

Catalytic Dehydrogenation of Cycloalkanes to Arenes by a Dihydrido Iridium P–C–P Pincer Complex

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Received July 25, 1996

The dehydrogenation of alkanes through catalytic reforming is the leading commercial method of producing arenes.¹ Platinum (often with a rhenium promoter) on alumina catalysts employed in this reaction require temperatures of 450–550 °C.¹ During the past decade, there has been steady progress in the development of soluble transition metal complexes as catalysts for the dehydrogenation of alkanes to alkenes at moderate conditions.^{2–4} However, there have been few extensions of these systems to the production of arenes. Pioneering studies by Shilov showed that K₂PtCl₄ catalyzes the reaction of H₂-PtCl₆ with cycloalkanes to produce a mixture of arenes, alcohols, and chlorinated species at 100–120 °C in aqueous trifluoroacetic acid.² Pd(O₂CCF₃)₂ has been reported to catalyze the dehydrogenation of cyclohexene to benzene⁶ but reacts with cyclohexane only stoichiometrically in the presence of CF₃COOH to produce benzene.³ Ru(styrene)₂(PPh₃)₂, [Ir(COD)(PPh₃)₂]⁺, and [Ir(COD)(P(*p*-FC₆H₄)₃)₂]⁺ catalyze the dehydrogenation of cyclohexene to benzene but are unreactive with cyclohexane,^{8,9} while PdSO₄ in the presence of H₂SO₄ effects only the stoichiometric conversion of cyclohexane to benzene.¹⁰ Crabtree has found an oxidative addition type system in which IrH₂{O₂CCF₃}(PPrⁱ₃)₂ effects the dehydrogenation of alkanes to arenes at 150 °C in the presence of the hydrogen acceptor, *tert*-butylethylene (tbe).⁵ This system fails to turnover catalytically because hydrogenolysis of the phosphine P–C bonds occurs at

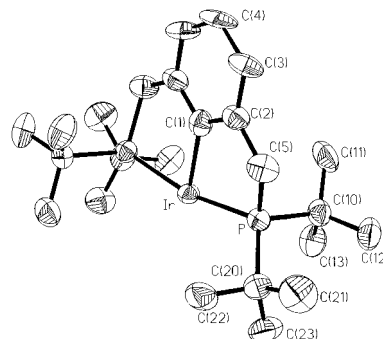
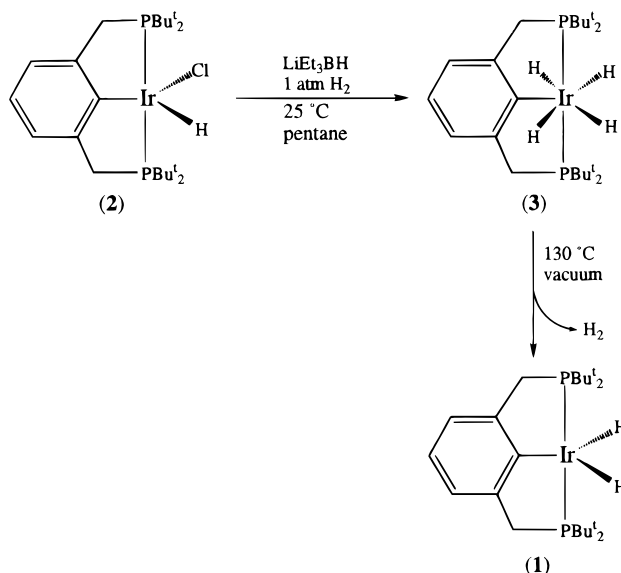


Figure 1. Projection of IrH₂{C₆H₃-2,6-(CH₂PBt₂)₂} (**1**) with the thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (deg): Ir–C(1), 2.12(1); Ir–P, 2.308(2); P–Ir–C(1), 82.41(6); P–Ir–P(a), 164.8(1). The hydrogen atoms are omitted for clarity.

Scheme 1



the temperatures of 135 °C or above required for the release of the arenes from the intermediate complexes. We recently found that the iridium P–C–P pincer complex IrH₂{C₆H₃-2,6-(CH₂PBt₂)₂} (**1**) is a highly active, homogeneous catalyst for the transfer dehydrogenation of cyclooctane with unusual long-term stability at temperatures as high as 200 °C.⁴ This reactivity has now been extended to the catalytic transfer dehydrogenation of cycloalkanes to arenes. We report this novel catalytic activity as well as the results of an X-ray structure determination of **1**.

As seen in Scheme 1, treatment of a pentane solution of the hydrochloride complex IrHCl{C₆H₃-2,6-(CH₂PBt₂)₂} (**2**) under 1 atm of hydrogen with LiEt₃H at 25 °C produces the white tetrahydrido complex IrH₄{C₆H₃-2,6-(CH₂PBt₂)₂} (**3**) in 85% yield.¹¹ The brown dihydrido complex **1**¹² is obtained quantitatively upon heating finely powdered **3** to 130 °C *en vacuo*.

(11) The spectroscopic and analytical data previously reported⁴ for **1** are for the tetrahydride complex **3**.

(12) For **1**: ¹H NMR (400 MHz, cyclohexane-*d*₁₂) δ 7.11 (d, *J*_{HH} = 7.7 Hz, 2H, *m*-H), 6.89 (t, *J*_{HH} = 7.7 Hz, 1H, *p*-H), 3.56 (vt, *J*_{PH} = 3.5 Hz, 4H, CH₂), 1.28 (vt, *J*_{PH} = 6.2 Hz, 18H, CH₃), –18.89 (t, *J*_{PH} = 8.1 Hz, 2H, IrH); ³¹P{¹H} NMR (161.9 MHz, cyclohexane-*d*₁₂) δ 86.1 (s).

(13) Dark orange crystals of **1** were obtained from slow evaporation of a pentane solution: tetragonal P4₂, Z = 2, a = b = 11.710(4) Å, c = 9.701(5) Å, V = 1330.2(9) Å³; 137 parameters were refined on 1744 reflections having I > 2σ(I); R (R_w) = 3.05 (6.21)%, GOF = 0.920. The refined Flack parameter suggested twinning, and twin component was included with the twinning law of 1,0,0,0, –1,0,0,0, –1. The twin component refined to a ratio 733:267(4), and its inclusion lowered R and decreased the dispersion in chemically equivalent carbon–carbon distances. Chirality is established by the final Flack parameter of 0.02(3). The hydride could not be reliably located.

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Table 1. Catalytic Dehydrogenation with **1**

substrate	time (h)	<i>T</i> (°C)	products (mol/mol of 1)	dehydrogenated/hydrogenated C–C bonds
cyclohexane	1	150	cyclohexene (44)	0.98
cyclohexane	0.5	200	benzene (54), tba (211)	1.02
methylcyclohexane	1	150	cyclohexene (86)	0.97
methylcyclohexane	1	200	benzene (77), tba (310)	0.96
methylcyclohexane	120	150	methylcyclohexenes: 1 (8), 3 (20), 4 (41)	0.97
decalin	72	150	toluene (11), tba (105)	0.96
decalin	1	200	methylcyclohexenes: 1 (27), 3 (39), 4 (70)	0.96
			toluene (54), tba (310)	0.97
			methylcyclohexenes: 1 (67), 3 (13), 4 (25)	0.97
			toluene (65), tba (310)	0.96
			octahydronaphthalenes (24)	0.96
			tetrahydronaphthalene (8)	0.96
			naphthalene (4), tba (71)	0.96
			octahydronaphthalenes (69)	0.96
			tetrahydronaphthalene (16)	0.96
			naphthalene (7), tba (159)	0.96

An X-ray structure determination was carried out on a single crystal of **1** in order to verify the structural composition.¹³ A diagram of the determined molecular structure and selected bond distances and angles are presented in Figure 1.

The activity of **1** as a catalyst for transfer dehydrogenation was investigated using solutions of cycloalkanes (4.0 mL), the (0.20 mL, 1.55 mmol), and **1** (3 mg, 0.005 mmol). The results of the catalytic dehydrogenation experiments are summarized in Table 1. The solutions were sealed in tubes under argon, and fully immersed in an oil bath for the prescribed reaction times. The orange solutions became red upon heating but did not further darken or discolor during the reaction period. The reaction was unaffected by the addition of metallic mercury to the solution, indicating that metallic iridium is not involved in the hydrogen transfer.¹⁴ The products were identified by GC-MS¹⁵ analysis and quantified by gas chromatography.¹⁵ As seen in Table 1, our quantification balances the number of dehydrogenated C–C bonds within 4% to the amount of the hydrogenated to *tert*-butylethane (tba) in all experiments. The rates of the dehydrogenation of cyclohexane and methylcyclohexane are comparable to those previously found for the dehydrogenation of cyclooctane to cyclooctene by **1**.⁴ The dehydrogenation of decalin required longer reaction times to yield products in adequate amounts for accurate quantification. This reduced reactivity reflects the stringent steric constraints at the metal center.

The solutions containing **1** remained active to the limit of complete hydrogenation of the hydrogen acceptor. The 5-day

experiment with methylcyclohexane shows that the total number of unsaturated C–C bonds does not change after the tba acceptor has been consumed. However, the distribution of dehydrogenated products continues to shift toward the trisubstituted, 1-methylcyclohexene, and toluene as a result of the 3- and 4-methylcyclohexenes acting hydrogen acceptors. As previously found for the dehydrogenation of cyclooctane by **1**, the system is inhibited at the tba to catalyst ratios greater than 350:1. Thus, high turnover numbers can be achieved only in solutions containing a limited amount of tba, which must be added periodically. The dehydrogenation activity resumes following incremental additions of tba (0.20 mL, 1.55 mmol). However, the products apparently compete with the tba for coordination to the iridium center. After 1000 total turnovers, there is no increase in the total amount of dehydrogenated products.

To our knowledge, this is the first report of a system for the conversion of cycloalkanes to arenes which is completely catalytic in precious metal. The unique reactivity can be ascribed to the P–C–P ligand, which renders the metal center reactive with saturated hydrocarbons but restricts its access to the ligand P–C bonds. This work illustrates that P–C–P pincer complexes can transverse previously inaccessible catalytic pathways.

Acknowledgment. M.K. is the 1995 J. J. Zuckermann fellow. The support of this research by the U.S. Department of Energy Hydrogen Program is gratefully acknowledged. We thank Dr. Regine Herbst-Irmer of the University of Goettingen for assistance with the analysis of the X-ray data.

Supporting Information Available: Tables of crystal data, thermal parameters, bond distances, bond angles, and atomic coordinates for IrH₂{C₆H₃-2,6-(CH₂PBu₂)₂} (**1**) (5 pages). See any current masthead page for ordering and Internet access instructions.

JA962560X

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(15) GC analyses were performed on a temperature-programmed (cyclohexane, 35 °C isothermal for 1 min, 5°/min to 70 °C; methylcyclohexane, 45 °C isothermal for 1 min; 5°/min to 100 °C; decalin, 60 °C isothermal for 1 min, 5°/min to 175 °C) Hewlett Packard 5890 gas chromatograph using a 250 μm × 25 m OV-1 capillary column. For GC-MS analyses, the column was coupled to a VG 70SE dual sector high-resolution mass spectrometer.