New bidentate cationic and zwitterionic relatives of Crabtree's hydrogenation catalyst†

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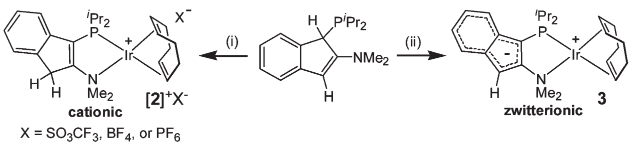
Inspired by the monodentate P,N ligation strategy featured in Crabtree's catalyst [(COD)Ir(PCy$_3$)(Py)]$^+$PF$_6$$^-$ ([1]$^+$PF$_6$$^-$), a new class of bidentate cationic ([2]$^+$X$^-$) and zwitterionic (3) Ir complexes have been developed, which are capable of mediating the hydrogenation of alkenes under mild conditions and in a wider range of solvents than is possible for [1]$^+$PF$_6$$^-$.

The metal-mediated hydrogenation of an alkene-containing substrate represents an important synthetic step in a wide range of prominent bench-top and industrial processes.[1] In this context, Crabtree's catalyst, [(COD)Ir(PCy$_3$)(Py)]$^+$PF$_6$$^-$ ([**1**]$^+$PF$_6$$^-$; COD = η^4-1,5-cyclooctadiene, Cy = cyclohexyl, Py = pyridine), has emerged as one of the most active homogeneous catalysts for alkene hydrogenation; in contrast to Ru- and Rh-based catalysts, [**1**]$^+$PF$_6$$^-$ is capable of reducing a range of substituted olefins under mild conditions (~1 atm H$_2$, 0 °C).[2] In evaluating the design features of [**1**]$^+$PF$_6$$^-$, Crabtree and co-workers noted that a formally cationic Ir center and a mixed P,N ancillary ligand set were needed to achieve optimal catalytic performance.[2] Building on this pioneering work, emphasis has shifted to the preparation of more rigid bidentate κ^2-*P*,*N* variants of [**1**]$^+$PF$_6$$^-$, in anticipation that these may be less susceptible to thermal decomposition or bimolecular deactivation.[2] Notably, chiral catalysts of this type have been developed that mediate the rather challenging asymmetric reduction of prochiral styrenes lacking directing functionalities.[3] In keeping with [**1**]$^+$PF$_6$$^-$, most bidentate [(COD)Ir(κ^2-*P*,*N*)]$^+$X$^-$ catalysts require the use of high-dielectric chlorinated solvents both to provide solubility and to maximize catalytic turnover.[4] As well, the nature of the counteranion (X) in such complexes has been shown to have a profound influence on the performance of the catalyst, often in a manner that cannot be predicted easily.[5]

In an effort to expand the scope and utility of Ir-mediated hydrogenation catalysis we became interested in comparing the structural and catalytic properties of cations of the type [**2**]$^+$X$^-$ with less-conventional zwitterions that feature a formally cationic Ir center counterbalanced by a 10π-electron indenide anion built into the backbone of a supporting κ^2-*P*,*N* ligand, as in the neutral complex **3** (Scheme 1).[6] We anticipated that formally charge-separated species such as **3** might combine the appealing catalytic activity of more traditional [(COD)Ir(κ^2-*P*,*N*)]$^+$X$^-$ catalysts with the desirable solubility properties associated with neutral complexes, while avoiding undesirable counteranion effects. The development of hydrocarbon-soluble zwitterionic Ir catalysts of this type is of particular interest, both in terms of providing a general means of circumventing the use of environmentally harmful chlorocarbon solvents for Ir-mediated alkene hydrogenations, and in light of the improved catalyst lifetime, reaction rate, and selectivity that might be achieved by employing a relatively inert, low-coordinating hydrocarbon as the reaction medium for such hydrogenations. Moreover, head-to-head reactivity studies involving [**2**]$^+$X$^-$ and the isostructural zwitterion **3** provide a rare opportunity to assess the impact on catalytic performance of adjusting only the electronic characteristics of an electrophilic Ir center on going from [**2**]$^+$X$^-$ to **3**, without substantially modifying the steric profile of the reactive metal coordination sphere.[7,8] Herein we describe the synthesis, structural characterization, and alkene hydrogenation capabilities of the new cationic complexes [**2**]$^+$X$^-$ (X = PF$_6$, BF$_4$ and SO$_3$CF$_3$), as well as the hydrocarbon-soluble complex **3** – the first formally zwitterionic analogue of Crabtree's catalyst.

The cationic complexes [**2**]$^+$X$^-$ were prepared from [(COD)IrCl]$_2$ and 1-P^{i}Pr$_2$-2-NMe$_2$-indene by use of AgX as the halide abstraction agent (X = PF$_6$, 78%; BF$_4$, 37%; and SO$_3$CF$_3$, 47%),‡ while the structurally analogous κ^2-*P*,*N* zwitterion (**3**) was prepared *via* lithiation of 1-P^{i}Pr$_2$-2-NMe$_2$-indene followed by treatment with [(COD)IrCl]$_2$ (93%). The structural formulations presented in Scheme 1 are based in part on data obtained from solution NMR spectroscopic studies, and in the case of [**2**]$^+$SO$_3$CF$_3$$^-$ and **3**, X-ray diffraction data (Fig. 1).§ The overall structural features of the Ir coordination spheres in [**2**]$^+$SO$_3$CF$_3$$^-$ and **3** are strikingly similar, with the Ir–P (2.299(1) Å) and Ir–N (2.192(4) Å) distances in the former differing only modestly from those found in the latter (2.3171(6) and 2.216(2) Å, respectively).[9] In contrast to the alternating bond lengths observed in the indene backbone of [**2**]$^+$SO$_3$CF$_3$$^-$, the carbocyclic framework of the κ^2-*P*,*N* ligand in **3** exhibits a much more delocalized structure



Scheme 1 Synthesis of new cationic and zwitterionic iridium catalyst complexes. *Reagents*: (i) 0.5 [(COD)IrCl]$_2$, AgX (X = PF$_6$, BF$_4$, or SO$_3$CF$_3$), then NEt$_3$ for X = PF$_6$ or SO$_3$CF$_3$; (ii) *n*-BuLi, then 0.5 [(COD)IrCl]$_2$ (COD = η^4-1,5-cyclooctadiene).

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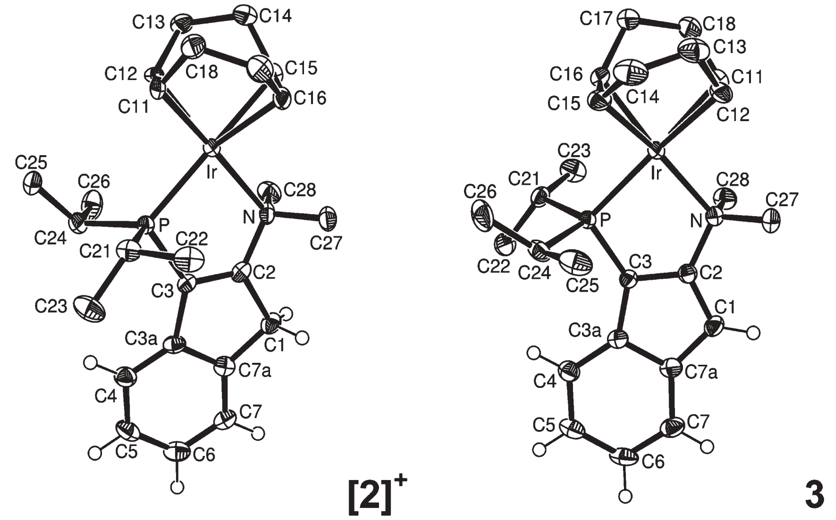

Fig. 1 ORTEP diagrams for [**2**]$^+$$SO_3CF_3^-$ and **3** shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; the anion in [**2**]$^+$$SO_3CF_3^-$ and selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for [**2**]$^+$$SO_3CF_3^-$: Ir–P 2.299(1), Ir–N 2.192(4), P–C3 1.807(5), N–C2 1.475(6), C1–C2 1.500(6), C2–C3 1.339(6), C3–C3a 1.491(6), C3a–C4 1.380(7), C4–C5 1.396(7), C5–C6 1.381(7), C6–C7 1.383(7), C7–C7a 1.390(6), C7a–C1 1.498(6), C3a–C7a 1.404(7); shortest Ir···SO_3CF_3 contact ~6.3 Å. Selected bond lengths (Å) for **3**: Ir–P 2.3171(6), Ir–N 2.216(2), P–C3 1.755(2), N–C2 1.478(3), C1–C2 1.381(3), C2–C3 1.413(3), C3–C3a 1.435(3), C3a–C4 1.406(3), C4–C5 1.374(4), C5–C6 1.411(4), C6–C7 1.370(4), C7–C7a 1.412(4), C7a–C1 1.424(4), C3a–C7a 1.440(3).

consistent with a 10π-electron indenide anion, as was observed in the corresponding Rh zwitterion.[6] However, while the formally zwitterionic **3** lacks a conventional resonance structure that places the anionic charge onto either of the N- or P-donor fragments, the shortening of the P–C3 distance on going from [**2**]$^+$$SO_3CF_3^-$ (1.807(5) Å) to **3** (1.755(2) Å) suggests that a less-conventional (and non-zwitterionic) resonance structure featuring a P=C3 bond and a negative charge on phosphorus may also contribute in **3**.[10]

The hydrogenation of styrene in CH_2Cl_2 (~1 atm H_2, 22 °C, 1.0 mol%) was examined in an initial effort to benchmark the catalytic performance of [**2**]$^+$$X^-$ and **3** against that of [**1**]$^+$$PF_6^-$ (Table 1). Complexes [**1**]$^+$$PF_6^-$ and [**2**]$^+$$PF_6^-$ proved equally effective, with clean conversion to ethylbenzene observed after 15 min (entries 1-1 and 1-2). Whereas quantitative reduction was also achieved after 30 min by employing [**2**]$^+$$BF_4^-$ (entry 1-3),[11] complete consumption of styrene was not observed for hydrogenations mediated by [**2**]$^+$$SO_3CF_3^-$ even after 4 h (entry 1-4). The dependence of the counteranion (*i.e.* $PF_6^- > BF_4^- > SO_3CF_3^-$) on catalytic activity in this series of complexes mirrors that noted in some other [(COD)Ir(κ^2-*P*,*N*)]$^+$$X^-$ catalyst systems.[5] In stark contrast to the negligible catalytic hydrogenation activity typically observed for neutral square-planar Ir complexes such as $(PPh_3)_3IrCl$,[12] the charge-neutral zwitterion **3** proved capable of reducing styrene to a significant extent (54% over 0.5 h, entry 1-5), and with a faster initial rate than was found for [**2**]$^+$$SO_3CF_3^-$. These observations indicate that the lower total productivity of **3** relative to [**1**]$^+$$PF_6^-$ and [**2**]$^+$$X^-$ may reflect the instability of **3** under these reaction conditions, rather than the inherent activity of this zwitterionic catalyst. Encouraged by these preliminary catalytic results, the hydrogenation of styrene in various solvents and at a lower catalyst loading (0.5 mol%) was also examined. Reactions employing [**1**]$^+$$PF_6^-$ and [**2**]$^+$$PF_6^-$ in CH_2Cl_2 were quantitative, although [**2**]$^+$$PF_6^-$ exhibited both a faster initial rate and a reduced total reaction time (entries 1-6 and 1-7). Clean reductions were also observed for reactions employing [**2**]$^+$$PF_6^-$ in THF rather than CH_2Cl_2, albeit at the cost of increased reaction time; in contrast, [**1**]$^+$$PF_6^-$ is only partially soluble in THF and the complete consumption of styrene was not achieved (entries 1-8 and 1-9). Interestingly, complex **3** performed similarly well in both CH_2Cl_2 and THF (entries 1-10 and 1-11), providing comparable yields and even faster initial rates at the 0.5 mol% catalyst loading level than were observed at the 1.0 mol% level (entry 1-5). Whereas [**1**]$^+$$PF_6^-$ and [**2**]$^+$$X^-$ are insoluble in all hydrocarbons, the benzene-soluble zwitterion (**3**) exhibited moderate catalytic activity both in this solvent (entry 1-12), as well as in aliphatic hydrocarbons (entry 1-13). By comparison, negligible styrene conversion (<3%) was achieved in benzene in the presence of catalytic amounts of the non-zwitterionic neutral species (COD)Ir(Cl)(κ^1-1-$P^i$$Pr_2$-2-$NMe_2$-indene),¶ which supports the

Table 1 Styrene hydrogenation results[a]

Entry	Catalyst	Solvent	Yield (%)	t^c/h	TON/TOF[d]
1-1	[**1**]$^+$$PF_6^-$	CH_2Cl_2	>99	0.25	100/400
1-2	[**2**]$^+$$PF_6^-$	CH_2Cl_2	>99	0.25	100/400
1-3	[**2**]$^+$$BF_4^-$	CH_2Cl_2	>99	0.5	100/280
1-4	[**2**]$^+$$SO_3CF_3^-$	CH_2Cl_2	97	4	97/165
1-5	**3**	CH_2Cl_2	54	0.5	55/210
1-6	[**1**]$^+$$PF_6^-$	CH_2Cl_2	>99	4	200/630
1-7	[**2**]$^+$$PF_6^-$	CH_2Cl_2	>99	0.5	200/740
1-8	[**1**]$^+$$PF_6^-$	THF[b]	91	4	183/415
1-9	[**2**]$^+$$PF_6^-$	THF	>99	4	200/400
1-10	**3**	CH_2Cl_2	56	4	113/355
1-11	**3**	THF	58	4	116/305
1-12	**3**	C_6H_6	37	4	75/165
1-13	**3**	Hexanes[b]	17	4	34/35

[a] *Conditions*: 22 °C and ~1 atm H_2; entries 1–5: 1.0 mol% and entries 6–13: 0.5 mol%. [b] Catalyst was not completely soluble in this solvent. [c] Time at which the conversion (yield) was achieved. [d] TON = moles alkane produced/moles catalyst and turnover frequency (TOF) at 0.25 h.

Table 2 Hydrogenation of substituted alkenes in CH$_2$Cl$_2$^{a}

Entry	Catalyst	Substrate	Yield (%)	t^b/h	TON/TOF^c
2-1	[**1**]$^+$PF$_6^-$	Cyclohexene	>99	0.25	200/800
2-2	[**2**]$^+$PF$_6^-$	Cyclohexene	>99	0.5	196/755
2-3	**3**	Cyclohexene	26	4	52/170
2-4	[**1**]$^+$PF$_6^-$	1-Methylcyclohexene	97	4	194/490
2-5	[**2**]$^+$PF$_6^-$	1-Methylcyclohexene	83	4	167/120

^{a} *Conditions*: 22 °C, ∼1 atm H$_2$, and 0.5 mol%. ^{b} Time at which the conversion (yield) was achieved. ^{c} TON = moles alkane produced/moles catalyst and turnover frequency (TOF) at 0.25 h.

view that the catalytic activity displayed by **3** can be attributed to the charge-separated nature of this neutral complex. In surveying the ability of these complexes to mediate the reduction of more substituted alkenes in CH$_2$Cl$_2$ under analogous conditions (Table 2), [**2**]$^+$PF$_6^-$ proved capable of quantitatively hydrogenating cyclohexene at a rate only slightly below that of [**1**]$^+$PF$_6^-$ (entries 2-1 and 2-2), and partial conversion was also noted for reactions employing **3** as a catalyst (26%, entry 2-3). However, while [**2**]$^+$PF$_6^-$ remained somewhat competitive with [**1**]$^+$PF$_6^-$ with respect to the reduction of 1-methylcyclohexene (entries 2-4 and 2-5), the zwitterion **3** proved incapable of reducing this trisubstituted alkene to any extent, either in CH$_2$Cl$_2$ or benzene.

The results detailed herein confirm that the κ^2-*P*,*N* ancillary ligand in [**2**]$^+$X$^-$ supports a coordination environment that is conducive to the Ir-mediated hydrogenation of olefins; notably, the catalytic performance of [**2**]$^+$PF$_6^-$ was found to be competitive with, and in some cases superior to, that of Crabtree's catalyst, [**1**]$^+$PF$_6^-$. The formally zwitterionic **3** has also proven to be an active catalyst for olefin hydrogenation under very mild conditions (∼1 atm H$_2$, 22 °C). While the catalytic abilities of **3** were found to be inferior to those of the more traditional catalyst salts [**2**]$^+$X$^-$ and [**1**]$^+$PF$_6^-$ under the conditions examined, the neutral character of **3** enabled hydrogenations to be carried out in a range of solvents, including hydrocarbons in which the cationic species are insoluble. In light of the nearly isostructural relationship that exists between the Ir coordination spheres in [**2**]$^+$X$^-$ and **3**, their disparate catalytic abilities can in principle be ascribed to differences associated with the electronic characteristics of the Ir centers in these complexes. Whereas [**2**]$^+$PF$_6^-$ is a highly active hydrogenation catalyst that has proven capable of reducing even trisubstituted alkenes, the electrophilicity of the formally cationic Ir center in the structurally analogous zwitterion **3** is apparently attenuated, possibly due to partial delocalization of the ancillary ligand anionic charge onto the P-donor fragment (*vide supra*). Based on these observations, we are currently developing more lipophilic analogues of **3** with the specific aim to augment the electrophilic character of the Ir center by discouraging charge delocalization onto the pnictogen donor fragments. Our progress in this regard, and in the study of chiral derivatives of [**2**]$^+$X$^-$ and **3**, will be the subject of future reports.

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Notes and references

‡ Attempts to prepare [**2**]$^+$B(C$_6$F$_5$)$_4^-$ by employing Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$ as the halide abstracting reagent generated intractable dark solids that gave rise to numerous ^{31}P NMR resonances. All isolated [**2**]$^+$X$^-$ complexes exhibited identical ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR features for [**2**]$^+$.

§ Both structures are space group = $P2_1/n$ (monoclinic) and Z = 4; D/R/P = data/restraints/parameters and GOF = goodness of fit. *Crystal data* for [**2**]$^+$SO$_3$CF$_3^-$: a = 9.9608(6), b = 20.271(1), c = 14.0988(9) Å, β = 103.575(1)°, V = 2767.2(3) Å^3, D/R/P = 5676/0/325, GOF = 1.002, R_1 = 0.0315, wR_2 = 0.0654. *Crystal data* for **3**: a = 9.6714(5), b = 16.9783(9), c = 14.5080(7) Å, β = 109.4177(7)°, V = 2246.8(2) Å^3, D/R/P = 4579/0/253, GOF = 1.086, R_1 = 0.0174, wR_2 = 0.0426. CCDC 270594 and 270595. See http://dx.doi.org/10.1039/b510253g for crystallographic data in CIF or other electronic format.

¶ This compound was prepared *in-situ* based on methods established for the synthesis of the Rh analogue.[6]

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