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Note

Dehydrogenation of cyclohexenes to cyclohexadienes by $[(PPh_3)_2Rh]^+$. The isolation of an intermediate in the dehydrogenation of cyclohexane to benzene: crystal structure of $[(\eta^4\text{-}C_6H_8)Rh(PPh_3)_2][closo\text{-}CB_{11}H_6Br_6]$

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Abstract

Treatment of the arene bridged dimer $[(PPh_3)_2Rh]_2[closo\text{-}CB_{11}H_6Br_6]_2$ with eight equivalents of cyclohexene affords $[(\eta^4\text{-}C_6H_8)Rh(PPh_3)_2][closo\text{-}CB_{11}H_6Br_6]$ with the concomitant formation of one equivalent of cyclohexane, while 1-methylcyclohexane and 4-methylcyclohexane both give 2-methylcyclohexa-1,3-diene complexes; all of these products are intermediates in the catalytic dehydrogenation pathway of cyclohexane to benzene.

Keywords: Dehydrogenation; Cyclohexene; C–H activation; Rhodium; X-ray structure

1. Introduction

The catalytic dehydrogenation of alkanes and cycloalkanes mediated by late transition metal complexes has been of interest since the first report by Crabtree over two decades ago, in which $[IrH_2(Me_2CO)_2(PPh_3)_2]^+$ dehydrogenates cyclopentanes to cyclopentadienyls using a hydrogen acceptor [1]. Since then, other hydrogen acceptor and acceptor-less systems have been discovered [2,3]. In particular, recent work by Jensen has shown that Iridium PCP-pincer complexes give highly active and robust catalysts for alkane activation [3]. Scheme 1 shows an abbreviated mechanistic pathway for the transfer dehydrogenation of cyclohexane to benzene.

In this, or related,[4] catalytic cycles, products arising from intermediates **A**, [4] **B**, [3–5] **E**, [6–8] and **F** [3,6,9] have been observed. The π-allyl intermediate **C** is inferred by the report of rapid isomerisation of 4-methycyclohexene to 1-methylcyclohexene in the dehydrogenation of cyclohexenes by $[IrH_2(Me_2CO)_2(PPh_3)_2][SbF_6]$ [7]. However, hexadiene intermediate **D** has, to our knowledge, not been observed in this process although it has often been postulated [7,8,10], which is surprising given that many stable conjugated diene complexes are known. There is a single report of terminal alkenes being transfer hydrogenated to dienes [11].

We have recently reported that changing the 'least coordinating' counterion in the Schrock–Osborn hydrogenation system, $[(PPh_3)_2Rh(nbd)][Y]$ (nbd = norbornadiene), from $[Y] = [BF_4]^-$ to $[closo\text{-}CB_{11}H_6Br_6]^-$ results in a dramatic increase of catalyst efficiency in the hydrogenation of hindered alkenes, suggesting that the anion may play some role in the catalytic cycle [12]. Interested in possible, observable, intermediates or catalyst precursors in this process, we have investigated the reaction of the catalytically active species $[(PPh_3)\{(\eta^6\text{-}C_5H_6)PPh_2\}Rh]_2[Y]_2$, complex (**I**), with cyclohexenes in the absence of hydrogen in anticipation of observing simple olefin complexes. We report here that while these are not observed, transfer dehydrogenation of cyclohexenes to cyclohexandienes occurs instead,

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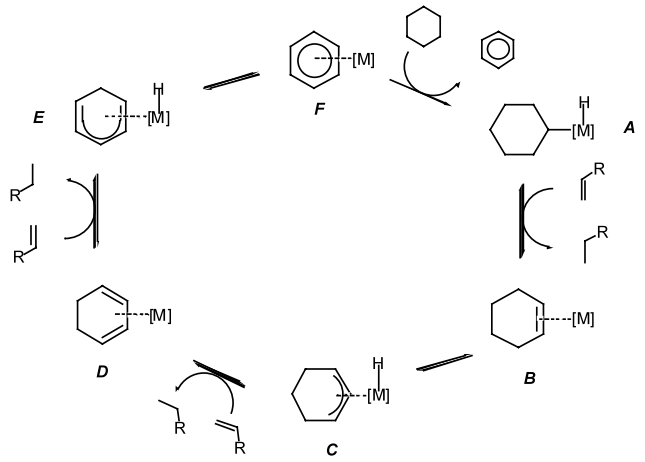


Scheme 1.

affording the isolation of a hexadiene intermediate **D** (Scheme 1) in the dehydrogenation of cyclohexane.

2. Results and discussion

Addition of eight equivalents cyclohexene to a CH_2Cl_2 solution of $[(PPh_3)\{(\eta^6\text{-}C_5H_6)PPh_2\}Rh]_2[closo\text{-}CB_{11}H_6Br_6]_2$ (**I**) [12] results in the isolation of the new complex $[(\eta^4\text{-}C_6H_8)Rh(PPh_3)_2][closo\text{-}CB_{11}H_6Br_6]$ (**1**) in good yield after 48 h at room temperature, this transformation being one in which cyclohexene has been dehydrogenated to cyclohexadiene. Monitoring the reaction by ^{1}H- and $^{31}P\{^1H\}$-NMR spectroscopy in CD_2Cl_2 solution showed the progressive formation of **1** with no intermediates detected. Concurrent evolution of one equivalent of cyclohexane (by ^{1}H-NMR and GC) was also observed, which is fully consistent with cyclohexene also acting as a hydrogen acceptor in the dehydrogenation process.

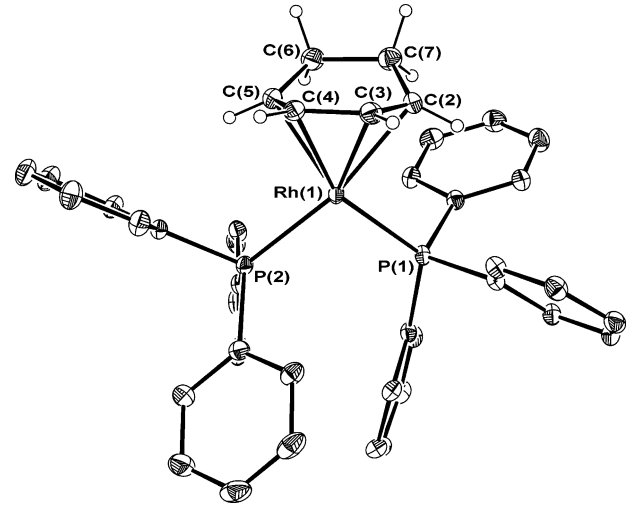
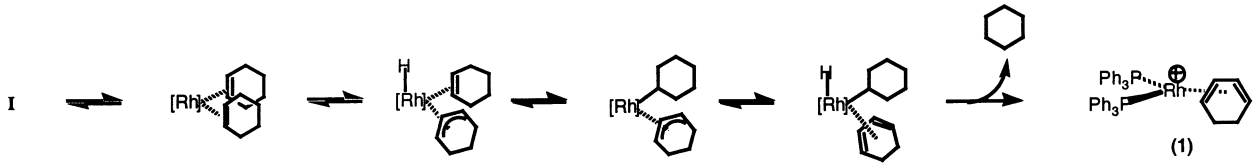


Fig. 1. Cationic component of complex **1**. Thermal ellipsoids are shown at the 30% probability level. Phenyl hydrogen atoms are omitted for clarity. Selected bonds lengths (Å) and angles (°): Rh(1)–C(2) 2.291(3), Rh(1)–C(3)–2.186(3), Rh(1)–C(4) 2.157(3), Rh(1)–C(5) 2.200(3), C(2)–C(3) 1.384(5), C(3)–C(4) 1.437(5), C(4)–C(5) 1.389(5), C(5)–C(6) 1.488(5), C(2)–C(7) 1.490(5), P(1)–Rh(1)–P(2) 100.59(3).

The solid-state structure of **1** has been determined (Fig. 1) and shows a η^4-coordinated diene bound to a $\{Rh(PPh_3)_2\}^+$ fragment. The carborane counterion is not associated with the cation. Bond lengths and angles are unremarkable and similar to other reported Rh-cyclohexadiene species [13]. Solution NMR spectra are fully consistent with the solid-state structure, exhibiting a doublet [δ 29.5, J(RhP) 177 Hz] in the $^{31}P\{^1H\}$-NMR spectrum and two, integral 2H, peaks observed in the ^{1}H-NMR spectrum for the diene protons at δ 5.5 [C(3,4)] and δ 3.9 [C(2,5)]. A ^1H–^1H COSY spectrum confirmed this assignment.

A suggested mechanism for the formation of **1**, which closely follows those proposed previously [3,7], is given in Scheme 2. Dehydrogenation of cyclohexene to benzene using *tert*-butylethene [7] or cyclohexene [8] as the sacrificial hydrogen acceptor has been reported, however, the intermediate in this process which complex **1** represents, structure **D** Scheme 1, has not been observed previously. A small, but significant, amount (ca. 10%) of coordinated benzene species is also observed in the ^{1}H-NMR spectra of the reaction mixture, along with **1**. It is likely that this occurs due to a combination of the further dehydrogenation of diene to benzene along with P–C_{aryl} bond cleavage, in a similar manner to related iridium systems [6]. Heating the sample (d_2-dichloroethane) did not result in catalytic turnover, nor did addition to the reaction of the hydrogen acceptor *tert*-butylethene. Substituting the carborane anion for $[BF_4]^-$ did not result in any appreciable difference in rate, but significantly more benzene coordinated product was observed. Using the anion $[closo\text{-}CB_{11}H_{12}]^-$ did not result in any reaction, only unchanged $(PPh_3)_2Rh(closo\text{-}CB_{11}H_{12})$ was recovered after 48 h. This is consistent with this unsubstituted carborane being significantly more coordinating than both $[closo\text{-}CB_{11}H_6Br_6]^-$ and $[BF_4]^-$ [12].



Scheme 2.

Replacing cyclohexene for the isomers 1-methylcyclohexene or 4-methylcyclohexene in the reaction afforded the same product in each case, namely 2-methyl-1,3-cyclohexadiene coordinated to a $\{(PPh_3)_2Rh\}^+$ fragment: $[(\eta^4\text{-2-Me-}C_6H_4)Rh(PPh_3)_2][closo\text{-}CB_{11}H_6Br_6]$, (**2**), which was fully characterised by multinuclear NMR spectroscopy (including COSY and NOESY experiments). In accord with the transfer dehydrogenation mechanism, methylcyclohexane was also formed (GC, ^{1}H-NMR). Two phosphorus environments are now observed in the $^{31}P\{^1H\}$-NMR spectrum of **2** at δ 30.8 and 27.7, consistent with the asymmetry induced by the coordinated diene. Dehydrogenation of these sterically hindered alkenes was very slow with eight equivalents of methylcyclohexene, so ca. 30 equivalents were used resulting in a reaction time of 48 h at room temperature. ^{1}H-NMR spectroscopy showed that 4-methylcyclohexene was initially isomerised to 1-methylcyclohexene by **I** relatively rapidly (Scheme 3), with the dehydrogenation to 2-methylcyclohexadiene significantly slower (days). Isomerisation of methylcyclohexenes prior to dehydrogenation to toluene as has been observed previously in related Iridium systems [7].

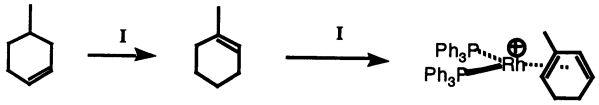
Further dehydrogenation to toluene was considerably slower than diene formation, diagnostic peaks due to coordinated toluene only observed in ca. 10% of the total after 48 h at room temperature. However, heating the sample (CD_2Cl_2, sealed NMR tube, 40 °C, 2 h) did result in an increase in the toluene species to ca. 20% but the benzene-coordinated complex that results from degradation of the phosphine also increased in total concentration to ca. 30%.

3. Conclusions

Addition of cyclohexenes to the Schrock–Osborn hydrogenation catalyst $[(PPh_3)_2Rh]^+$ does not result in the observation of an olefin complex but transfer dehydrogenation of cyclohexanes to cyclohexadienes occurs instead. The resulting complexes are intermediates on the mechanistic pathway for the dehydrogenation of cyclohexane to benzene.

4. Experimental

All manipulations were carried out under an atmosphere of argon using standard Schlenk line techniques. Solvents were dried according to standard procedures and distilled under nitrogen. NMR solvents were dried over CaH_2 for at least 24 h, vacuum distilled and freeze-pump thawed prior to use. Cyclohexene, 1-methylcyclohexene and 4-methylcyclohexene were passed through a column of activated alumina and freeze-pump thawed prior to use. Gas Chromatography was performed on a Perkin-Elmer Autosystem XL. NMR spectra were recorded on either a Brüker 300 MHz or a Varian 400 MHz spectrometer. ^{1}H-NMR spectra were referenced using residual protio solvents, $^{13}C\{^1H\}$-NMR spectra were reference to CD_2Cl_2 (internal) and $^{31}P\{^1H\}$-NMR spectra were referenced to an external H_3PO_4 reference. All NMR spectra were recorded at room temperature (r.t.). Coupling constants are quoted in Hz. $[(Ph_3P)_2Rh(C_7H_8)][Y]$ $\{[Y] = [BF_4], [closo\text{-}CB_{11}H_6Br_6]\}$ was prepared by the reported routes [12]. Both the new compounds **1** and **2**, displayed ^{11}B-NMR spectra that showed resonances due to uncoordinated [*closo*-$CB_{11}H_6Br_6$] [14].



Scheme 3.

4.1. $[(Ph_3P)_2Rh(\eta^4\text{-}C_6H_8)][closo\text{-}CB_{11}H_6Br_6]$ (**1**)

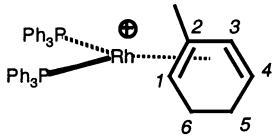
$[(Ph_3P)_2Rh(C_7H_8)][closo\text{-}CB_{11}H_6Br_6]$ (40 mg, 0.03 mmol) was dissolved in CD_2Cl_2 (1 cm^3) in a Young's NMR tube and placed under an H_2 atmosphere for 0.5 h. The solution was monitored via ^{1}H-NMR spectroscopy until all starting material had reacted to $[(PPh_3)\{(\eta^6\text{-}C_5H_6)PPh_2\}Rh]_2[closo\text{-}CB_{11}H_6Br_6]_2$. The system was then freeze-pumped thawed three times and placed under argon and C_6H_{10} (25 μl, 0.24 mmol) was added to the solution via syringe. The reaction was monitored via ^{1}H- and $^{31}P\{^1H\}$-NMR spectroscopy for 48 h until all the starting material had been consumed. Crystals suitable for a single crystal X-ray structure study, were grown by diluting a CH_2Cl_2 solution of **1** with an equal volume of hexane and cooling at 0°C for several days. Yield 0.03 g (75%). Analysis for $C_{43}H_{44}B_{11}Br_6P_2Rh$ requires C, 39.01; H, 3.35. Found: C, 39.9; H, 3.82%.

Spectroscopic data for (**1**): δ^1H (300 MHz, CD_2Cl_2) 7.2 (m, 30H C_6H_5), 5.5 (br s, 2H, C_6H_8, C(3,4)), 3.9 (br s, 2H, C_6H_8, C(2,5)), 2.4 (br s, CH_{cage}), 1.2 [d, 2H J(HH) 5, C_6H_8], 1.0 [d, 2H J(HH) 5, C_6H_8]. $\delta^{31}P\{^1H\}$ (121MHz, CD_2Cl_2) 29.5 [d, J(RhP) 177]. $\delta^{13}C\{^1H\}$ (100 MHz, CD_2Cl_2) 142.0 (C_6H_5), 138.3 (s, C_6H_5), 126.6 (s, C_6H_5), 93.3 (s, C_6H_8), 88.6 (s, C_6H_8), 42 (s, CH_{cage}), 20.6 (s, C_6H_8).

4.2. $[(Ph_3P)_2Rh(\eta^4\text{-}C_7H_{10})][closo\text{-}CB_{11}H_6Br_6]$ (**2**)

$[(Ph_3P)_2Rh(C_7H_8)][closo\text{-}CB_{11}H_6Br_6]$ (40 mg, 0.03 mmol) was dissolved in CD_2Cl_2 (1 cm^3) in a Young's NMR tube and placed under an H_2 atmosphere for 0.5 h. The solution was monitored via ^{1}H-NMR spectroscopy until all starting material had reacted to $[(PPh_3)\{(\eta^6\text{-}C_5H_6)PPh_2\}Rh]_2[closo\text{-}CB_{11}H_6Br_6]_2$. The

system was then freeze-pumped thawed three times and placed under argon and 1-methylcyclohexene (C_7H_{12}) (130 μl, 1.00 mmol) was added to the solution via syringe. The reaction was monitored via ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy for 48 h until all the starting material had been consumed. Despite repeated attempts analytically pure material for **2** was not obtained. Unfortunately, mass spectrometry (FAB+, 3-noba matrix) did not afford the molecular ion with only the fragment $[Rh(PPh_3)_2]^+$ was observed. Identification by NMR spectroscopy (^{1}H–^{1}H COSY, ^{1}H-NOESY) was unambiguous, however.



Spectroscopic data for (**2**): δ^1H (300 MHz, CD_2Cl_2) 7.2 (m, 30H C_6H_5), 4.5 (s br, 1H, H(3)), 4.0 (s br, 1H, H(4)), 3.7 (s br, 1H, H(1)), 2.4 (br s, 1H CH_{cage}), 1.8 (s, 3H, CH_3), 1.79 (m, 1H), 1.4 (m, 1H), 1.1 (m, 1H), 0.9 (m, 1H). δ^{31}P{^{1}H} (121 MHz, CD_2Cl_2) 30.8 [dd, J(RhP) 170, J(PP) 33], 27.7 [dd, J(RhP) 181, J(PP) 33].

4.3. X-ray crystallography

The crystal structure data for compound (**1**) was collected on a Nonius Kappa CCD. Structure solution, followed by full-matrix least-squares refinement was performed using the SHELX suite of programs throughout [15]. Plots were produced using ORTEX [16].

Crystal data for (**1**): $C_{45}H_{48}B_{11}C_{14}P_2Rh$, $M = 1493.85$, $\lambda = 0.71073$ Å, triclinic, $P\bar{1}$, $a = 12.3970(10)$, $b = 15.6110(10)$, $c = 16.1060(2)$ Å, $\alpha = 67.920(1)$, $\beta = 87.446(1)$, $\gamma = 73.900(1)^\circ$, $U = 2768.86(4)$ Å^3, $Z = 2$, $D_{calc} = 1.792$ g cm^{-1}, $\mu = 4.922$ mm^{-1}, $F(000) = 1452$, crystal $0.3 \times 0.25 \times 0.13$ mm, 16 151 unique reflections ($R_{int} = 0.0722$), $R_1 = 0.0417$, $wR_2 = 0.0960$ [$I > 2\sigma(I)$].

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 188813 for compound **1**.

Acknowledgements

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References

[1] R.H. Crabtree, M.F. Mellea, J.M. Mihelcic, J.M. Quirk, J. Am. Chem. Soc. 104 (1982) 107.
[2] (a) R.H. Crabtree, Dalton Trans. (2001) 2437.;
(b) J.A. Maguire, W.T. Boese, A.S. Goldman, M.E. Goldman, Coord. Chem. Rev. 97 (1990) 179.
[3] C.M. Jensen, Chem. Commun. (1999) 2443.
[4] G.P. Rosini, S. Soubra, M. Vixamar, S. Wang, A.S. Goldman, J. Organomet. Chem. 554 (1998) 41.
[5] M.J. Burk, R.H. Crabtree, J. Am. Chem. Soc. 109 (1987) 8025.
[6] R.H. Crabtree, C.P. Parnell, R.J. Uriarte, Organometallics 6 (1987) 696.
[7] R.H. Crabtree, C.P. Parnell, Organometallics 4 (1985) 519.
[8] B.N. Chaudret, D.J. Cole-Hamilton, G. Wilkinson, Acta Chem. Scand. A 32 (1978) 763.
[9] B.N. Chaudret, F. Dahan, X.D. He, Chem. Commun. (1990) 1111.
[10] B.M. Trost, P.J. Metzner, J. Am. Chem. Soc. 102 (1980) 3572.
[11] M.G. Clerici, S. Di Gioacchino, F. Maspero, E. Perrotti, Z. Zanobi, J. Organomet. Chem. 84 (1975) 379.
[12] A. Rifat, N.J. Patmore, M.F. Mahon, A.S. Weller, Organometallics 21 (2002) 2856.
[13] P. Budzelaar, N.N.P. Moonen, R. de Gelder, J.M.M. Smits, A.W. Gal, Chem. Eur. J. 6 (2000) 2740.
[14] T. Jelinek, J. Plesek, S. Hermanek, B. Stibr, Collect. Czech. Chem. Commun. 51 (1986) 819.
[15] G.M. Sheldrick, SHELXL-97. University of Göttingen. A computer program for refinement of crystal structures.
[16] P. McArdle, J. Appl. Crystallogr. 28 (1995) 65.