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Notes

Catalytic Alkene Hydroboration Mediated by Cationic and Formally Zwitterionic Rhodium(I) and Iridium(I) Derivatives of a P,N-Substituted Indene

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*Summary: Cationic (**2a**,**b**) and formally zwitterionic (**3a**,**b**) Rh(I) and Ir(I) complexes supported by P,N-substituted indene or indenide ligands (respectively) have been employed in the selective hydroboration of substituted vinylarenes with pinacolborane (HBpin, pin = 1,2-$O_2C_2Me_4$). Notably, **3a**,**b** exhibited remarkably high, but differing, selectivities in the hydroboration of 1-phenylpropene.*

Introduction

Cationic square-planar complexes of the heavier group 9 metals are among the most effective and widely used classes of homogeneous catalysts for the addition of E−H and E−E bonds (E = main-group element) to unsaturated organic substrates.[1] While the design and construction of new cationic catalysts of this type continues to facilitate advancements in metal-mediated synthesis,[2] such discrete salts often display poor solubility in low-polarity media and can be rendered catalytically inactive in strongly coordinating solvents.[3] Furthermore, the strategic design of group 9 cationic catalysts is complicated by the fact that the accompanying outer-sphere counteranion influences the solubility and reactivity properties of the catalyst.[4] In this context, structurally related and formally zwitterionic group 9 species that feature formal charge separation between a cationic metal fragment and an associated anionic ancillary ligand are emerging as a complementary class of catalysts.[5] While the first zwitterionic Rh complexes explored in catalytic applications involving E−H and/or E−E bond activation were those supported by η^6-tetraphenylborate and related ligands,[6] other classes of Rh zwitterions in which the anionic charge carrier is a substituted carborane,[7] sulfate,[8] or borate[9] fragment have been developed and in some cases have exhibited desirable catalytic properties. Conversely, Ir zwitterions are much less common,[10] and their reactivity properties have not been explored in a systematic manner.

With the goal of establishing new classes of metal complexes that exhibit interesting and synthetically useful reactivity patterns with substrate E−H and/or E−E bonds, one of our groups has reported previously that **1a** can be employed in the preparation of cationic complexes such as **2a**,**b**, as well as structurally related

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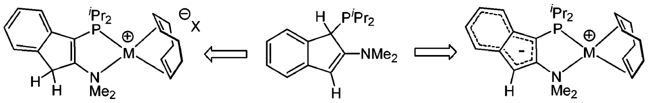
Scheme 1. Cationic and Zwitterionic κ^2-*P*,*N* Rh(I) and Ir(I) Complexes Derived from 1a



cationic
2a, M = Rh, X = PF_6
2b, M = Ir, X = PF_6

1a

zwitterionic
3a, M = Rh
3b, M = Ir

and formally zwitterionic species, including **3a**,**b** (Scheme 1).[11] Whereas **2a**,**b** can be compared with other more traditional group 9 [(COD)M(κ^2-*P*,*N*)]$^+$X$^-$ salts, the zwitterions **3a**,**b** constitute an unusual class of substituted indenyl−metal complexes,[12] which are comprised of a formally cationic [(COD)M]$^+$ fragment counterbalanced by an uncoordinated 10-π-electron indenide unit that is incorporated into the backbone of the κ^2-*P*,*N* ancillary ligand framework. Preliminary reactivity studies revealed the catalytic utility of **2a** and **3a** in alkene hydrosilylation reactions, and of **2b** and **3b** for alkene hydrogenation.[11c,d] In an effort to assess further the ability of these Rh and Ir complexes to mediate the addition of E−H and E−E bonds to unsaturated substrates, we turned our attention to the hydroboration and diboration of alkenes. Herein we report on the results of this catalytic survey and related reactivity studies, which suggest that **2a**,**b** and **3a**,**b** can be viewed as a complementary family of catalyst complexes for vinylarene hydroboration, especially when pinacolborane is employed (HBpin; pin = 1,2-$O_2C_2Me_4$). Notably, the successful application of **3b** in this context represents the first reported hydroboration reaction mediated by a formally zwitterionic Ir complex.

Results and Discussion

The addition of B−H bonds to unsaturated organic molecules represents an important synthetic methodology in organic chemistry.[13] While BH_3 adds rapidly to alkenes at −80 °C, alternative hydroborating agents such as catecholborane (HBcat; cat = 1,2-$O_2C_6H_4$) and HBpin are slow to react, even at elevated temperatures.[14] However, the reluctance of these $(RO)_2BH$ reagents to add to alkenes can allow for hydroborations to be carried out under the control of a catalyst.[15] Following a report by Männig and Nöth,[16] who demonstrated that Rh complexes could be used to catalyze the hydroboration of alkenes with HBcat under mild conditions and in some cases with selectivity differing from that of the uncatalyzed reaction, Rh and Ir complexes have emerged as the most effective catalysts for the addition of HBcat or HBpin to vinylarenes.[15,17] Nevertheless, achieving high levels of selectivity in such metal-catalyzed hydroboration reactions can still represent a significant challenge; in addition to the typical linear and less common branched hydroboration B−H addition products, borylated olefins and hydrogenated products are also observed frequently in such metal-catalyzed transformations. In the context of comparing and contrasting the catalytic abilities of our cationic (**2a**,**b**) and formally zwitterionic (**3a**,**b**) group 9 catalyst complexes, we viewed vinylarene hydroboration as representing an appealing prototype for metal-mediated E−H bond additions in which product selectivity can be difficult to achieve.[15,17,18]

Our initial catalytic studies (room temperature, THF-d_8, 2 mol % catalyst) examined the hydroboration of monosubstituted vinylarenes (4-vinylanisole and 4-fluorostyrene) with either HBcat or HBpin, catalyzed by **2a**,**b** or **3a**,**b**. Catalytic reactions were monitored by use of multinuclear magnetic resonance techniques, which allowed for the identification of numerous boron-containing species,[6f] including linear and branched hydroboration products and mono- and diborated species derived from dehydrogenative borylation reaction pathways,[19] as well as the corresponding substituted ethylbenzene arising from the hydrogenation of the vinylarene substrate. In turning our

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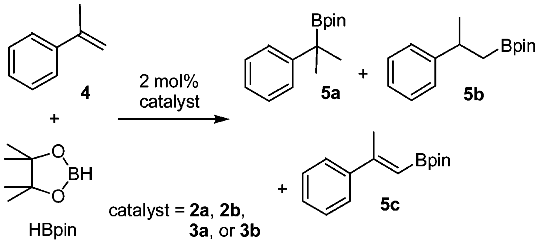
Scheme 2. Metal-Catalyzed Hydroboration of 2-Phenylpropene (4) using HBpin



Scheme 3. Metal-Catalyzed Hydroboration of 1-Phenylpropene (6) using HBpin

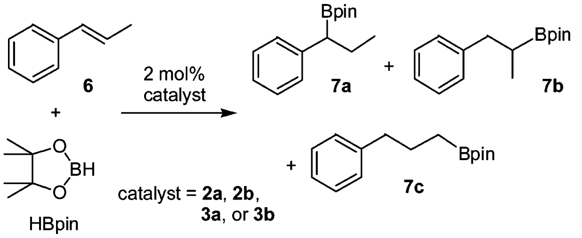


Table 1. Product Distribution Data for the Metal-Catalyzed Hydroboration of 2-Phenylpropene (4) and 1-Phenylpropene (6) with Hbpin[a]

	catalyst			
product	2a	3a	2b	3b
5a	0	30	0	0
5b	90	70	60	>95
5c	10	0	40	0
7a	80	>95	0[b]	0[b]
7b	20	0	0[b]	0[b]
7c	0	0	>95[b]	>95[b]

[a] Except where noted, reactions were carried out at room temperature in THF-d_8 with 2 mol % catalyst. Product distributions were determined based on ^{1}H NMR spectroscopic data after 72 h, at which point quantitative consumption of the vinylarene substrate was achieved. See the Supporting Information for complete experimental details. [b] Reaction carried out in refluxing toluene.

attention to disubstituted alkene substrates, the hydroboration of 2-phenylpropene (α-methylstyrene, **4**) mediated by **2a**,**b** or **3a**,**b** was investigated under similar conditions. Reactions of HBcat with **4** once again gave a complex mixture of products arising from competing hydroboration, dehydrogenative borylation, and hydrogenation reaction pathways. However, greatly enhanced selectivity was achieved when the less reactive HBpin was employed (Scheme 2), with each of the catalyst complexes exhibiting a preference for the linear addition product, **5b** (Table 1). Whereas the cationic Rh complex **2a** proved to be more selective than the structurally analogous zwitterion **3a**, the opposite trend was observed in the Ir system, with the formally zwitterionic catalyst **3b** producing **5b** exclusively. Notably, while significant quantities of the alkenyl boronate ester **5c** were generated in reactions employing the cationic catalyst complexes **2a**,**b**, such products arising from dehydrogenative borylation were not detected in reactions mediated by their formally zwitterionic relatives **3a**,**b**. In an effort to identify potential intermediates in these metal-catalyzed hydroborations, complexes **2a**,**b** and **3a**,**b** were treated separately with HBpin and B_2pin_2 (vide infra) and the progress of each reaction was monitored by use of ^{31}P NMR techniques. Unfortunately, under all experimental conditions surveyed (1 or 10 equiv HBpin or B_2pin_2; room temperature or 60 °C), complex reaction mixtures resulted, from which no pure materials could be obtained.

Encouraged by the catalytic results involving 2-phenylpropene (**4**), the metal-mediated hydroboration of 1-phenylpropene (β-methylstyrene, **6**) with HBpin was examined (room temperature, THF-d_8, 2 mol % catalyst), as depicted in Scheme 3. While the cationic Rh catalyst **2a** exhibited excellent selectivity for the hydroboration product **7a** (Table 1), the structurally related zwitterion **3a** proved superior, generating **7a** exclusively. Conversely, poor substrate conversions were achieved under analogous conditions employing **2b** and **3b**. However, both of these Ir catalyst complexes performed well at elevated temperatures (refluxing toluene, 2 mol % catalyst), affording the terminally substituted borane **7c** quantitatively. Product **7c** presumably arises from an initial metal-mediated isomerization of the double bond in **6** to give the corresponding α-olefin (3-phenylpropene), followed by a regioselective hydroboration step. While the isomerization of 3-phenylpropene to 1-phenylpropene (**6**) under similar conditions is common,[20] the apparent reverse rearrangement of **6** to 3-phenylpropene (ultimately leading to **7c**) has not been observed previously in metal-catalyzed hydroboration reactions. In contrast to the selectivity achieved in these reactions employing HBpin, complex product mixtures were generated in analogous hydroborations employing HBcat. In addition, in evaluating the utility of **2a**,**b** or **3a**,**b** in mediating the diboration[21] of the vinylarenes featured herein using either B_2cat_2 or B_2pin_2, complex product distributions arising from competing diboration, dehydrogenative borylation, hydroboration, and hydrogenation pathways were obtained, as has been observed previously in reactivity studies involving some other catalyst systems.[19i]

Control experiments conducted in the course of the aforementioned alkene hydroboration studies confirmed the stability of **2a**,**b** and **3a**,**b** in either THF or toluene at room temperature for a minimum of 72 h. However, the remarkably similar catalytic performance exhibited by **2b** and **3b** in the selective hydroboration of 1-phenylpropene (**6**) with HBpin at elevated temperatures prompted us to investigate the extent to which these Ir species might access a common reactive intermediate upon heating in solution. In this regard, we observed that heating of the formally zwitterionic **3b** in THF at 60 °C for 72 h resulted in the partial conversion (ca. 25%) to a single new phosphorus-containing species (**8**; $\delta(^{31}P)$ 14). Significant quantities of **8**, along with another as yet unidentified phosphorus-containing species ($\delta(^{31}P)$ 61), were also produced in toluene under similar conditions. Although we have thus far been unsuccessful in our efforts to isolate sufficient amounts of analytically pure **8** to allow for the comprehensive characterization of this complex, in one instance we were able to obtain a minute quantity of

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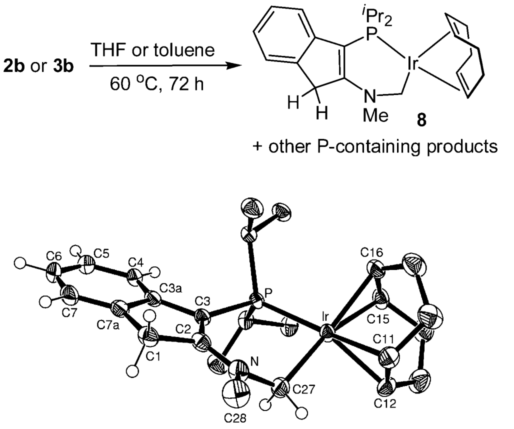

Figure 1. Formation of **8** from **2b** or **3b**. The ORTEP diagram for **8** is shown with 50% displacement ellipsoids; selected hydrogen atoms have been omitted for clarity.

pure **8** in crystalline form from pentane, which allowed for the spectroscopic (^{1}H and ^{31}P NMR) and X-ray crystallographic identification of **8** as the cyclometalation product depicted in Figure 1.[22] The generation of **8** from **3b** can be viewed as proceeding by way of an initial C−H activation step involving the NMe$_2$ fragment, followed by net transfer of a proton (either intra- or intermolecular) from the formally cationic Ir center to the indenide backbone of the ancillary ligand. We have observed similar cyclometalation processes in our examination of Pt and Ru coordination complexes of P,N-substituted indenes.[11b,23]

Whereas the cationic complex **2b** proved to be more thermally robust than **3b**, with only 10% decomposition observed after 72 h at 60 °C in THF or toluene (^{31}P NMR), once again **8** was identified as one of the thermolysis products. In this case, **8** can be viewed as arising from an initial insertion of Ir into a C−H bond of the NMe$_2$ unit in **2b**, followed by net loss of HPF$_6$. Notably, treatment of either **2b** or **3b** with NEt$_3$ for 12 h at room temperature in THF resulted in the consumption of the Ir starting complex, along with the formation of **8** as the major product. Nonetheless, all of our efforts to isolate pure **8** from such reactions have met with only limited success, and as such we are unable to comment regarding the catalytic competence of **8**. Unlike **2b** and **3b**, both of the Rh complexes **2a** and **3a** exhibited excellent thermal stability under similar experimental conditions, with no decomposition observed for **2a** and <5% decomposition detected in the case of **3a** (^{31}P NMR). As well, no reaction was observed upon exposure of **2a** or **3a** to NEt$_3$ for 12 h at room temperature in THF.

Summary and Conclusions

The cationic Rh and Ir complexes **2a**,**b**, as well as their formally zwitterionic relatives **3a**,**b**, have proven capable of mediating the selective hydroboration of disubstituted vinylarenes with pinacolborane (HBpin). To the best of our knowledge, the successful application of **3b** in this context represents the first reported hydroboration reaction mediated by a formally zwitterionic Ir complex. Despite the structurally similar metal coordination environments that are found in these cationic and formally zwitterionic complexes, some notable reactivity differences were observed both within and between the Rh and Ir cation/zwitterion pairs **2a**/**3a** and **2b**/**3b**. Particularly interesting was the selectivity observed in the hydroboration of 1-phenylpropene (**6**) with HBpin; while the branched product (**7a**) was favored when using one of the Rh catalysts (**2a** or **3a**), the linear product (**7c**) was formed exclusively in reactions mediated by either of the Ir catalysts (**2b** or **3b**). The observation that the formally zwitterionic catalysts (**3a**,**b**) provided either comparable or improved catalytic performance versus their cationic relatives (**2a**,**b**) in this transformation provides further evidence that such zwitterions represent an effective class of neutral catalyst complexes for the addition of E−H bonds to unsaturated substrates, whose reactivity properties are in some cases complementary to those of more traditional group 9 [(COD)M(κ^2-*P*,*N*)]$^+$X$^-$ salts.

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Supporting Information Available: Text giving complete experimental details and a CIF file giving single-crystal X-ray diffraction data for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] (a) Spectroscopic data for **8**: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.24 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H or C7-H), 7.18 (d, $^3J_{HH}$ = 6.5 Hz, 1H, C7-H or C4-H), 7.02 (t, $^3J_{HH}$ = 7.8 Hz, 1H, C5-H or C6-H), 6.76 (t, $^3J_{HH}$ = 7.3 Hz, 1H, C6-H or C5-H), 4.11 (br m, 2H, COD), 3.91 (br m, 2H, COD), 3.51 (s, 2H, C1(H)$_2$ or N-CH$_2$-Ir), 3.47 (s, 2H, NCH$_2$−Ir or C1(H)$_2$), 3.18−2.98 (m, 5H, NMe and P(C*H*Me$_a$Me$_b$)$_2$), 2.13−2.05 (m, 4H, COD), 1.85 (m, 2H, COD), 1.74 (m, 2H, COD), 1.27 (d of d, 6H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 15.0 Hz, P(CH*Me$_a$*Me$_b$)$_2$), 1.14 (d of d, 6H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 15.0 Hz, P(CHMe$_a$*Me$_b$*)$_2$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 13.7. (b) Selected crystallographic data for **8**: empirical formula, C$_{25}$H$_{37}$NPIr; formula weight, 574.73; crystal dimensions, 0.47 × 0.40 × 0.39; crystal system, monoclinic; space group, $P2_1/n$ (No. 14); a = 11.0069(8) Å; b = 9.2904(7) Å; c = 21.893(2) Å; β = 97.828(1)°; V = 2217.8(3) Å^3; Z = 4; ρ_{calcd} = 1.721 g cm^{-3}; μ = 6.103 mm^{-1}; 2θ limit = 52.82° with $-13 \le h \le 13$, $-11 \le k \le 11$, $-27 \le l \le 27$; total no. of data collected, 16 692; no. of independent reflections, 4539; no. of observed reflections, 4167; absorption correction, multiscan (SADABS); range of transmission, 0.1994−0.1616; no. of data/restraints/parameters, 4539/0/254; R1 ($F_o^2 \ge 2\sigma(F_o^2)$) = 0.0193; wR2 ($F_o^2 \ge 3\sigma(F_o^2)$) = 0.0505; goodness of fit, 1.037; largest peak, hole 1.193, −0.672 e Å^{-3}. Selected interatomic distances (Å) for **8**: Ir−P, 2.3314(7); Ir−C27, 2.088(3); Ir···N, 3.064; Ir−C11, 2.168(3); Ir−C12, 2.156(3); Ir−C15, 2.200(3); Ir−C16, 2.181(3); N−C2, 1.341(4); N−C27, 1.471(4); N−C28, 1.444(4); C1−C2, 1.519(4); C2−C3, 1.383(4).

[23] Wile, B. M.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 1959.