated structure factors (Table 6S) (20 pages). Ordering information is given on any current masthead page.

(Alkyne)(2,2′-bipyridine)copper(I) Complexes. Controlled Formation of $[Cu(bpy)(alkyne)]^+$ and $\{[Cu(bpy)]_2(alkyne)\}^{2+}$

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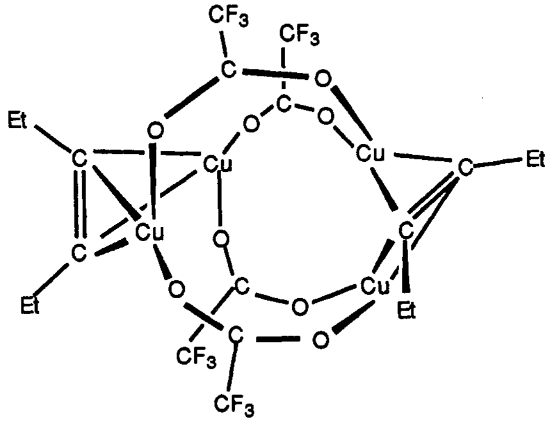
Received July 8, 1991

The addition of 1 equiv of 2,2′-bipyridine (bpy) to a solution of $Cu(NCMe)_4X$ (X = PF_6^-, SbF_6^-) followed by addition of an excess of alkyne (alkyne = 3-hexyne, 1-pentyne, methyl 2-butynoate, diphenylacetylene, diethyl acetylenedicarboxylate, phenylacetylene) leads to the preparation of [Cu(bpy)(alkyne)]X complexes in good yield. In order to isolate pure products, the alkyne complexes must be precipitated in the presence of excess alkyne. The alkyne ligands are labile in solution, exchanging rapidly on the NMR time scale. Competition studies show that the relative affinities of the alkynes (and ethylene) for copper in this system are $C_2H_4 \sim HC{\equiv}CPr > EtC{\equiv}CEt \sim$ DEAD $> HC{\equiv}CPh > MeC{\equiv}CCO_2Me > PhC{\equiv}CPh$. Repeated precipitation from solutions that initially contain [Cu(bpy)(alkyne)]X (alkyne = diethyl acetylenedicarboxylate, phenylacetylene) complexes in the absence of added alkyne leads to the isolation of $\{[Cu(bpy)]_2(alkyne)\}X_2$, complexes with a 2:1 copper:alkyne stoichiometry.

Introduction

Continuing our interest in the synthesis and reactivity of η^2-alkyne complexes of the transition metals,[1] we have recently reported the preparation and characterization of neutral adducts of copper(I) trifluoroacetate.[2] In addition to the preparation of the expected $[Cu(O_2CCF_3)(alkyne)]_2$ complexes,[3] we reported that tetranuclear complexes with a copper:alkyne ratio of 4:2, $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-alkyne})_2$, can also be prepared. In certain cases, these alkyne-deficient complexes form even in the presence of excess alkyne. In fact, the copper to alkyne stoichiometry (either 4:2 or 2:2) can be controlled by the choice of alkyne or variations in the purification procedures. The solid-state structure of $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-}EtC{\equiv}CEt)_2$ shows that in these unusual tetranuclear complexes each of the alkyne ligands bridge two copper atoms that are not directly bridged by other ligands (structure A). This surprising tendency for the formation of complexes with the $Cu_2(\mu\text{-alkyne})$ bonding arrangement has been noted by others.[4,5] While most transition elements do form stable complexes containing bridging alkynes,[6] the copper subgroup had been a notable exception until these recent studies.



A

Reported here are the results of studies extending this chemistry to cationic (2,2′-bipyridine)copper(I) derivatives. As observed in the trifluoroacetate system, complexes with both 1:1 and 2:1 copper:alkyne ratios can be prepared. The only similar alkyne complex of copper(I) was reported by Thompson and Whitney.[7] They have prepared and

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