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Homogeneous catalysis of the hydrogenation of 9,10-dimethylanthracene to 1,2-dihydro-9,10-dimethylanthracene by $[RuH(PPh_3)_2(9,10\text{-dimethylanthracene})]^+$ †

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Abstract

The cationic ruthenium arene complex, $[RuH(PPh_3)_2(\eta^6\text{-}9,10\text{-dimethylanthracene})]^+$ (**1**), serves as a catalyst for the hydrogenation of 9,10-dimethylanthracene (**2**), initially to 1,2-dihydro-9,10-dimethylanthracene (**3**), followed by hydrogenation of the latter to 1,2,3,4-tetrahydro-9,10-dimethylanthracene (**4**). The first step, i.e., **2** → **3**, obeys the rate-law $-d[\mathbf{2}]/dt = k_{cat}[\mathbf{1}][H_2]$, where $k_{cat} = (1.5 \pm 0.1) \times 10^{-3}$ M^{-1} s^{-1} at 25°C in $CDCl_3$.

Only a few homogeneous catalysts for the hydrogenation of arenes have been reported, notably those derived from the precursors, $[RuH_5(PPh_3)_2]^-$ [1], $[RuH_4(PPh_3)_2]$ [2], $[\overline{Rh(Ph_2PCH_2CH_2PPh_2)}(MeOH)_2]^+$ [3], $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ [4], $[HCo(CO)_4]$ [5] and $[Co(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}_3]$ [6]. Since alkenes typically are hydrogenated more readily than arenes by such catalysts, it is not surprising that "olefinic" intermediates, i.e., compounds containing partially hydrogenated rings, are not detected in these systems [7*]. In this communication we describe the homogeneous hydrogenation of 9,10-dimethylanthracene [10*] to the olefinic product, 1,2-dihydro-9,10-dimethylanthracene, catalyzed by $[RuH(PPh_3)_2(9,10\text{-dimethylanthracene})]^+$. We call attention to the marked distinction of this selectivity compared with earlier examples of the homogeneous catalytic hydrogenation of anthracene to 9,10-dihydroanthracene [5] and 1,2,3,4-tetrahydroanthracene [1–3], in the latter cases without detection of 1,2-dihydro intermediates.

$[RuH(PPh_3)_2(\eta^6\text{-}Me_2An)]^+[O_3SCF_3]^-$ (**1**, Me_2An = 9,10-dimethylanthracene) [11*] was found to catalyze the hydrogenation of 9,10-dimethylanthracene in

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† Dedicated to the memory of the late Professor Piero Pino.

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

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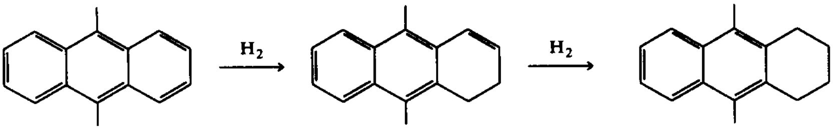
CH_2Cl_2 or $CHCl_3$ solution at 25 °C in accord with the following sequence of steps. **2**, **3** and **4** were separable by GLC.



Me_2An (**2**) $\quad$ 1,2-H_2Me_2An (**3**) $\quad$ 1,2,3,4-H_4Me_2An (**4**) $\quad$ (1)

Stopping the reaction prior to completion yielded the intermediate **3** with high selectivity. Thus, reaction of 1.55 mmol **2** in CH_2Cl_2 (10 ml) with H_2 (1 atm) for 12 days at 25 °C resulted in a mixture containing 64% unreacted **2**, 32% **3** and 4% **4**, as determined by GLC (**3** also identified by GLC–MS). The corresponding reaction with D_2 yielded 1,2-D_2-9,10-dimethylanthracene without detectable deuterium scrambling. Hydrogenation of a mixture of **2**, **3** and **4** at 25 °C, with $[RuH_4(PPh_3)_3]$ as catalyst, resulted in conversion of **3** to **4** without significant change in the concentration of **2**.

The time dependencies of the concentrations of **2**, **3** and **4** in a representative catalytic experiment are depicted in Fig. 1. From the shapes of the plots it is clear that **4** derives from the hydrogenation of the intermediate dihydro compound, **3**, rather than directly from **2**. During the reaction, the catalyst was gradually deactivated toward hydrogenation of **2**, probably by reversible displacement of Me_2An from **1** by **3** to form an inactive $[RuH(PPh_3)_2(\mathbf{3})]^+$ complex. The accompanying appearance of a new ^1H signal at δ −14.0 ppm (t, $^2J(HP) = 33$ Hz) and a new $^{31}P\{^1H\}$ signal at δ 48.1 ppm is consistent with this.

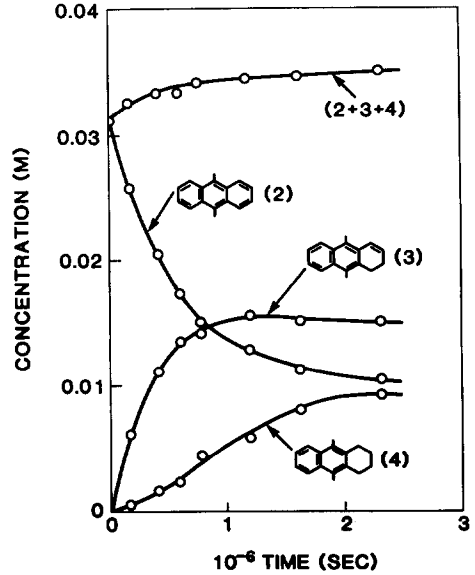


Fig. 1. Variation of the concentrations of **2**, **3** and **4** during the $[RuH(PPh_3)_2(Me_2An)]^+$-catalyzed hydrogenation of **2** in $CDCl_3$ at 25 °C. Initial concentrations: 5.3×10^{-3} *M* $[RuH(PPh_3)_2(Me_2An)]^+$, 3.1×10^{-2} *M* **2**; 732 Torr H_2.

The kinetics of the first stage of reaction 1, i.e., **2** → **3**, were monitored in $CDCl_3$ by measuring the initial rates of disappearance of **2** by ^1H NMR. The results, summarized in Fig. 2 and Table 1, are consistent with the rate-law, eq. 2:

$$-\mathrm{d}[\mathbf{2}]/\mathrm{d}t = k_{\mathrm{obsd}} = k_{\mathrm{cat}}\left[\mathrm{RuH(PPh_3)_2(Me_2An)}^+\right][\mathrm{H_2}][\mathrm{Me_2An}]^0 \qquad (2)$$

where $k_{\mathrm{cat}} = (1.5 \pm 0.1) \times 10^{-3}\ M^{-1}\ \mathrm{s}^{-1}$.

The results reported here do not permit elucidation of the detailed mechanism of these catalytic hydrogenation reactions. Clearly, the first step is hydrogenation of *one* of the double bonds in a terminal ring of **2**. Presumably, hydrogenation of the second double bond, i.e., of **3**, is disfavored by rapid displacement from the resulting ruthenium complex $[RuH(PPh_3)_2(\mathbf{3})]^+$, of **3** by **2** to form a more stable η^6-arene complex. A marked preference for η^6-arene vs η^2-alkene coordination is precedented for at least one other class of cationic complexes, i.e., [Rh(diphosphine)(unsat)]$^+$ (unsat = alkene or arene) [12]. Hydrogenation of one of the end rings of **2** also is expected to reduce the binding strength of the other end ring, as reflected, for example, in the related greater binding of anthracene vs naphthalene. Thus the equilibrium constant for reaction 3 was determined to be 0.041 in CD_2Cl_2 at 23° C.

$$\left[\mathrm{RuH(PPh_3)_2(Me_2An)}\right]^+ + \text{naphthalene} \rightleftharpoons$$

$$\left[\mathrm{RuH(PPh_3)_2(naphthalene)}\right]^+ + \mathrm{Me_2An} \qquad (3)$$

The selectivity toward 1,2-hydrogenation exhibited by $[RuH(PPh_3)_2(\mathbf{2})]^+$ contrasts with the 1,2,3,4-hydrogenation previously reported for $[RuH(PPh_3)_2(\text{anthracene})]^-$ [1,2]. This may be related to η^6-binding of anthracene in the former case vs η^4-binding in the latter, with correspondingly greater tendency for the intermediate 1,2-dihydro compound to be displaced in the former case.

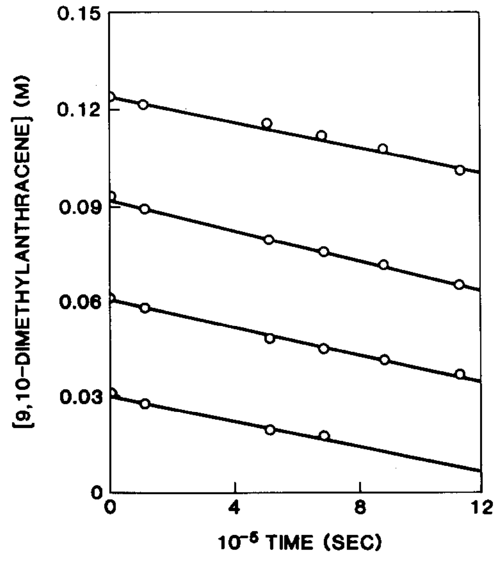


Fig. 2. Initial rate plots for the $[RuH(PPh_3)_2(Me_2An)]^+$-catalyzed hydrogenation of 9,10-dimethylanthracene (**2**) in $CDCl_3$ at 25° C. 5.2×10^{-3} *M* $[RuH(PPh_3)_2(Me_2An)]^+[O_3SCF_3]^-$; 732 Torr H_2.

Table 1

Kinetic data for the $[RuH(PPh_3)_2(Me_2An)]^+$-catalyzed hydrogenation of 9,10-dimethylanthracene (Me_2An) in $CDCl_3$ at 25 °C

10^3 $[RuH(PPh_3)_2(Me_2An)]^+$ (M)	10^2 $[Me_2An]$ (M)	H_2 pressure (Torr)	10^3 $[H_2]$ [a] (M)	10^8 k_{obsd} ($M\ s^{-1}$)	10^3 k_{cat} ($M^{-1}\ s^{-1}$)
5.21	3.10	732	2.64	1.91	1.39
5.21	6.19	732	2.64	2.15	1.56
5.21	9.29	732	2.64	2.38	1.73
5.21	12.4	732	2.64	2.02	1.47
5.38	3.10	732	2.64	2.01	1.42
5.38	3.10	572	2.06	1.58	1.43
5.38	3.10	412	1.49	1.03	1.29
10.32	3.07	732	2.64	3.91	1.44
5.16	3.07	732	2.64	3.07	(2.25) [b]
2.58	3.07	732	2.64	1.14	1.67
					Mean 1.49 ± 0.13

[a] Based on solubility of H_2 (0.0614 cm^3 H_2/cm^3 $CHCl_3$) from H. Stephen and T. Stephen (Eds.), *Solubilities of Inorganic and Organic Compounds*, Pergamon Press, Oxford, 1963, Table 1703. [b] Not included in computing mean value.

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10 9,10-Dimethylanthracene was used in these studies, rather than anthracene, because of its enhanced solubility and the utility of the methyl ^1H NMR signals.

11 Synthesis of $[RuH(PPh_3)_2\eta^6\text{-9,10-dimethylanthracene})]^+[O_3SCF_3]^-$ (1). In an inert atmosphere glove box, a 50 ml Schlenk flask was charged with 0.20 g (0.22 mmol) of $RuH_4(PPh_3)_3$. On the Schlenk line, 15 ml of CH_2Cl_2 was added to the flask by syringe under H_2 flush at −78 °C. After warming the mixture to dissolve the solid, CF_3SO_3H (23 μl, 0.26 mmol) was added at −78 °C, followed, after stirring for 5 min, by addition of 9,10-dimethylanthracene (50 mg, 0.24 mmol). After purging with N_2, the mixture was gradually warmed to room temperature and stirred for an additional hour. The solvent was removed and the resulting solid was washed with 3 × 15 ml of pentane. Vacuum drying afforded a brick-red solid. Yield; 0.17 g, 77%. ^1H NMR (CD_2Cl_2): δ 8.28 (m, 2H), 7.88 (m, 2H), 7.23 (t, $^3J(HH) = 7.2$ Hz, 6H), 7.04 (t, $^3J(HH) = 7.2$ Hz, 12H), 6.87 (br s, 12H), 6.27 (br s, 2H), 5.35 (br s, 2H), 2.34 (s, 6H), −15.9 (t, $^2J(HP) = 31$ Hz, 1H), ^{31}P NMR (CD_2Cl_2): δ 47.4 (s, $^2J(HP) = 29$ Hz).

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