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Preliminary communication

Synthesis and protonation of new 1,3-diene complexes of zerovalent ruthenium *

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Abstract

Complexes of general formula Ru(η^4-1,3-diene)(η^4-1,5-cyclooctadiene)(nitrile) are formed by reaction of various acyclic 1,3-dienes with Ru(η^6-naphthalene)(η^4-1,5-cyclooctadiene) (**1**) in the presence of nitriles. The coordinated nitrile is readily replaced by stronger π-acceptors such as CO, ^{t}BuNC, $P(OMe)_3$ and tertiary phosphines. In contrast, 1,3-cyclohexadiene reacts with **1** in the presence of benzonitrile to give Ru(1,3-C_6H_8)$_2$(NCPh). The mono-protonated salt obtained from the 2,3-dimethylbutadiene complex Ru(η^4-C_6H_{10})(η^4-1,5-C_8H_{12})(PEt_3) and HPF_6 contains an agostic methyl group whose rotation is almost frozen at −90°C.

It has been shown that coordinated naphthalene in the ruthenium(0) complex Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) (**1**) (1,5-C_8H_{12} = 1,5-cyclooctadiene) can be replaced under mild conditions by a variety of functionalized arenes to give arene-ruthenium(0) complexes, Ru(η^6-arene)(η^4-1,5-C_8H_{12}) [1,2]. The reaction is promoted by acetonitrile, which is thought to stabilize intermediate ruthenium(0)-naphthalene complexes of lower hapticity, and thus provides a useful alternative to syntheses based on Ru(η^6-C_8H_{10})(η^4-1,5-C_8H_{12})(C_8H_{10} = 1,3,5-cyclooctatriene) (**2**), for which the presence of hydrogen gas is necessary. We now find that, in the presence of a nitrile, the η^6-naphthalene in **1** is also readily replaced by 1,3-dienes, the nitrile being retained in the coordination sphere of the product.

A typical procedure is as follows. An excess of 2,3-dimethylbutadiene (2,3-C_6H_{10}) (0.20 ml, 1.77 mmol) is added to a slurry of **1** (300 mg, 0.89 mmol) in acetonitrile (4 ml). The mixture is stirred under nitrogen at room temperature for 3 h and evaporated to dryness in a vacuum. Naphthalene is removed by sublimation on to a −78°C probe. The solid residue is extracted with ether/hexane (1:1)

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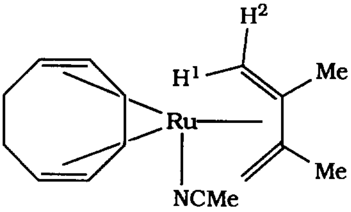
(8 ml) and the yellow-brown solution is filtered. Evaporation to ca. half-volume and cooling to −78°C for 2 days gives air-sensitive, gray crystals of Ru(η^4-2,3-C_6H_{10})(η^4-1,5-C_8H_{12})(NCMe) (**3**) (140–175 mg, 50–60%) [3*].



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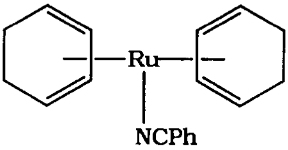
The corresponding Ru(η^4-1,3-diene)(η^4-1,5-C_8H_{12})(NCMe) complexes of 3-methyl-1,3-pentadiene (**4**) and isoprene (**5**) are obtained similarly. In the presence of acetonitrile, 1,3-cyclohexadiene (1,3-C_6H_8) displaces both naphthalene and 1,5-cyclooctadiene from **1**; the product is presumably Ru(1,3-C_6H_8)$_2$(NCMe), but its thermal sensitivity has prevented adequate characterization. The corresponding benzonitrile complex, Ru(1,3-C_6H_8)$_2$(NCPh) (**6**), is obtained as a brown solid [4*]. The analogous carbonyl complex, Ru(1,3-C_6H_8)$_2$(CO), has been isolated previously by thermal isomerization of Ru(η^5-C_6H_7)(η^3-C_6H_9)(CO), which is the initial product of reaction of CO at −196°C with the co-condensate of ruthenium atoms and either 1,3- or 1,4-cyclohexadiene [5].



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The CH_3CN resonance of **3** is broad at room temperature and it broadens further on addition of a small amount of acetonitrile, a feature indicative of rapid intermolecular exchange. This may also account for the failure to detect a resonance due to CH_3CN in the $^{13}C\{^1H\}$NMR spectra of **3** and **4**. Coordinated acetonitrile in **3** and **4** is easily replaced at room temperature by other ligands L [^{t}BuCN, PhCN, CO, ^{t}BuNC, PPh_3, PEt_3, P^nBu_3 and $P(OMe)_3$] to give stable, colorless or yellow complexes Ru(η^4-1,3-diene)(η^4-1,5-C_8H_{12})(L) in high yield. These compounds probably have a square pyramidal geometry similar to that found in the η^4-1,3,5-cyclooctatriene complex Ru(η^4-1,3,5-C_8H_{10})(η^4-1,5-C_8H_{12}){P(OMe)$_3$} [6] and in the *E*,*E*-dimethyl muconate complex Ru(η^4-$MeO_2CCH{=}CHCH{=}CHCO_2Me$)$_2${P(OMe)$_3$} [7].

Like their close relatives M(η^4-1,3-diene)L_3 (M = Fe, L = CO, P(OMe)$_3$; M = Ru; L = various tertiary phosphines or phosphites) [8–10], the new complexes are protonated by strong acids such as CF_3CO_2H or HPF_6 at the terminal carbon atom of the coordinated 1,3-diene to give agostic η^3-methallyl complexes. Addition of

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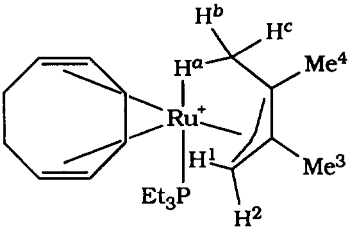
* Reference number with asterisk indicates a note in the list of references.

60% aqueous HPF_6 to a solution of the 2,3-dimethylbutadiene complex $Ru(\eta^4-C_6H_{10})(\eta^4-1,5-C_8H_{12})(L)$ ($L = PEt_3$) immediately precipitates the yellow salt $[Ru(\eta^3-C_6H_{11})(\eta^4-1,5-C_8H_{12})(PEt_3)]PF_6$ (7), which is stable in an inert atmosphere for ca. 24 h at room temperature [11*]. Similar but thermally less stable compounds are formed when L = CO, ${}^tBuNC$, PPh_3 and $P(OMe)_3$. A characteristic feature of the ^1H NMR spectrum of 7 in CD_2Cl_2 at 20°C is a broad singlet at δ -4.11 ppm corresponding to the agostic methyl protons H^a, H^b and H^c, which undergo rapid exchange as a consequence either of reversible Ru–H bond-breaking or of 'in-place' rotation of the methyl group [10]. There are also a complex multiplet at δ 0.12 ppm due to the inner allylic proton H^1, a singlet at δ 2.26 ppm due to the methyl protons Me^4, and a doublet at δ 2.53 ppm due to the methyl protons Me^3 (J_{13} 3.6 Hz). The olefinic protons of $1,5-C_8H_{12}$ appear as a pair of complex 2H-multiplets at δ 4.04 ppm and δ 3.2–3.0 ppm. The resonance due to the outer allylic proton H^2 cannot be located, and is probably masked by the PCH_2CH_3 multiplet at δ 1.1 ppm.



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On cooling to -40°C, the resonance at δ -4.11 collapses into the baseline and at -90°C one observes at 1 H-singlet at δ -12.6 ppm due to the agostic proton H^a and a 1 H-singlet at δ -1.1 ppm due to one of the remaining methyl protons, H^b or H^c; the other signals in the spectrum do not change between +20 and -90 °C. The singlet due to H^c or H^b would be expected to be at δ ca. 1.3 ppm and is probably buried beneath the CH_2 multiplets due to $1,5-C_8H_{12}$ and PEt_3. This observation of separate signals for the agostic methyl protons at low temperature as a consequence of slowing of the methyl group rotation is similar to that reported for the η^3-3-methylbutenyl and η^3-2,3-dimethylbutenyl iron complexes $[Fe(\eta^3\text{-dienyl})\{P(OMe)_3\}_3]BPh_4$ [8]. For η^3-butenyl ruthenium complexes of this type, broadening of the signal due to $H^{a,b,c}$ is evident at -80 °C, but separate signals are not observed [9].

Complex 1, which can now be synthesized in good yield [2,12], is clearly a useful precursor to new 1,3-diene complexes of ruthenium(0) whose chemistry and catalytic properties are currently being examined.

References and notes

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3 Anal. Found: C, 57.9; H, 7.8; N, 4.3. $C_{16}H_{25}NRu$ calc.: C, 57.8; H, 7.6; N, 4.2%. MS (70 eV) *m/z* 290 $[M - MeCN]^+$. IR (KBr) 2220 cm^{-1} [ν(CN)]. ^1H NMR (200 MHz, C_6D_6) δ 3.78–3.65 (m, 2H, =CH of C_8H_{12}), 2.84–2.40 (m, 6H, =CH, $2CH_2$ of C_8H_{12}), 2.22–1.92 (m, 10H, $2CH_2$ of C_8H_{12},

C*Me*=CH_2), 1.71 (s, 2H, H^2), 0.72 (s, 3H, CH_3CN), 0.52 (s, 2H, H^1). $^{13}C\{^1H\}$NMR (50 MHz, C_6D_6) δ 100.91 (C^2), 78.28, 72.22 (=CH of C_8H_{12}), 41.95 (C^1), 33.54, 31.98 (CH_2 of C_8H_{12}), 19.76 (C*Me*=CH_2).

4 Anal. Found: C, 64.2; H, 6.3; N, 3.7. $C_{19}H_{21}NRu$ calc.: C, 64.8; H, 6.0; N, 4.0%. MS(70 eV) m/z 258 $(M-\mathrm{PhCN})^+$. ^1H NMR (300 MHz, C_6D_6) δ 7.0–6.6 (m, 5H, C_6H_5), 4.24 (m, 4H, inner =CH of C_6H_8), 3.52 (m, 4 H, outer =CH of C_6H_8), 2.04 (approx. 1:2:2:1q, sepn 10.1, 15.7, 10.1 Hz, 8H, CH_2). Also unassigned broad singlet at δ 3.40 (approx. 4H), probably due to product of decomposition or polymerization. $^{13}C\{^1H\}$ NMR (50 MHz, C_6H_6) δ 76.71 (inner diene C), 54.50 (outer diene C), 22.72 (CH_2).

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