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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 $\text{Ru}(\eta^4\text{-1,3-diene})(\eta^4\text{-1,5-cyclooctadiene})(\text{nitrile})$ are formed by reaction of various acyclic 1,3-dienes with $\text{Ru}(\eta^6\text{-naphthalene})(\eta^4\text{-1,5-cyclooctadiene})$ (**1**) in the presence of nitriles. The coordinated nitrile is readily replaced by stronger π -acceptors such as CO, tBuNC , P(OMe)_3 and tertiary phosphines. In contrast, 1,3-cyclohexadiene reacts with **1** in the presence of benzonitrile to give $\text{Ru}(\eta^6\text{-C}_6\text{H}_8)_2(\text{NCPh})$. The mono-protonated salt obtained from the 2,3-dimethylbutadiene complex $\text{Ru}(\eta^4\text{-C}_6\text{H}_{10})(\eta^4\text{-1,5-C}_8\text{H}_{12})(\text{PEt}_3)$ and HPF_6 contains an agostic methyl group whose rotation is almost frozen at -90°C .

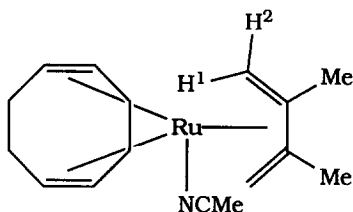
It has been shown that coordinated naphthalene in the ruthenium(0) complex $\text{Ru}(\eta^6\text{-C}_{10}\text{H}_8)(\eta^4\text{-1,5-C}_8\text{H}_{12})$ (**1**) ($\eta^4\text{-1,5-C}_8\text{H}_{12}$ = 1,5-cyclooctadiene) can be replaced under mild conditions by a variety of functionalized arenes to give arene-ruthenium(0) complexes, $\text{Ru}(\eta^6\text{-arene})(\eta^4\text{-1,5-C}_8\text{H}_{12})$ [**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 $\text{Ru}(\eta^6\text{-C}_8\text{H}_{10})(\eta^4\text{-1,5-C}_8\text{H}_{12})(\text{C}_8\text{H}_{10}$ = 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 ($2,3\text{-C}_6\text{H}_{10}$) (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)

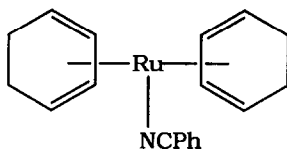
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* Dedicated to Professor Akio Yamamoto on the occasion of his retirement from the Tokyo Institute of Technology and in recognition of his contributions to organometallic chemistry.

(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 $\text{Ru}(\eta^4\text{-}2,3\text{-C}_6\text{H}_{10})(\eta^4\text{-}1,5\text{-C}_8\text{H}_{12})(\text{NCMe})$ (**3**) (140–175 mg, 50–60%) [3*].

**3**

The corresponding $\text{Ru}(\eta^4\text{-}1,3\text{-diene})(\eta^4\text{-}1,5\text{-C}_8\text{H}_{12})(\text{NCMe})$ complexes of 3-methyl-1,3-pentadiene (**4**) and isoprene (**5**) are obtained similarly. In the presence of acetonitrile, 1,3-cyclohexadiene ($1,3\text{-C}_6\text{H}_8$) displaces both naphthalene and 1,5-cyclooctadiene from **1**; the product is presumably $\text{Ru}(1,3\text{-C}_6\text{H}_8)_2(\text{NCMe})$, but its thermal sensitivity has prevented adequate characterization. The corresponding benzonitrile complex, $\text{Ru}(1,3\text{-C}_6\text{H}_8)_2(\text{NCPH})$ (**6**), is obtained as a brown solid [4*]. The analogous carbonyl complex, $\text{Ru}(1,3\text{-C}_6\text{H}_8)_2(\text{CO})$, has been isolated previously by thermal isomerization of $\text{Ru}(\eta^5\text{-C}_6\text{H}_7)(\eta^3\text{-C}_6\text{H}_9)(\text{CO})$, 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].

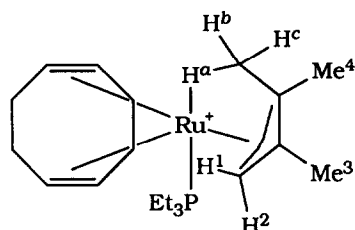
**6**

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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3** and **4**. Coordinated acetonitrile in **3** and **4** is easily replaced at room temperature by other ligands L [$^t\text{BuCN}$, PhCN , CO , $^t\text{BuNC}$, PPh_3 , PEt_3 , P^nBu_3 and P(OMe)_3] to give stable, colorless or yellow complexes $\text{Ru}(\eta^4\text{-}1,3\text{-diene})(\eta^4\text{-}1,5\text{-C}_8\text{H}_{12})(\text{L})$ in high yield. These compounds probably have a square pyramidal geometry similar to that found in the $\eta^4\text{-}1,3,5\text{-cyclooctatriene}$ complex $\text{Ru}(\eta^4\text{-}1,3,5\text{-C}_8\text{H}_{10})(\eta^4\text{-}1,5\text{-C}_8\text{H}_{12})(\text{P(OMe)}_3)_2$ [6] and in the *E,E*-dimethyl muconate complex $\text{Ru}(\eta^4\text{-MeO}_2\text{CCH=CHCH=CHCO}_2\text{Me})_2(\text{P(OMe)}_3)_2$ [7].

Like their close relatives $\text{M}(\eta^4\text{-}1,3\text{-diene})\text{L}_3$ ($\text{M} = \text{Fe}$, $\text{L} = \text{CO}$, P(OMe)_3 ; $\text{M} = \text{Ru}$; $\text{L} =$ various tertiary phosphines or phosphites) [8–10], the new complexes are protonated by strong acids such as $\text{CF}_3\text{CO}_2\text{H}$ or HPF_6 at the terminal carbon atom of the coordinated 1,3-diene to give agostic $\eta^3\text{-methallyl}$ complexes. Addition of

* 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 $\text{Ru}(\eta^4\text{-C}_6\text{H}_{10})(\eta^4\text{-1,5-C}_8\text{H}_{12})(\text{L})$ ($\text{L} = \text{PEt}_3$) immediately precipitates the yellow salt $[\text{Ru}(\eta^3\text{-C}_6\text{H}_{11})(\eta^4\text{-1,5-C}_8\text{H}_{12})(\text{PEt}_3)]\text{PF}_6$ (**7**), which is stable in an inert atmo-



7

sphere for ca. 24 h at room temperature [11*]. Similar but thermally less stable compounds are formed when $\text{L} = \text{CO}$, $t\text{BuNC}$, 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 $\delta -4.11$ 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 $\delta 0.12$ ppm due to the inner allylic proton H^1 , a singlet at $\delta 2.26$ ppm due to the methyl protons Me^4 , and a doublet at $\delta 2.53$ ppm due to the methyl protons Me^3 (J_{13} 3.6 Hz). The olefinic protons of $1,5\text{-C}_8\text{H}_{12}$ appear as a pair of complex 2H-multiplets at $\delta 4.04$ ppm and $\delta 3.2\text{--}3.0$ 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 $\delta 1.1$ ppm.

On cooling to -40°C , the resonance at $\delta -4.11$ collapses into the baseline and at -90°C one observes at 1 H-singlet at $\delta -12.6$ ppm due to the agostic proton H^a and a 1 H-singlet at $\delta -1.1$ 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 $1,5\text{-C}_8\text{H}_{12}$ 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 $\eta^3\text{-3-methylbutenyl}$ and $\eta^3\text{-2,3-dimethylbutenyl}$ iron complexes $[\text{Fe}(\eta^3\text{-dienyl})(\text{P(OMe)}_3)_3]\text{BPh}_4$ [8]. For $\eta^3\text{-butenyl}$ ruthenium complexes of this type, broadening of the signal due to $\text{H}^{a,b,c}$ 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. $\text{C}_{16}\text{H}_{25}\text{NRu}$ calc.: C, 57.8; H, 7.6; N, 4.2%. MS (70 eV) m/z 290 $[\text{M} - \text{MeCN}]^+$. IR (KBr) 2220 cm^{-1} [$\nu(\text{CN})$]. ^1H NMR (200 MHz, C_6D_6) δ 3.78–3.65 (m, 2H, $=\text{CH}$ of C_8H_{12}), 2.84–2.40 (m, 6H, $=\text{CH}$, 2CH_2 of C_8H_{12}), 2.22–1.92 (m, 10H, 2CH_2 of C_8H_{12} ,

- $CMe=CH_2$), 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 ($CMe=CH_2$).
- 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 ($M - PhCN$) $^+$. 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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