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Synthesis of conjugated diene complexes of ruthenium(0) derived from Ru(η^6-naphthalene)(η^4-1,5-COD): *Z* to *E* isomerisation of coordinated 1,3-pentadiene

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ABSTRACT

The naphthalene complex of zerovalent ruthenium, [Ru(η^6-$C_{10}H_8$)(η^4-1,5-COD)] (**1**), readily reacts with 1,3-dienes in the presence of a ligand (L) to produce complexes [Ru(η^4-*cisoid*-1,3-diene)(η^4-1,5-COD)(L)] [1,3-diene = butadiene, 2,3-dimethylbutadiene, isoprene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3-cyclohexadiene; L = MeCN, ^{t}BuCN, PhCN, NCC_6H_4CN, CO, ^{t}BuNC, pyridine, $P(OMe)_3$, $P(OPh)_3$, PMe_3, PEt_3, PPh_3, PCy_3]. The single-crystal X-ray structures of [Ru(η^4-*cisoid*-1,3-butadiene)(η^4-1,5-COD)(MeCN)] (**2a**) and [Ru{η^4-(*E*)-*cisoid*-1.3-pentadiene}(η^4-1,5-COD)(PPh_3)}] (*E*-**5l**) show the expected, approximately square pyramidal geometry about the metal atom, with the auxiliary ligand occupying the axial site. [Ru{η^4-(*Z*)-*cisoid*-1,3-pentadiene}(η^4-1,5-COD)(PPh_3)] (*Z*-**5l**) irreversibly isomerises to *E*-**5l** in benzene-d_6 at 30 °C, the reaction obeying a first-order rate law [$k = (2.89 \pm 0.06) \times 10^{-4}\ s^{-1}$]. This reaction is significantly retarded by addition of PPh_3 suggesting that a vacant site is required for the *E*/*Z* isomerisation.

1. Introduction

The lability of the coordinated naphthalene in [Ru(η^6-$C_{10}H_8$)(η^4-1,5-COD)] (**1**) [1–3] is responsible for the ability of this complex, especially in the presence of acetonitrile, to catalyse some important organic reactions, including alkene hydrogenation [3] and isomerisation [4,5], the selective tail-to-tail dimerisation of unsaturated compounds such as methyl acrylate [6,7], methyl methacrylate [8] and acrylonitrile [9], and cross dimerisations between butadiene and methyl methacrylate [10], and between 2,5-dihydrofuran and methyl methacrylate [11]. An excess of butadiene in the absence of acetonitrile completely displaces naphthalene from complex **1** to give *supine*, *prone*-[Ru(η^3:η^3-2,6-octadiene-1,8-diyl)(η^4-1,5-COD)] as a result of oxidative coupling of the butadiene units in an intermediate [Ru(η^4-*cisoid*-butadiene)(η^2-*transoid*-butadiene)(η^4-1,5-COD)] that can be detected at low temperature [12]. Similar mechanisms probably apply also to the other cross dimerisations mentioned above.

Addition of a compact Lewis base (L) to complex **1** causes facile ring slippage of the naphthalene to give isolable complexes [Ru(η^4-$C_{10}H_8$)(η^4-1,5-COD)(L)] [L = PMe_3, PEt_3, $P(OMe)_3$] and this decrease in hapticity encourages displacement of the naphthalene by incoming substrates [13]. As already reported briefly [14], acyclic 1,3-dienes such as 2,3-dimethylbutadiene in the presence of acetonitrile undergo this reaction to give labile complexes of the type [Ru(η^4-*cisoid*-1,3-diene)(η^4-1,5-COD)(NCMe)], from which acetonitrile is readily displaced by the ligands L.

We now present a full report on this work, including observations on the *Z* to *E* isomerisation of the 1,3-pentadiene complexes [15].

2. Results

2.1. Synthesis of conjugated diene complexes

The complexes prepared in this work are listed in Table 1 together with the ^{1}H NMR data of the coordinated 1,3-diene units.

Treatment of a slurry of [Ru(η^6-$C_{10}H_8$)(η^4-1,5-COD)] (**1**) in acetonitrile with a saturated solution of 1,3-butadiene in benzene gave [Ru(η^4-*cisoid*-1,3-butadiene)(η^4-1,5-COD)(NCMe)] (**2a**), which

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Abbreviation: COD, cyclooctadiene (C_8H_{12}).

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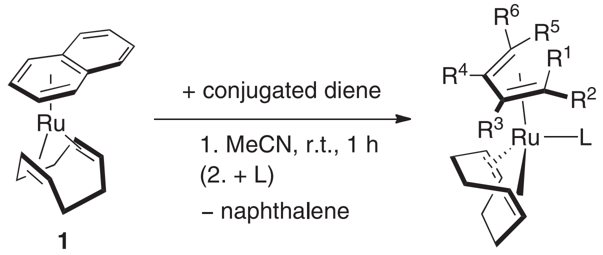

(1)

conjugated diene = butadiene (**2**)
2,3-dimethylbutadiene (**3**)
isoprene (**4**)
1,3-pentadiene (**5**)
2-methyl-1,3-pentadiene (**6**)
1,3-cyclohexadiene (**7**)

The suffix letters from a to m in compounds **2-7** stand for the following ligand L:

L = MeCN (a), ^{t}BuCN (b), PhCN (c),
NCC_6H_4CN (d), CO (e), ^{t}BuNC (f),
NC_5H_5 (g), $P(OMe)_3$ (h), $P(OPh)_3$ (i),
PMe_3 (j), PEt_3 (k), PPh_3 (l), PCy_3 (m)

was isolated as air-sensitive, thermally unstable brown crystals in 34% yield (Eq. (1)).

The crystalline solid could be stored under nitrogen at dry-ice temperature for a few weeks. Although the ^{1}H and ^{13}C NMR spectra were in agreement with the formulation, elemental analyses were not completely satisfactory owing to the instability and sensitivity of the solid. After many attempts, a single-crystal of **2a** suitable for X-ray analysis was finally obtained. The molecular structure of **2a** is depicted in Fig. 1 and selected bond distances and angles are listed in Table 2.

The crystallographic analysis clearly shows a *cisoid*-η^4-coordination of the 1,3-butadiene fragment at the Ru centre. If the midpoints of the olefinic double bonds are regarded as coordination sites, the molecular structure of **2a** can be described as being a five-coordinate, approximately square pyramid, with the nitrile ligand in the axial position. It is similar to that observed in $[Ru(\eta^4\text{-}1,3,5\text{-}C_8H_{10})(\eta^4\text{-}1,5\text{-COD})\{P(OPh)_3\}]$ [16], $[Ru(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-COD})(L)]$ [L = PMe_3, PEt_3, $P(OMe)_3$] [13], and numerous $Fe(\eta^4\text{-}1,3\text{-diene})(CO)_3$ complexes [17,18]. The Ru–C distances to the 1,3-diene unit fall in the range 2.176–2.191 Å and are similar to those observed in the compounds cited above and in $[Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-butadiene})]$ [19]. The distance C(2)–C(3) between the central atoms of the 1,3-diene [1.421(5) Å] is the same as the terminal C–C distances [1.419(7), 1.416(5) Å] within the standard deviation, a pattern that is generally similar to that observed in the $Fe(\eta^4\text{-}1,3\text{-diene})(CO)_3$ complexes and different from the short-long-short pattern observed in $[Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-butadiene})]$ [19]. The observed pattern is consistent with the usual assumption of a minor contribution to the metal-diene bond of an ene-diyl extreme (Chart 1).

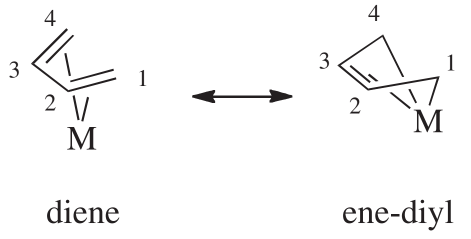

Chart1.

In an attempt to distinguish between these extremes, Müller *et al.* [19] have employed the parameter Δd, which is the difference between the average of the outer Ru–C (Ru–C(1) and Ru–C(4)) and inner Ru–C (Ru–C(2) and Ru–C(3)) distances, and the C(1)–Ru–C(4) angle (α). For the diene form, Δd lies between −0.1 and +0.1 Å, and α between 75° and 90°. For **2a**, the Δd and α values are estimated to be +0.009 Å and 79.33°, respectively. Therefore, according to this analysis, the diene extreme is the main contributor to the bonding in **2a**.

Similar complexes containing either acetonitrile or other nitriles were obtained from 2,3-dimethylbutadiene (**3a**–**d**), isoprene (**4a**, **4c**), (*E*)- and (*Z*)-1,3-pentadiene (**5a**), (*E*)-2-methyl-1,3-pentadiene [(*E*)-**6a**, **6c**, **6f**] and 1,3-cyclohexadiene (**7c**). The benzonitrile complexes are slightly more stable than those of acetonitrile or *t*-butyl cyanide.

Spectroscopic evidence shows that the coordinated nitriles are very labile. The EI-mass spectra do not show molecular ion peaks but, for example, a peak at *m*/*z* 291 in the spectra of the 2,3-dimethylbutadiene complexes **3a**–**d** can be assigned to the fragment $[Ru(C_6H_{10})(C_8H_{12})]^+$ and there are also intense peaks arising from the nitrile. The IR spectra show a ν(CN) band at *ca.* 2220–2240 cm^{-1}, close to the value for the free nitrile (2222–2260 cm^{-1}) [20]. The red 1,4-phthalonitrile 2,3-dimethylbutadiene complex **3d** shows only one ν(CN) band at 2220 cm^{-1} (2234 cm^{-1} for free phthalonitrile), even though only one of the CN groups is presumed to be coordinated. Although a dinuclear structure bridged by 1,4-phthalonitrile is a possible alternative, the elemental analysis of **3d** clearly supports a mononuclear formulation. Coordination of a nitrile through nitrogen usually causes an observable high frequency shift; a shift to lower frequency occurs only when the metal centre has a strong back-bonding ability [21]. We assume that the bands due to free and coordinated CN in **3d** probably overlap.

The ^{1}H NMR spectra of the acyclic 1,3-diene complexes show resonances characteristic of η^4-coordination at δ *ca.* 0.5 and 1.7 due to the inner and outer protons of the terminal methylene groups. They are shielded considerably relative to the corresponding resonances of the free dienes and resemble those of other *cisoid*-1,3-diene complexes of ruthenium(0), *e.g.*, $[Ru(\eta^6\text{-arene})(\eta^4\text{-}1,3\text{-diene})]$ [19,22] and $[Ru(L)(\eta^4\text{-}1,3\text{-diene})_2]$ [L = CO, PPh_3, $P(OMe)_3$] [23–25]. The 1,5-COD olefinic protons usually appear as two well-