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Exploring the utility of neutral Rh(I) and Ir(I) κ^2-(*P*,*O*)MCOD catalyst complexes for the addition of triethylsilane to styrene

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Dedicated to Professor Brian James, in honor of his outstanding contributions to the fields of inorganic chemistry and homogeneous catalysis.

Abstract

The ability of neutral Rh and Ir phosphinoenolate complexes of the type (COD)M(κ^2-3-P^iPr$_2$-2-*O*-indene) (M = Rh, **2a**; M = Ir, **2b**; COD = η^4-1,5-cyclooctadiene) to mediate the addition of triethylsilane to styrene was explored under various reaction conditions in which the solvent, temperature and substrate ratio were altered. Throughout the course of these catalytic studies, head-to-head performance comparisons were made with Wilkinson's catalyst ($(PPh_3)_3RhCl$; **3**) and Crabtree's catalyst ($[(COD)Ir(PCy_3)(Py)]^+PF_6^-$; Cy = cyclohexyl; Py = pyridine; **4**). While **2a** proved to be an active catalyst for dehydrogenative silylation, exhibiting selectivity for *E*-1-triethylsilyl-2-phenylethene (**5a**) comparable to that of **3** under appropriate conditions, the Ir analogue **2b** displayed rather poor catalytic productivity. In contrast, **4** exhibited good catalytic activity, generating **5a** as well as 1-triethylsilyl-1-phenylethane (**5c**) as major products. Crystallographic data for **2a** · 0.25CH$_2$Cl$_2$ are also reported.

Keywords: Rhodium; Iridium; P,O-ligands; Hydrosilylation; Dehydrogenative silylation; Catalysis

1. Introduction

The study of transition metal complexes supported by mixed donor chelating ligands is an active and fruitful area of chemical research [1–3]. One reason for the interest in such complexes arises from the fact that the incorporation of an asymmetric chelate binding environment around the transition metal can facilitate substrate activation, and can provide selectivity in subsequent transformations occurring within the metal coordination sphere [1–3]. The synthetic utility of Rh and Ir catalyst complexes stabilized by mixed donor ligands has been demonstrated for many transformations involving the activation of E–H bonds (E = main group element) in small molecule substrates, including (but not limited to) hydrogenation, hydrosilylation, hydroboration, and hydroformylation reactions [2]. One class of mixed donor ligands that has found widespread use are phosphorus–oxygen ligands, which bind in a κ^2-*P*,*O* fashion to the metal [3]. Nickel catalysts of this type, including κ^2-[Ph$_2$*P*CH$_2$C(=O)*O*]NiCOD (COD = η^4-1,5-cyclooctadiene), are employed in the shell higher olefin process (SHOP), which represents a multi-billion dollar a year industry globally for the production of ethene oligomers [3].

In this context, our research group is focused on the development of new classes of reactive transition metal coordination complexes supported by donor-substituted indene ligands, including 1-P^{i}Pr$_2$-2-NMe$_2$-indene, 2-NMe$_2$-3-P^{i}Pr$_2$-indene, and related derivatives, in anticipation that these complexes will function effectively as catalysts for substrate transformations involving E–H bond activation steps [4–10]. These ligands have proven capable of supporting both neutral and cationic metal

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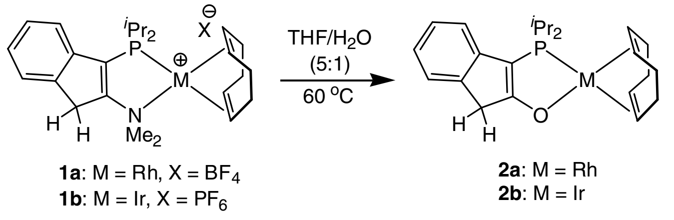
fragments in a κ^2-*P*,*N* fashion, and upon deprotonation of the indene backbone and introduction of a cationic metal fragment, zwitterionic κ^2-*P*,*N* complexes [4,9,10]. Our interest in developing charge-neutral zwitterionic group 9 complexes of this type arises from our desire to identify new neutral group 9 catalyst complexes that possess the advantageous reactivity traits of more conventional cationic systems, while circumventing the low solubility, thermal instability, and other limitations that can be associated with Rh(I) and Ir(I) salts. Preliminary studies have revealed that the zwitterion (COD)Rh(κ^2-3-P^iPr$_2$-2-*N*Me$_2$-indenide) is an effective catalyst for C–H/Si–H dehydrogenative cross-coupling [4], while the Ir analogue exhibits modest catalytic activity for alkene hydrogenation [10].

In addition to studying the catalytic reactivity of these κ^2-*P*,*N* zwitterionic species, we recently discovered that cationic [(COD)M(κ^2-3-P^iPr$_2$-2-*N*Me$_2$-indene)]$^+$X$^-$ (M = Rh, X = BF$_4$, **1a**; M = Ir, X = PF$_6$, **1b**) complexes are readily converted to the corresponding neutral κ^2-*P*,*O* phosphinoenolate complexes, **2a** and **2b**, upon thermolysis in a THF/water mixture (Scheme 1) [11]. Interestingly, complex **2b** represents the most active neutral square-planar Ir(I) alkene hydrogenation catalyst known, functioning under mild catalytic conditions (~1 atm H$_2$, 22 °C) and most effectively in aliphatic hydrocarbons; in contrast, the Rh congener **2a** exhibits poor activity for alkene hydrogenation [11].

Intrigued by these preliminary results, we turned our attention to the addition of triethylsilane to styrene as a means of evaluating further the catalytic abilities of **2a** and **2b**. The hydrosilylation of unsaturated substrates mediated by a transition metal catalyst complex has been the focus of active research for several decades, owing to the utility of the resulting organosilanes in applications ranging from the preparation of silicon-containing polymers to the synthesis of bioactive compounds [12–15]. Herein we report the crystallographic characterization of **2a**, and discuss the catalytic addition of triethylsilane to styrene mediated by **2a** and **2b**, noting high conversion and selectivity of **2a** for the dehydrogenative silylation product, *E*-1-triethylsilyl-2-phenylethene, as well as poor overall catalytic performance exhibited by **2b**. These catalytic results are placed in the context of analogous reactions mediated by Wilkinson's catalyst ((PPh$_3$)$_3$RhCl; **3**) and Crabtree's catalyst ([(COD)Ir(PCy$_3$)(Py)]$^+$PF$_6$$^-$; Cy = cyclohexyl; Py = pyridine; **4**).



Scheme 1. Synthesis of the neutral phosphinoenolate Rh(I) and Ir(I) complexes (**2a**, **2b**) from P,N-cationic metal precursors (**1a**, **1b**).

2. Experimental

2.1. General considerations

Unless stated otherwise, all manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within a glovebox apparatus manufactured by mBraun Inc., utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. The non-deuterated solvents tetrahydrofuran, benzene, hexanes, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system manufactured by mBraun Inc. Tetrahydrofuran was purified over two alumina-packed columns, while benzene, hexanes, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. All solvents used within the glovebox were stored over activated 3 Å molecular sieves for 24 h prior to use. 1,2-Dichloroethane, styrene and triethylsilane (Aldrich) were degassed by using three repeated freeze–pump–thaw cycles and dried over activated 3 Å molecular sieves for 7 days prior to use. Complexes **2a** [11], **2b** [11], and Wilkinson's catalyst ((PPh$_3$)$_3$RhCl; **3**) [16] were prepared employing published methods, while Crabtree's catalyst ([(COD)Ir(PCy$_3$)(Py)]$^+$PF$_6$$^-$; **4**) was obtained from Strem.

2.2. General protocol for hydrosilylation experiments

The protocol used for these reactions employing 5.0 mol% catalyst loading (relative to Et$_3$SiH) in benzene with a styrene to silane ratio of 5:1 run at 60 °C is provided as a representative procedure. A solution of the catalyst compound in benzene (0.005 M in 4.5 mL solvent) was allowed to equilibrate for 5 min, at which point the alkene (0.5 M in 4.5 mL) was added by use of an Eppendorf pipette. The vial was then sealed and shaken vigorously for 15 s. Subsequently, Et$_3$SiH (0.1 M in 4.5 mL) was added to the reaction mixture by use of an Eppendorf pipette, and the vial was then sealed and shaken as before. Aliquots (1 mL) of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line, submerged in a temperature-controlled oil bath (60 °C), and magnetic stirring of the solutions was initiated. In the case of **2a**, clear yellow homogeneous solutions were observed throughout; for **2b**, clear red solutions developed during the course of the catalytic reactions. At the desired sampling time, the reactor cell was opened to air and ~1 mL of pentane was added via Pasteur pipette. The resultant mixtures were then filtered through a short Al$_2$O$_3$ column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC–MS [17,18], while quantitative data were obtained from GC–FID analysis; tabulated data represent the average of at least two runs.