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Catalysis of the hydrogenation of benzophenone by polyhydride complexes of tris(triphenylphosphine)ruthenium *

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Abstract

The following reactions have been identified in THF solution (P=PPh_3): (1) $[RuH_4P_3]$ (**3**) + $Ph_2C{=}O \rightarrow [RuH_2P_3(THF)]$ (**4**) + Ph_2CHOH. (2) **4** + $H_2 \rightarrow$ **3**. (3) **4** + $2Ph_2C{=}O \rightarrow [RuH(O{=}CPhC_6H_4)P_3]$ (**5**) + Ph_2CHOH. (4) **5** + $2H_2 \rightarrow$ **4** + Ph_2CHOH. (5) $[RuH_3P_3]^-$ (**1**) + $Ph_2C{=}O \rightarrow$ **4** + Ph_2CHO^-. (6) **3** + $Ph_2CHO^- \rightarrow$ **1** + Ph_2CHOH. Each of the following combination of steps constitutes one of a set of interconnected catalytic cycles for the hydrogenation of $Ph_2C{=}O$ to Ph_2CHOH: (1) + (2); (3) + (4); (2) + (6) + (5).

Introduction

Recently we described the hydrogenation of cyclohexanone (eq. 3) with catalysts derived from the neutral and anionic ruthenium polyhydride complexes, $[RuH_4P_3]$ and $[RuH_3P_3]^-$ (P=PPh_3), respectively [1]. Hydrogenation was shown to proceed through the catalytic cycle depicted by eq. 1 and 2, in which the first step is rate-determining. $[RuH_3P_3]^-$ apparently is not itself effective as a catalyst for the hydrogenation of cyclohexanone but during an induction period is converted to an active catalyst, presumably $[RuH_4P_3]$, which is formed by protonation of $[RuH_3P_3]^-$ by cyclohexanol (eq. 4).

$$[RuH_4P_3] + \text{cyclo-}C_6H_{10}O \rightarrow [RuH_2P_3S] + \text{cyclo-}C_6H_{11}OH \quad (1)$$
$$(S = \text{THF or cyclo-}C_6H_{10}O)$$

$$[RuH_2P_3S] + H_2 \rightarrow [RuH_4P_3] \quad (2)$$

* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

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$$\text{cyclo-}C_6H_{10}O + H_2 \xrightarrow{[RuH_4P_3]} \text{cyclo-}C_6H_{11}OH \quad (3)$$

$$[RuH_3P_3]^- + \text{cyclo-}C_6H_{11}OH \rightleftharpoons [RuH_4P_3] + \text{cyclo-}C_6H_{11}O^- \quad (4)$$

In this paper we describe the extension of these studies to the catalytic hydrogenation of benzophenone, a system which exhibits somewhat different and more complex behaviour.

Experimental

General

All manipulations were conducted with rigorous exclusion of air and moisture, by use of a high vacuum line (10^{-4}–10^{-5} torr), an argon-filled Schlenck line, and a nitrogen-filled glove box (Vacuum Atmospheres). Solvents and reagents were stored in the glove box.

Materials

Benzophenone was recrystallized from ether/hexane (10 g/20 ml; 1/1 v/v) in an H-tube under argon. Potassium diphenylmethoxide was prepared from the corresponding alcohol as described by Morton and Claff [2] but with $K[HBEt_3]$ in place of KNH_2 as the base. Other reagents and solvents were purified as previously described [1].

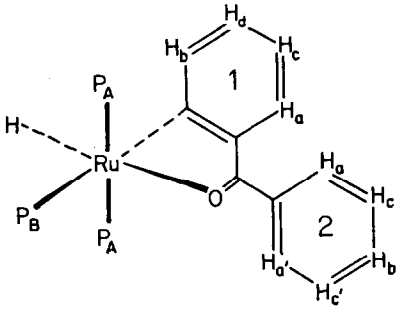
K[*fac*-RuH_3P_3] (**1**), $[RuH_2P_3(N_2)]$ (**2**), $[RuH_4P_3]$ (**3**) and $[RuH_2P_3(THF)]$ (**4**) were prepared (the latter in situ) as previously described [1].

mer-$[\overline{RuH(O{=}CPhC_6H_4)}P_3$ (**5**) [3]. To a 100 ml flask equipped with an O-ring ball joint and stopcock assembly, was added 2.2 mmol **1** or **2** (prepared in situ from $[RuH_2P_3(N_2)]$ and H_2) and 15.9 mmol benzophenone. Dry degassed THF was transferred into the flask from a reservoir containing a sodium ketyl solution of THF. The resulting solution was stirred for 12 h at 45 °C. Evaporation to ca. 15 ml, followed by addition of 40 ml of hexane, yielded a red oil which crystallized slowly. Filtration and washing with hexane yielded 1.5 g of crude **5**, this was dissolved in benzene (30 ml) and the solution filtered. Addition of octane and slow evaporation of the solvent yielded 0.9 g (60%) of red crystalline **5**. ^1H NMR (C_6D_6): δ −14.67 (td, 1H, RuH, $J(P_A–H) \sim 30$ Hz, $J(P_B–H) \sim 15$ Hz), 6.28 (br t, 1H, $H_d(1)$, $J \sim 7$ Hz), 6.51 (br t, 1H, $H_c(1)$, $J \sim 7$ Hz), 6.83 (br t, 12H, *meta* protons of P_APh_3, $J \sim 7$ Hz), 6.88 (overlapping t's, 13H, *meta*-protons of P_BPh_3, *para*-protons of P_APh_3 and $H_b(1)$, 6.95 (br t, 3H, *para*-protons of P_BPh_3, $J \sim 7$ Hz), 7.26 (m, 3H, $H_b(2)$, $H_c(2)$, $H_{c'}(2)$), 7.34 (m, 12H, *ortho*-protons of P_APh_3), 7.46 (br d, 2H, $H_a(2)$, $H_{a'}(2)$, $J \sim 7$ Hz), 7.52 (br d, 1H, $H_a(1)$, $J \sim 7$ Hz), 7.76 (br t, 6H, *ortho*-protons of P_BPh_3) (assignments based on selective decoupling experiments). $^{31}P\{^1H\}$ NMR(C_6D_6): 43.5 (t, 1P, P_B, J ($P_A–P_B$) ~ 23 Hz), 53.2 (d, 2P, P_A). These signals split into a doublet of triplets and a doublet of doublets, respectively, upon selective decoupling of the aryl protons. IR (Nujol): 1938 (m, Ru–H), 1583 cm^{-1} (w, C=O).

$[\overline{RuH(O{=}CPh_2C_6H_4)}P_2(CO)]$ (**6**). **5** (0.41 g, (0.37 mmol) and 10 ml of benzene were placed in a 100 ml N_2-filled flask equipped with an O-ring ball joint and stopcock assembly. The solution was frozen, the flask evacuated, and carbon monoxide (1 atm) admitted. The stopcock was closed to seal the flask, then the solution was stirred for 30 min at 25 °C, during which the color changed from red to

yellow. The volume was reduced to 15 ml by evaporation and 15 ml of hexane was added to give a yellow precipitate, which was washed with hexane (3 × 10 ml) to yield 0.26 g (80%) of **6**. ^{1}H NMR (C_6D_6): δ − 14.1 (t, 1H, Ru-H, J(P–H) ~ 15 Hz), 6.49 (br t, 1H, $H_c(1)$ or $H_d(1)$, J ~ 7 Hz), 6.58 (br t, 1H, $H_c(1)$ or $H_d(1)$, J ~ 7 Hz), 6.95 (m, 18H, *meta*- and *para*-PPh_3 protons), 7.08 (m, 5H, $H_a(2)$, $H_{a'}(2)$, $H_b(2)$, $H_{b'}(2)$, $H_c(2)$), 7.26 (d, 1H, $H_a(1)$ or $H_b(1)$, J 7 ~ Hz), 7.56 (d, 1H, $H_a(1)$ or $H_b(1)$, J ~ 7 Hz), 7.64 (m, 12H, *ortho*-PPh_3 protons). $^{31}P\{^1H\}$ NMR (C_6D_6): 53.6 (s, split into a doublet on selective decoupling of the aryl protons). IR (Nujol): 1987(m) (Ru–H), 1910(s) (CO), 1553(w) cm^{-1} (C=O).

Procedures. All reactions were performed in THF-d_8 solution and monitored by ^{1}H NMR spectroscopy (University of Chicago 500 MHz spectrometer). ^{31}P NMR spectra were recorded with a Nicolet 200 MHz spectrometer. Chemical shifts are expressed in ppm upfield from $Si(CH_3)_4$(^{1}H) or 85% H_3PO_4(^{31}P). Infrared spectra were recorded with a Perkin–Elmer 283 or Nicolet MX-5 FT1R spectrophotometer.



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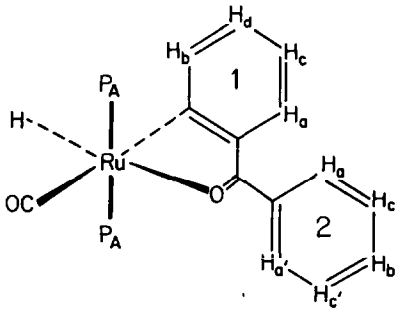

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Results and discussion

Reaction of [Ru$_4$(PPh$_3$)$_3$] with Ph$_2$CHO$^-$. Reaction of [RuH_4P_3] (0.022 M) with an excess of K[Ph_2CHO] (0.30 M) in THF-d_8 at 25 °C resulted in immediate and quantitative conversion into [$RuH_3P_3^-$] (0.021 M) and Ph_2CHOH (0.018 M), in accord with eq. 5. The corresponding reaction of 0.022 M [RuH_4P_3] with 0.017 M Ph_2CHO^- yielded a final solution containing 0.012 M [RuH_4P_3], 0.010 M [$RuH_3P_3^-$], 0.007 M Ph_2CHO^- and 0.010 M Ph_2CHOH. This provides evidence for the reversibility of reaction 5 and yields a value of 1.2 for the equilibrium constant $K_4^{eq} = [RuH_3P_3^-][Ph_2CHOH]/[RuH_4P_3][Ph_2CHO^-]$. Similar reversibility has been reported previously for the reaction of [RuH_4P_3] with cyclo-$C_6H_{11}O^-$ [1].

$$[RuH_4P_3] + Ph_2CHO^- \rightleftharpoons [RuH_3P_3]^- + Ph_2CHOH \quad (5)$$

Reaction of [RuH$_4$(PPh$_3$)$_3$] with Ph$_2$C=O. Reaction of [RuH_4P_3] (0.012 M) with an excess of $Ph_2C{=}O$ (0.17 M) at 45 °C for 36 min resulted in complete (> 90%) conversion into [$\overline{RuH(O{=}CPhC_6H_4)P_3}$] and formation of Ph_2CHOH (0.023 M by NMR; 0.025 by GC) in accord with eq. 7. Reaction of 0.019 M [RuH_4P_3] with an equivalent concentration (0.019 M) of $Ph_2C{=}O$ yielded, after 26 h at 45 °C 0.0044 M (24%) unreacted [RuH_4P_3], 0.0086 M (48%) of [RuH_2P_3(THF)] and 0.0046 M (25%) [$\overline{RuH(O{=}CPhC_6H_4)P_3}$], together with 0.017 M Ph_2CHOH. This provided convincing evidence that reaction 8 proceeds through the stepwise sequence of eq. 6 and 7.

$$[RuH_4P_3] + Ph_2C{=}O \rightarrow [RuH_2P_3(THF)] + Ph_2CHOH \quad (6)$$

$$[RuH_2P_3(THF)] + 2Ph_2C{=}O \rightarrow [\overline{RuH(O{=}CPhC_6H_4)}P_3] + Ph_2CHOH \quad (7)$$

$$[RuH_4P_3] + 3Ph_2C{=}O \rightarrow [\overline{RuH(O{=}CPhC_6H_4)}P_3] + 2Ph_2CHOH \quad (8)$$

$[\overline{RuH(O{=}CPhC_6H_4)}P_3]$ was prepared and characterized previously by Cole-Hamilton and Wilkinson [3]. This compound arises in our studies in a somewhat different context and we report here (see Experimental) an alternative synthesis. Treatment of a benzene solution of $[\overline{RuH(O{=}CPhC_6H_4)}P_3]$ with CO (see Experimental) resulted in displacement of the unique equatorial PPh_3 ligand by CO and formation of $[\overline{RuH(O{=}CPhC_6H_4)}P_2(CO)]$ (**6**). Several analogues of **6**, including the structurally characterized complex $[\overline{RuCl(O{=}C(p\text{-}MePh)(C_6H_3Me)}(PMe_2Ph)_2]$, have recently been reported [4].

Reaction of $[RuH_3P_3]^-$ with $Ph_2C{=}O$. Reaction of 0.024 *M* $[RuH_3P_3]^-$ with an excess of $Ph_2C{=}O$ (0.33 *M*) in THF-d_8 yielded after 1.7 h at 45°C, 0.017 *M* $[\overline{RuH(O{=}CPhC_6H_4)}P_3]$ and 0.0007 *M* $[RuH_2P_3]$, as well as 0.022 *M* Ph_2CHO^- and 0.024 *M* Ph_2CHOH, in accord with eq. 8. Reaction of 0.070 *M* $[RuH_3P_3]^-$ with ca. 0.5 equiv. (~0.035 *M*) $Ph_2C{=}O$ yielded, after 8.5 h at 45°C, 0.030 *M* (43%) unreacted $[RuH_3P_3]^-$, 0.006 *M* $[RuH_4P_3]$ and 0.022 *M* $[RuH_2P_3(THF)]$, together with 0.036 *M* Ph_2CHO^- and 0.012 *M* Ph_2CHOH (by ^1H NMR). This is consistent with the stepwise reaction sequence corresponding to eq. 9 followed by eq. 7, yielding the overall reaction 10.

$$[RuH_3P_3]^- + Ph_2C{=}O \rightarrow [RuH_2P_3(THF)] + Ph_2CHO^- \quad (9)$$

$$[RuH_3P_3]^- + 3Ph_2C{=}O \rightarrow [\overline{RuH(O{=}CPhC_6H_4)}P_3] + Ph_2CHOH + Ph_2CHO^- \quad (10)$$

Reactions of $[RuH_2P_3(THF)]$ and $[\overline{RuH(O{=}CPhC_6H_4)}P_3]$ with H_2. Reaction of $[RuH_2P_3(THF)]$ and $[\overline{RuH(O{=}CPhC_6H_4)}P_3]$ with H_2 (1 atm) in THF-d_8 at 25°C, resulted in rapid conversion (< 5 min) into $[RuH_4P_3]$ (~70 and ~80%, respectively, monitored by ^1H NMR spectroscopy) in accord with eq. 11 and 12.

$$[RuH_2P_3(THF)] + H_2 \rightarrow [RuH_4P_3] \quad (11)$$

$$[\overline{RuH(O{=}CPhC_6H_4)}P_3] + 3H_2 \rightarrow [RuH_4P_3] + Ph_2CHOH \quad (12)$$

Catalytic hydrogenation of benzophenone. The stoichiometric reactions identified in these studies can be combined to define three catalytic cycles for the hydrogenation of benzophenone. These correspond to the combinations of eq. 6 and 11, eq. 7 and 12, and eq. 9, 11 and 5, respectively. The superposition of these catalytic cycles is depicted in Fig. 1, in which they are seen to be connected through the common intermediate, $[RuH_2(PPh_3)_2(THF)]$ (abbreviated $[RuH_2P_3]$). The necessary kinetic studies have not yet been performed to determine the overall catalytic behavior and the relative contributions of these different pathways.

The catalytic hydrogenation of benzophenone differs in two striking respects from that of cyclohexanone described earlier [1], namely:

(1) The operation of the catalytic cycle involving the metallated intermediate, $[\overline{RuH(O{=}CPhC_6H_4)}P_3]$. This reflects the well recognized widespread tendency of ruthenium to undergo metallation reactions with aromatic C–H bonds [5].

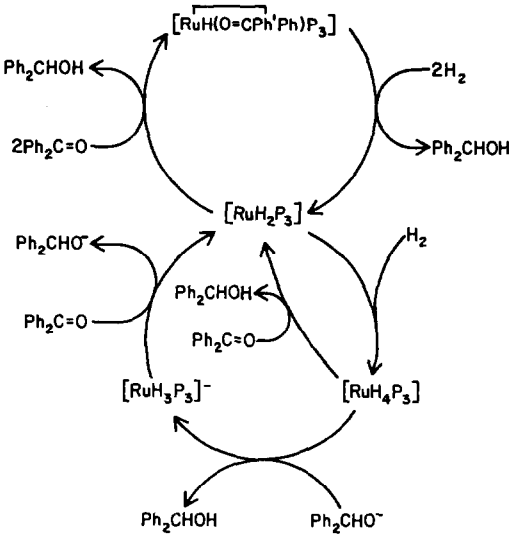

Fig. 1. Catalytic cycles for the $[RuH_4P_3]$-, $[RuH_2P_3]$- and $[RuH_3P_3]^-$-catalyzed hydrogenation of benzophenone ($P = PPh_3$).

(2) The operation of a catalytic cycle involving the anionic catalyst, $[RuH_3P_3]^-$, which was found to be inactive for the hydrogenation of cyclohexanone. This is plausibly interpreted in terms of the greater electrophilicity of benzophenone.

Acknowledgment

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