A Rare Example of Efficient Alkene Hydrogenation Mediated by a Neutral Iridium(I) Complex under Mild Conditions

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*Summary: The synthesis and characterization of two new square-planar (COD)M(κ^2-P,O-phosphinoenolate) complexes (M = Rh, **3a**; M = Ir, **3b**; COD = η^4-1,5-cyclooctadiene) are described. Complex **3b** represents an unusual example of a neutral (not cationic) square-planar Ir(I) complex that is capable of mediating the reduction of alkenes under mild benchtop conditions (∼1 atm of H_2, 22 °C) in the presence of high-polarity (THF, CH_2Cl_2, CH_3CN) and low-polarity solvents (hexanes, benzene).*

The metal-catalyzed addition of dihydrogen to alkenes is an atom-economical synthetic methodology that is used extensively in academic and industrial settings.[1] Among the diversity of transition-metal-based homogeneous alkene hydrogenation catalysts that have been developed, cationic square-planar Ir(I) species such as Crabtree's catalyst, $[(COD)Ir(PCy_3)(Py)]^+PF_6^-$ (**1**: COD = η^4-1,5-cyclooctadiene, Cy = cyclohexyl, Py = pyridine),[2] are unique with respect to the efficiency with which they can reduce highly substituted olefins that lack polar functional groups. However, the use of such catalysts often requires high-dielectric reaction media because of the polar nature of Ir(I) salts,[3a] and catalysis mediated by these salts is often completely inhibited by coordinating solvents (e.g. CH_3CN).[2c,4] In addition, the performance of cationic Ir(I) hydrogenation catalysts is influenced by the nature of the accompanying counteranion,[5] and many such complexes, including **1**,[2a,b] are thermally unstable. Alternatively, the use of more lipophilic, neutral square-planar Ir(I) catalyst complexes represents a potential way in which to exploit the beneficial catalytic abilities of Ir(I) salts, while avoiding the limited solvent compatibility, thermal instability, and counteranion issues associated with related cationic catalysts. However, the development of neutral Ir(I) alkene hydrogenation catalysts has received scant attention in the literature, due in part to the widely held belief that a formally cationic Ir(I) center is required in order to achieve an appropriate level of catalytic productivity. Indeed, it is extremely rare for neutral Ir(I) species to function as alkene hydrogenation catalysts under mild conditions;[6a] for example, while Wilkinson's complex ($RhCl(PPh_3)_3$) is effective in mediating the reduction of some classes of olefins,[6b] the Ir analogue is completely inactive.[6c]

Given the inherent limitations of cationic square-planar Ir(I) catalysts, and in light of the possible reactivity benefits that might be realized by conducting Ir-mediated alkene hydrogenations in low-coordinating aliphatic hydrocarbons, we became interested in identifying neutral, alkane-soluble Ir(I) complexes which exhibit the desirable catalytic properties of Ir(I) salts and which function effectively under mild benchtop conditions within solvents of varying polarity.[3b,7a] One approach we are exploring is the development of formally zwitterionic variants of **1**. While modest catalytic turnover was achieved by use of the zwitterion (COD)Ir(κ^2-3-P^iPr_2-2-NMe_2-indenide) (**2**) in benzene, THF, and CH_2Cl_2, this complex exhibited both limited solubility and attenuated catalytic activity in aliphatic hydrocarbons[7a] and proved intolerant to CH_3CN.[8] Building on the hard (N) and soft (P) donor ligand pairing featured in **1**, and given the established utility of P,O ligands in tuning the reactivity properties of metal complexes,[9,10] we also became interested in surveying the catalytic properties of κ^2-*P*,*O*-phosphinoenolate complexes. Within the few reports that feature Rh(I) complexes of this type as alkene hydrogenation catalysts, the feasibility of employing an aliphatic hydrocarbon reaction medium was not evaluated,[11] and the hydrogenation of alkenes mediated by analogous Ir(I) complexes has yet to be documented. Herein we report the synthesis and characterization of the new phosphinoenolate complexes **3a** (M = Rh) and **3b** (M = Ir).

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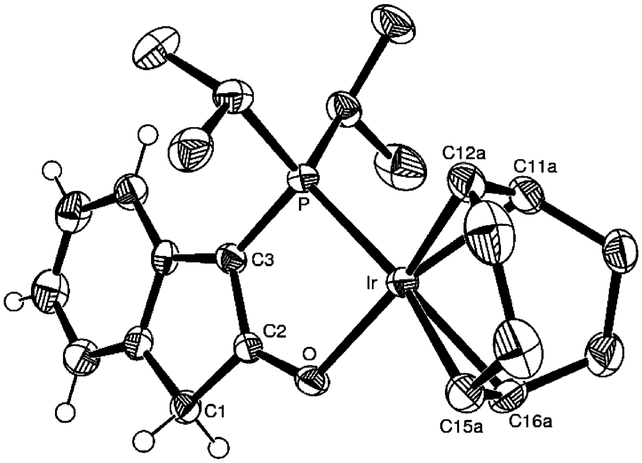
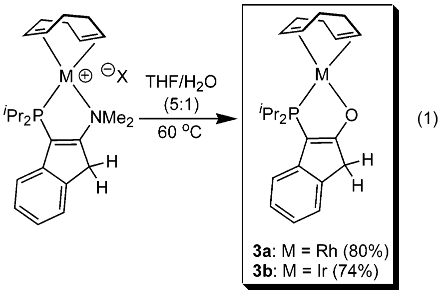


Figure 1. Crystallographically determined structure of **3b** shown with 50% displacement ellipsoids. Only one of the two crystallographically independent molecules is shown, and selected H atoms have been omitted for clarity. Selected interatomic distances (Å): Ir−P, 2.320(1); Ir−O, 2.058(3); Ir−C11a, 2.117(5); Ir−C12a, 2.099(6); Ir−C15a, 2.181(5); Ir−C16a, 2.164(5); P−C3, 1.779(5); O−C2, 1.302(6); C1−C2, 1.514(7); C2−C3, 1.380(7).

Notably, **3b** is thermally robust and mediates the hydrogenation of alkenes under mild benchtop conditions (~1 atm of H_2, 22 °C) in the presence of a range of solvents (hexanes, benzene, THF, CH_2Cl_2, and CH_3CN). To the best of our knowledge, **3b** is the most active neutral, square-planar Ir(I) alkene hydrogenation catalyst known.

In the course of surveying the reactivity properties of $[(COD)M(\kappa^2$-3-P^iPr$_2$-2-NMe$_2$-indene)]$^+X^-$ (M = Rh, Ir)[7] we noted that heating in a THF/H_2O mixture (5:1, 60 °C, 48 h) resulted in clean conversion to the neutral κ^2-*P*,*O* species **3a** and **3b** (eq 1). These new complexes were isolated and characterized spectroscopically and, in the case of **3b**, also by use of X-ray diffraction methods (Figure 1).[12] The C2−C3 (1.380(7) Å) and O−C2 (1.302(6) Å) distances in this complex are consistent with a phosphinoenolate structural formulation, and the overall geometric features in **3b** mirror those observed in related complexes.[13] While the direct insertion of Rh- and Ir-based fragments into C−N bonds has been observed,[14] we instead view the formation of **3a** and **3b** as arising by way of an enamine hydrolysis reaction involving 3-P^iPr$_2$-2-NMe$_2$-indene, in which the coordinated [CODM]$^+$ fragment functions as a Lewis acid;[15] we are currently exploring the mechanism of this transformation. Interestingly, the enamine 1-P^iPr$_2$-2-NMe$_2$-indene is not hydrolyzed under similar conditions. In contrast to the temperature-sensitive nature of **1**,[2a,b] no decomposition was observed for complex **3b** upon heating in toluene over two weeks at 100 °C.



3a: M = Rh (80%)
3b: M = Ir (74%)

(1)

Table 1. Alkene Hydrogenation Mediated by 3b[a]

entry	amt of **3b** (mol %)	substrate/solvent	yield (%)	TOF[b]
1	1.0	styrene/CH_2Cl_2	68	125
2	1.0	styrene/THF	>99	170
3	1.0	styrene/C_6H_6	>99	185
4	1.0	styrene/hexanes	>99	400
5	1.0	styrene/~4:3 C_6H_6−CH_3CN	29	30
6	0.5	styrene/hexanes	>99	590
7	0.5	styrene/hexanes (open air setup)[c,d]	>99	480
8	0.1	styrene/hexanes	35	645
9	0.5	cyclohexene/hexanes	57	260
10	0.5	1-methylcyclohexene/hexanes	7	35

[a] Conditions: 22 °C, ~1 atm of H_2, 4 h (except for entry 4, 0.25 h). [b] TOF = ((mol of product)/(mol of catalyst))/h, measured at 0.25 h. [c] The reagents, catalyst, and solvent were handled in the open air, and no efforts were made to purify the hexanes prior to use. [d] Solutions of **3b** in C_6D_6 stored under air are stable for a minimum of 4 h (^{31}P NMR).

Preliminary reactivity studies revealed that **3b** is a competent catalyst for styrene hydrogenation in a range of solvents and under mild conditions (22 °C, ~1 atm of H_2, 1.0 mol %; Table 1). While incomplete conversion was observed in CH_2Cl_2 (68%; entry 1), clean reductions were achieved after 4 h in both THF (entry 2) and benzene (entry 3). Remarkably, in hexanes **3b** proved capable of quantitatively reducing styrene after only 0.25 h (entry 4), at double the initial rate observed in CH_2Cl_2, THF, or benzene; this catalytic performance rivals that of the benchmark complex **1** in CH_2Cl_2.[2,7a] Whereas **1**[2c] and other cationic Ir(I) species, as well as the zwitterion **2**,[8b] are catalytically inactive in the presence of CH_3CN, the reduction of styrene mediated by **3b** proceeded to some extent in a mixture of C_6H_6 and CH_3CN (entry 5). The clean reduction of styrene was still achieved upon lowering the loading of **3b** to 0.5 mol % (entry 6), and no significant loss of catalytic activity occurred when the hydrogenation was conducted on the benchtop without the rigorous exclusion of oxygen and using hexanes that had not been dried (entry 7). Modest catalytic productivity (35%) was also detected at the 0.1 mol % **3b** loading level (entry 8). While complex **3b** proved capable of reducing cyclohexene to a significant extent (57%, entry 9), minimal conversion was achieved for the hydrogenation of 1-methylcyclohexene (7%, entry 10). By comparison, the Rh(I) complex **3a** proved vastly inferior to **3b**, with less than 10% styrene conversion observed after 4 h employing 5.0 mol % **3a** in either CH_2Cl_2 or hexanes.

In contrast to the preponderance of evidence suggesting that square-planar Ir(I) complexes must be formally cationic in order to function effectively as homogeneous alkene hydrogenation catalysts, we have identified an unusual example of a neutral, square-planar Ir(I) complex (**3b**) that mediates the hydrogenation of alkenes under mild conditions (~1 atm of H_2, 22 °C) and without the need for rigorous inert-atmosphere techniques. The solubility and stability profiles of this neutral Ir(I) complex provide practical advantages over traditional cationic Ir(I) complexes; while **1** is temperature-sensitive, functions almost exclusively in chlorocarbons, and is intolerant to coordinating

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(12) (a) Full experimental details, including spectroscopic characterization data for **3a** and **3b** are provided in the Supporting Information. (b) Selected crystal data for **3b**: monoclinic ($P2_1/c$); $a = 23.180(2)$ Å; $b = 7.4095(8)$ Å; $c = 26.823(3)$ Å; $\beta = 113.899(2)°$; $V = 4211.8(8)$ Å^3; data/parameters = 8649/469; GOF = 1.060; R1 = 0.0345; wR2 = 0.0744.

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solvents, the neutral complex **3b** is thermally robust and exhibits optimal catalytic performance in aliphatic hydrocarbons while remaining active in other polar and nonpolar media.

Having established the viability of employing neutral square-planar Ir(I) complexes as alkene hydrogenation catalysts, we are currently pursuing derivatives of **3b** that mediate the reduction of tri- and tetrasubstituted alkenes. We are also developing chiral variants of **3b** as part of this effort. We anticipate that enhanced rates and enantioselectivities may be achieved for asymmetric alkene hydrogenations mediated by such chiral Ir(I) catalysts in aliphatic hydrocarbons, relative to those obtained by use of traditional cationic Ir(I) catalyst complexes in more polar media. Our progress in these areas will be the subject of future reports.

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Supporting Information Available: Text and tables giving experimental details and characterization data for **3a** and **3b**, as well as crystallographic data for **3b**; crystallographic data are also available as a CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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