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Preliminary communication

HIGHLY FLUXIONAL *tetrahapto*-CYCLOOCTATETRAENE COMPLEXES OF RUTHENIUM(0)

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Summary

In complexes of the type Ru(arene)(cot) (cot = cyclooctatetraene) the cyclooctatetraene ring is 1—4-η-bonded as shown by X-ray diffraction study of the hexamethylbenzene derivative, and the barrier to intramolecular exchange of the bound and unbound halves of the eight-membered ring is unusually low (< 6 kcal/mol).

The reaction of cyclooctatetraene dianion with diolefinruthenium(II) complexes such as $[RuCl_2(nbd)]_n$** gives η^6-cyclooctatetraeneruthenium(0) complexes such as Ru(nbd)(η^6-cot); addition of CO or various phosphorus-donor ligands (L) induces a change in the bonding mode of cyclooctatetraene to give Ru(nbd)(1—4-η-cot)(L) [1]. We find that 1—4-η-cyclooctatetraene complexes can be obtained directly by reaction of areneruthenium(II) complexes $[RuCl_2(arene)]_2$ or $[RuCl_2(arene)(py)]$ [2—4] with M_2(cot) (M = Li, Na, K) to give 30—50% yields of the orange-yellow, air-sensitive, crystalline compounds Ru(arene)(cot) (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6). The proton resonances of coordinated cyclooctatetraene are singlets at room temperature (Table 1), indicative either of planar η^8- or fluxional η^4-coordination, and the IR spectra show a low intensity ν(C=C) absorption at 1530 cm^{-1} which suggests that the second alternative is correct cf. 1562 cm^{-1} for $Fe(CO)_3$(1—4-η-cot) [5] and 1527 cm^{-1} for the η^4-ring in Fe(1—4-η-cot)(1—6-η-cot) [6]. In contrast, ν(C=C) for the uncomplexed double bonds of 1,2,5,6-η-cyclooctatetraene is about 1630 cm^{-1} [7].

The presence of a 1—4-η-cyclooctatetraene ring is confirmed by single crystal X-ray structural analysis of Ru(hmb)(cot), crystals of which are monoclinic with

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**Abbreviations: cot = cyclooctatetraene; nbd = norbornadiene [bicyclo[2.2.1]hepta-2,5-diene]; py = pyridine; hmb = hexamethylbenzene (C_6Me_6).

TABLE 1

NMR DATA FOR Ru(arene)(cot) COMPLEXES[a]

Compound	Arene resonances	Cot resonances
$Ru(C_6H_6)(C_8H_8)$[b]	(^1H) 5.29(s)	4.67(s)
$Ru(1,3,5\text{-}C_6H_3Me_3)(C_8H_8)$[b]	(^1H) 5.48(s, aromatic H) 8.19(s, $C\underline{H}_3$)	4.80(s)
$Ru(C_6Me_6)(C_8H_8)$[c,d]	(^1H) 7.87(s, $C\underline{H}_3$) (^{13}C $\{^1H\}$) 91.27(C_6), 17.27(CH_3)	5.09(s) 91.59($\underline{C}_8$)

[a] Proton chemical shifts (τ, ppm) measured at 100 MHz, and carbon chemical shifts (δ, ppm) measured at 67.89 MHz relative to internal TMS. [b] In C_6D_6 at ca. 34°C; it remained unchanged down to −145°C in CHF_2Cl/CF_2Cl_2. [c] ^1H NMR spectrum in $CDCl_3$ at ca. 34°C; it remained unchanged down to −145°C in CHF_2Cl/CF_2Cl_2. [d] $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2 at −120°C.

a 8.846, *b* 18.062, *c* 10.818 Å, β 91.5°, $Z = 4$, space group $P2_1/n$. Unit cell dimensions and reflection intensities were measured on a Picker FACS-I automatic four-circle diffractometer using Cu-K_α radiation. The structure was solved by conventional "heavy atom" methods and full matrix least-squares refinement using the 1931 reflections with $I > 3\sigma(I)$ converged with an R of 0.054. The molecular geometry is illustrated in Fig. 1.

The arene ring is planar to within experimental error, the maximum deviation from the mean plane being 0.03 Å; the mean Ru—C (hmb) distance (2.22 Å) is close to the Ru—(η^6-hmb) distance of 2.25 Å in Ru(η^4-hmb) (η^6-hmb) [8]. The geometry of the η^4-cyclooctatetraene ring is similar to that found in $M(CO)_3$(cot) (M = Fe, Ru) [9, 10], Fe(CO)(cot)(C_4H_6) [11] and Fe(η^4-cot)(η^6-cot) [12], the dihedral angle between the mean planes of the coordinated and uncoordinated halves of the ring in Ru(hmb)(cot) (39.6°) being in the same range as in these complexes. The mean distances from the metal atom to the terminal and central carbon atoms of the coordinated diene are 2.25 and 2.14 Å respectively, which are comparable with the corresponding values of 2.27 and 2.18 Å in $Ru(CO)_3$(cot) [10].

Despite the similarity of geometry of the eight-membered ring in $Ru(CO)_3$(cot) and Ru(hmb)(cot), the latter complex has a considerably lower barrier to intramolecular rearrangement. In Ru(hmb)(cot), the cot proton resonance remains a sharp singlet even at −145°C, whereas $Ru(CO)_3$ (cot) reaches its limiting ^1H

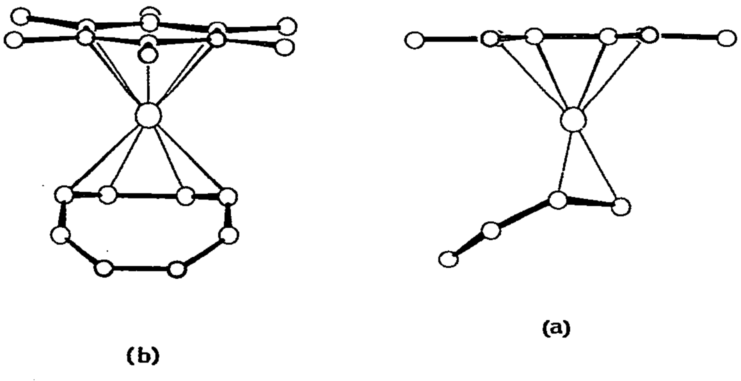

Fig. 1. Molecular geometry of Ru(hmb)(cot) projected (a) on to the approximate molecular mirror plane and (b) in a plane perpendicular to it.

spectrum at about −140°C [13]. Likewise, the exchange-averaged ^{13}C cyclooctatetraene resonance of Ru(hmb)(cot) measured at 67.89 MHz is a sharp singlet even at −120°C (Table 1), whereas for $Ru(CO)_3(cot)$ a limiting 25.03 MHz ^{13}C NMR spectrum is obtained at the same temperature [14]. Assuming the average chemical shift difference between coordinated and uncoordinated carbon atoms in the slow exchange limit and the frequency factors to be the same for the two complexes, we can place an upper limit of 6 kcal/mol on the Arrhenius activation energy of the presumed 1,2-shift of the cyclooctatetraene ring in Ru(hmb)(cot) cf. 8.6 kcal/mol for the corresponding process in $Ru(CO)_3(cot)$ [14]. The barrier to the ring shift in Ru(hmb)(cot) is probably of the same order as the barrier to internal rotation about the metal—arene ring axis cf. values of about 5 kcal/mol for reorientation of the five-membered rings in substituted ferrocenes [15, 16]. We are examining the variable temperature NMR spectra of other cyclic olefin complexes in an effort to discover the factors responsible for the highly fluxional behaviour of Ru(arene)(cot) complexes.

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