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Synthesis and reactivity of 2-(*tert*-butylcyclopentadienyl)-indenyl dinuclear ruthenium complex [η^5:η^5-(^{t}BuC$_5$H$_3$)(C$_9$H$_6$)]Ru$_2$(CO)$_4$: Halogen induced Ru cleavage from indenyl ring

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ABSTRACT

Thermal reaction of $Ru_3(CO)_{12}$ with unsymmetrical Fv ligand 2-(*tert*-butylcyclopentadienyl)-indene provided [η^5:η^5-(^{t}BuC$_5$H$_3$)(C$_9$H$_6$)]Ru$_2$(CO)$_4$ (**2**) in good yield. When **2** reacted with three or more equivalent of halogen X_2, compounds [(η^5-^{t}BuC$_5$H$_3$)(C$_9$H$_6$X)]Ru(CO)$_2$X (X = Br, **3**; I, **4**) were isolated in moderate yield. In complexes **3** and **4** only the Cp rings were coordinated with Ru(CO)$_2$X, along with uncomplexed halogenated-indenyl rings. All the new complexes have been fully characterized. X-ray characterization of **2**, **3**, and **4** are also provided.

1. Introduction

Dinuclear fulvalene [η^5:η^5-CpCp (Fv), Cp = C$_5$H$_4$, cyclopentadienyl ring] complexes, in which the Cp moieties are directly attached to each other without a bridging group, have been extensively explored in the last two decades [1–4]. Fulvalene can act as good ligand for many bimetallic complexes in part due to the strong bonding of its Cp rings to transition metals. The properties of Fv bimetallic complexes are quite different from those of Cp analogues might attribute to several reasons: (a) the Fv ligands act as frameworks for dinuclear metal complexes that are resistant to fragmentation and maintain two metal centers in close proximity even after the M–M bond cleavage; (b) the Fv ligands are forced to bend away from planarity to accommodate the M–M bonds, and the resulting distortions of the ligands in turn case unique reactivity; (c) the two metal centers can communicate through the π-bond system of the Fv ligand regardless whether the existence of M–M bond or not, and whether the metals are oriented *cis* or *trans* with respect to the ligand [1,3,5].

The process for the haptotropic rearrangement of coordinated cyclic polyenyl ligand is casually termed "ring slippage" and has been reviewed for the cyclopentadienyl (Cp) and indenyl (Ind) ligands [6,7]. Transition metal complexes containing the indenyl ligand have received much attention due to their enhanced reactivity and catalytic ability as compared to the cyclopentadienyl analogues. Basolo and co-workers called this phenomenon the "indenyl effect" [8]. They attributed it to the ease of slippage from a nominally 18-electron η^5 structure to a 16-electron η^3 species, assisted by restoration of full aromaticity to the benzene ring.

The indenyl analogue to Fv ligand – dibenzofulvalene – was reported with its iron and group 6 metal complexes by Kerber and Waldbaum [9,10]. Later, Gaede and Tews demonstrated the synthesis of bridged dibenzofulvalene ligand and its Mo, Fe, Co, Rh, and Ir complexes [11,12]. However, the fulvalene ligands with unsymmetrical backbones, such as 2-(cyclopentadienyl)-indenyl species, were less explored. Only two complexes *rac*-Fc(η^5-C$_9$H$_6$)$_2$Fe and *rac*-Fc(η^5-C$_9$H$_6$)$_2$ZrCl$_2$ based on such unsymmetrical Fv foundation were reported before [13].

In this study, we will report the synthesis of [η^5:η^5-(^{t}BuC$_5$H$_3$)(C$_9$H$_6$)]Ru$_2$(CO)$_4$ (**2**) by reaction of 2-(*tert*-butylcyclopentadienyl)-indene (**1**) with $Ru_3(CO)_{12}$ and its subsequent reactions with halogens (Br$_2$, I$_2$). The latter reactions provide rare examples of halogen induced metal cleavage from indenyl ring.

2. Experimental

2.1. General considerations

Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon prior to use. Melting points were uncorrected. ^{1}H NMR spectra were recorded on a Bruker AV300, or Varian Mercury VX300, or Varian Mercury Plus 400 instrument. IR spectra

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were recorded as KBr disks on a Nicolet 380 FT-IR spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. 2-(*tert*-Butylcyclopentadienyl)-indene (**1**) [14] were prepared according to the literature method.

2.2. Reaction of 1 with $Ru_3(CO)_{12}$ and synthesis of $[\eta^5:\eta^5\text{-}(^tBuC_5H_3)(C_9H_6)]Ru_2(CO)_4$ (2)

A solution of **1** (94 mg, 0.40 mmol) and $Ru_3(CO)_{12}$ (160 mg, 0.25 mmol) in toluene (30 mL) was refluxed for 6 h. After removal of solvent the residue was chromatographed on an alumina column. Elution with petroleum ether–CH_2Cl_2 (3/1, v/v) gave a yellow band, which afforded **2** (128 mg, 62% yield) as yellow crystals. M.p. 243 °C (dec.). Anal. Calc. for $C_{22}H_{18}O_4Ru_2$: C, 48.17; H, 3.11. Found: C, 48.36; H, 3.48%. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34 (m, 2H, Ar-H), 7.19 (m, 2H, Ar-H), 5.53 (m, 1H, Cp-H), 4.63 (s, 2H, Ind-CH), 4.15 (t, 1H, Cp-H), 4.04 (s, 1H, Cp-H), 1.22(m, 9H, CMe_3); IR (ν_{CO}, cm^{-1}): 2006(s), 1952(s).

2.3. Reaction of complex 2 with Br_2 and synthesis of $[(\eta^5\text{-}^tBuC_5H_3)(C_9H_6Br)]Ru(CO)_2Br$ (3)

A solution of complex **2** (60 mg, 0.110 mmol) and Br_2 (0.33 mmol, ~5% solution in benzene) in benzene (30 mL) was stirred for 2 h at room temperature. The reaction was monitored by TLC and stopped when complex **2** was used up completely. After removal of solvent the residue was chromatographed on a silica column using CH_2Cl_2 as eluent, which afforded complex **3** (25 mg, 41% yield) as yellow crystals as a mixture of two isomers in ~3:2 ratio at 20 °C. M.p. 157–158 °C. Anal. Calc. for $C_{20}H_{18}Br_2O_2Ru$: C, 43.58; H, 3.29. Found: C, 43.31; H, 3.45%. ^1H NMR ($CDCl_3$, 400 MHz): For isomer **a**, δ 7.52 (m, 1H, Ar-H), 7.33 (m, 1H, Ar-H), 7.30 (m, 2H, Ar-H), 7.13 (m, 1H, C*H*=CCHBr), 5.88 (br s, 1H, CH=CC*H*Br), 5.74 (br s, 1H, Cp-H), 5.64 (br s, 1H, Cp-H), 5.35 (br s, 1H, Cp-H), 1.26 (m, 9H, CMe_3). For isomer **b**, δ 7.52 (m, 1H, Ar-H), 7.33(m, 1H, Ar-H), 7.30 (m, 2H, Ar-H), 7.12 (m, 1H, C*H*=CCHBr), 5.98 (br s, 1H, CH=CC*H*Br), 5.60 (br s, 1H, Cp-H), 5.52 (br s, 1H, Cp-H), 5.30 (br s, 1H, Cp-H), 1.27 (m, 9H, CMe_3); IR (ν_{CO}, cm^{-1}) of a mixture of isomers: 2035(s), 1986 (s).

2.4. Reaction of complex 2 with I_2 and synthesis of $[(\eta^5\text{-}^tBuC_5H_3)(C_9H_6I)]Ru(CO)_2I$ (4)

A solution of complex **2** (57 mg, 0.105 mmol) and I_2 (79 mg, 0.315 mmol) in benzene (30 mL) was stirred for 1 h at room temperature. The reaction was monitored by TLC and stopped when complex **2** was used up completely. After removal of solvent the residue was chromatographed on a silica column using petroleum ether–CH_2Cl_2 (1/1, v/v) as eluent, which afforded complex **4** (46 mg, 68% yield) as brown-red crystals as a mixture of two isomers in ~1:3 ratio at 20 °C. M.p. 140 °C (dec.). Anal. Calc. for $C_{20}H_{18}I_2O_2Ru$: C, 37.23; H, 2.81. Found: C, 37.00; H, 3.03%. ^1H NMR ($C_6D_6CD_3$, 300 M): For isomer **a**, δ 7.25 (br s, 1H, Ar-H), 6.98 (m, 1H, Ar-H), 6.94 (m, 2H, Ar-H), 6.71 (s, 1H, C*H*=CCHI), 5.71 (t, 1H, Cp-H), 5.50 (br s, 1H, CH=CC*H*I), 4.95 (m, 1H, Cp-H), 4.57 (m, 1H, Cp-H), 1.00 (s, 9H, CMe_3). For isomer **b**, δ 7.24 (d, *J* = 3.21 Hz, 1H, Ar-H), 6.99 (m, 1H, Ar-H), 6.96 (br s, 2H, Ar-H), 6.57 (s, 1H, C*H*=CCHI), 5.74 (s, 1H, CH=CC*H*I), 5.43 (m, 1H, Cp-H), 5.32 (t, 1H, Cp-H), 4.62 (m, 1H, Cp-H), 0.93 (s, 9H, CMe_3). IR (ν_{CO}, cm^{-1}) of a mixture of isomers: 2039(s), 1987 (s).

2.5. Crystallographic studies

Single crystals of all complexes suitable for X-ray diffraction were obtained from hexane/CH_2Cl_2. Data collection of complexes **2** and **4** were performed on a Bruker SMART 1000 at 294(2) K, while **3** was performed on a Rigaku Saturn 70 equipped with a rotating anode system at 113(2) K, using graphite-monochromated Mo Kα radiation (ω-2θ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were using the SHELXTL-97 program system. The molecular structure of **2** contained one CH_2Cl_2 of solvation. The crystal data and summary of X-ray data collection are presented in Table 1.

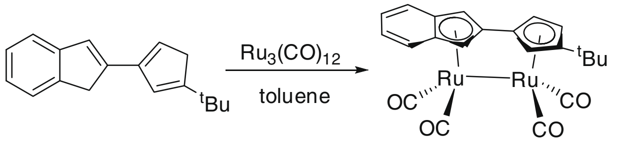
Table 1
Summary of crystallographic data for **2 · 0.5 CH_2Cl_2**, **3**, and **4**.

	2 · 0.5 CH_2Cl_2	**3**	**4**
Empirical formula	$C_{22.50}H_{19}ClO_4Ru_2$	$C_{20}H_{18}Br_2O_2Ru$	$C_{20}H_{18}I_2O_2Ru$
Formula weight	590.97	551.23	645.21
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Fdd*2	$P\bar{1}$	$P\bar{1}$
a (Å)	23.254(4)	8.4827(17)	8.6348(17)
b (Å)	44.351(9)	8.9187(18)	8.6911(17)
c (Å)	8.4715(13)	13.671(3)	14.642(3)
α (°)	90	82.53(3)	80.41(3)
β (°)	90	78.08(3)	83.06(3)
γ (°)	90	72.36(3)	68.82(3)
V ($Å^3$)	8737(3)	961.8(3)	1008.0(3)
Z	16	2	2
$D_{calc.}$ (g cm^{-3})	1.797	1.903	2.126
μ (mm^{-1})	1.531	4.979	3.850
F(000)	4656	536	608
Crystal size (mm)	0.22 × 0.20 × 0.14	0.14 × 0.14 × 0.10	0.12 × 0.10 × 0.08
Maximum 2θ (°)	50.04	50.04	55.74
Number of reflections collected	11176	5585	7213
Number of independent reflections [$R_{(int)}$]	3859 [0.0427]	3381 [0.0501]	4718 [0.0481]
Number of parameters	271	226	229
Goodness-of-fit on F^2	0.963	1.047	0.977
R_1, wR_2 [$I > 2\sigma(I)$]	0.0269, 0.0573	0.0491, 0.0984	0.0434, 0.1047
R_1, wR_2 (all data)	0.0344, 0.0610	0.0670, 0.1043	0.0563, 0.1097
Largest peak in final difference map (e $Å^3$)	0.300	1.357	1.669

3. Results and discussion

3.1. Synthesis and X-ray structure of $[\eta^5:\eta^5\text{-}(^tBuC_5H_3)(C_9H_6)]Ru_2(CO)_4$

Reaction of $Ru_3(CO)_{12}$ with the unsymmetrical Fv ligand 2-(*tert*-butylcyclopentadienyl)-indene (**1**) in refluxing toluene afforded the normal Fv dinuclear ruthenium complex $[\eta^5:\eta^5\text{-}(^tBuC_5H_3)(C_9H_6)]Ru_2(CO)_4$ (**2**) in good yield (Scheme 1). The reaction can be also conducted in heptane and xylene, just with relatively lower yields. Complex **2** has been completely characterized, including by a single crystal X-ray diffraction study. The ^1H NMR studies showed three multiplets for three Cp protons at δ 5.53, 4.15, and 4.04 ppm [15–17], a singlet for two five-membered ring protons



1 **2**

Scheme 1.