J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Olefin Isomerization and Hydrosilylation Catalysis by Lewis Acidic Organofluorophosphonium Salts

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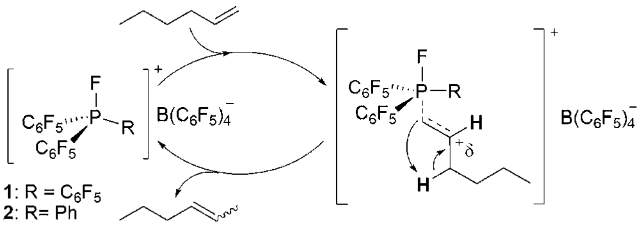
Supporting Information

ABSTRACT: Organofluorophosphonium salts of the formula $[(C_6F_5)_{3-x}Ph_xPF][B(C_6F_5)_4]$ ($x = 0, 1$) exhibit Lewis acidity derived from a low-lying σ^* orbital at P opposite F. This acidity is evidenced by the reactions of these salts with olefins, which catalyze the rapid isomerization of 1-hexene to 2-hexene, the cationic polymerization of isobutylene, and the Friedel–Crafts-type dimerization of 1,1-diphenylethylene. In the presence of hydrosilanes, olefins and alkynes undergo efficient hydrosilylation catalysis to the alkylsilanes. Experimental and computational considerations of the mechanism are consistent with the sequential activation and 1,2-addition of hydrosilane across the unsaturated C–C bonds.

Despite the extensive use of phosphorus compounds as Lewis bases in organometallic chemistry and catalysis, there are a few examples of such species exhibiting Lewis acidity. Gudat,[1] Burford,[2] Yoshifuji,[3] Bertrand,[4] and others have explored phosphenium cations as Lewis acids. Such P(III) centers are predicted to exhibit fluorophilicities comparable to known neutral Lewis acids.[5] P(V) centers such as those in ylide reagents are Lewis acidic, prompting their classic reactions with ketones,[6] whereas phosphonium cations mediate additions to polar unsaturates[7] and Diels–Alder reactions.[8] More recently, the Lewis acidity of phosphonium cations has been exploited by Gabbaï and co-workers to enhance the fluoride ion selectivity of adjacent B/P electrophiles.[9] Targeting further applications of Lewis acidic phosphonium cations, we incorporated electron-withdrawing aryl substituents, recognizing that these groups would offer additional stabilization of the σ^* LUMO at P.[10,11] This feature, together with the cationic charge, was expected to generate a highly electrophilic center. Indeed, the species $[(C_6F_5)_{3-x}Ph_xPF][B(C_6F_5)_4]$ (**1**, $x = 0$; **2**, $x = 1$) have been shown to exhibit Lewis acidity, binding the oxygen-donors DMF and Et_3PO.[11] The latter result indicated that the salt **1** is more Lewis acidic than $B(C_6F_5)_3$.[11] This characteristic renders these species sufficiently fluorophilic to effect C–F bond activations of fluoroalkanes via hydrodefluorination catalysis.[11] Given their Lewis acidity, we herein report the reactivity of organofluorophosphonium salts with olefins and alkynes, demonstrating their unique ability to effect olefin isomerization and hydrosilylation of olefins and alkynes.

The reaction of 1-hexene with phosphonium salt **1** was investigated. For example, using 1 mol % **1** in CD_2Cl_2, nearly complete conversion of 1-hexene to 2-hexene was observed within <1 h at ambient temperature. This reaction is slowed under dilute conditions. ^1H and $^{13}C\{^1H\}$ NMR spectra indicate the formation of both *cis*- and *trans*-2-hexene as the major products (Scheme 1) along with small quantities of polyolefin (see Supporting Information). Clearly, this observation suggests a direct interaction of the **1** with the olefin. In this regard, it is interesting to note that electrophilic boranes, which are less Lewis acidic than **1**, have been shown to exhibit van der Waals interactions with olefins.[12,13] Thus, isomerization of the terminal olefin is thought to proceed via its interaction with the Lewis acidic phosphonium center, generating an incipient carbocation that can undergo a 1,3-proton migration (Scheme 1). In a separate experiment, *cis*-2-hexene was added to a C_6D_5Br solution containing **1**. After 2 h the partial isomerization to *trans*-2-hexene was observed spectroscopically, indicating that **1** also catalyzes the *cis*/*trans* isomerization of an internal olefin.

Scheme 1. Phosphonium-Catalyzed Isomerization of 1-Hexene to 2-Hexene



In a similar fashion, a stirred CH_2Cl_2 solution of **1** at −78 °C was subjected to 1 atm of isobutylene for 30 min. From the resulting viscous mixture, poly(isobutylene) was isolated. GPC data showed M_W of 4.0×10^5 Da, with a polydispersity of 1.7. ^1H and $^{13}C\{^1H\}$ NMR analysis were consistent with the linear polymer being the major component.[10] Interaction of isobutylene with **1** is thought to produce a relatively stable tertiary carbocation that facilitates rapid cationic polymerization. In contrast, the analogous reaction of 1,1-diphenylethylene with 1.5 mol % **1** in CH_2Cl_2 resulted in a Friedel–Crafts-type cyclodimerization product. Such reactivity is known to occur in the presence of Lewis acids including $B(C_6F_5)_3$.[14,15]

Having observed interactions of fluorophosphonium salts with olefins, trials to effect olefin hydosilylation catalysis were undertaken. In an initial run, Et_3SiH and 1-hexene were added to a CD_2Cl_2 solution containing 1.5 mol % of catalyst **1**. ^1H and $^{13}C\{^1H\}$ NMR spectroscopic analyses of the mixture showed

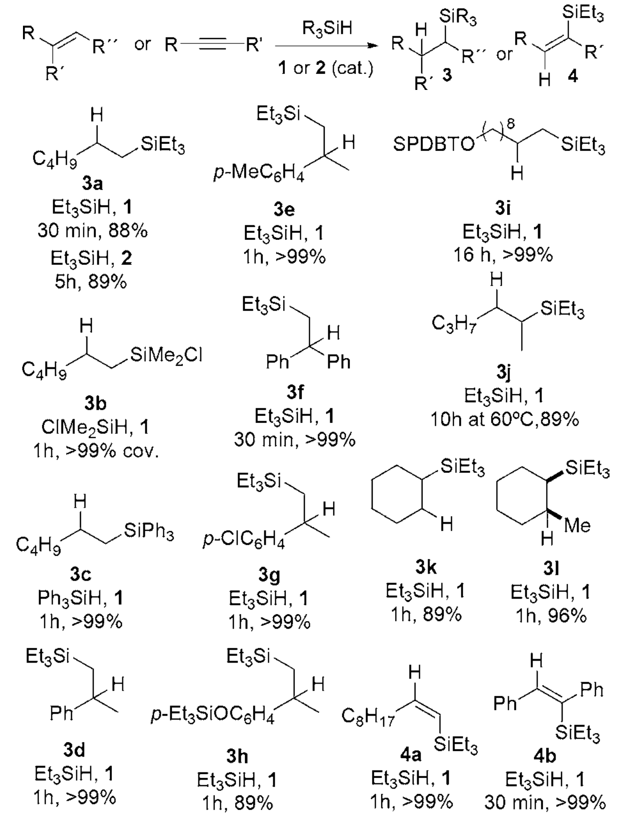
Received: October 9, 2013
Published: November 20, 2013

ACS Publications © 2013 American Chemical Society

dx.doi.org/10.1021/ja410379x | J. Am. Chem. Soc. 2013, 135, 18308–18310

that the reaction was complete after 30 min, and the product triethyl(hexyl)silane (**3a**) was isolated in 88% yield (Table 1).

Table 1. Hydrosilylation Reactions[a]



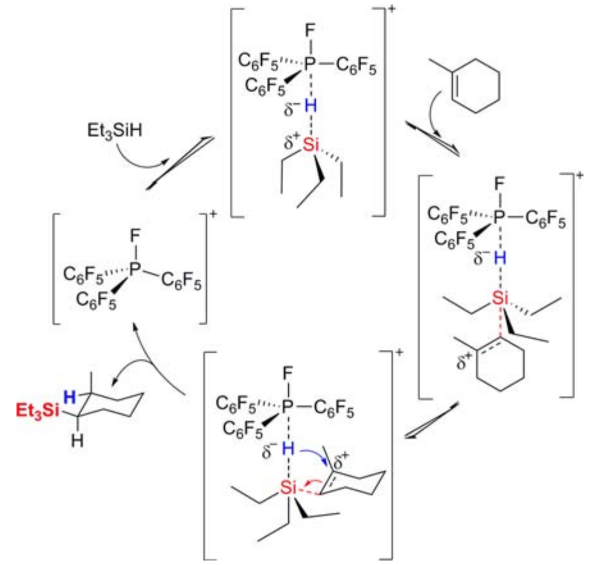
[a] Hydrosilane/olefin mixtures were added to **1** or **2** in CH_2Cl_2, CD_2Cl_2, or C_6D_5Br and left at ambient temperature, except for **3j** (left at 60 °C). Isolated yields are reported, except for **3b** (determined by ^1H NMR).

Using the less-electrophilic phosphonium salt **2** in an analogous reaction required that the catalyst loading be increased to 9 mol % to achieve complete conversion after 5 h. Similar hydrosilylations of 1-hexene were also carried out using silanes Me_2ClSiH or Ph_3SiH in the presence of 1.5 mol % **1**, resulting in excellent product yields. The above protocol was compatible with styrenes, resulting in their complete conversions and near-quantitative yields in all cases (Table 1). It is noteworthy that the *p*-chloro-substituted product (**3g**) is accessible, allowing the possibility of further functionalization of the arene. In the case of *p*-methoxy-*α*-methylstyrene, **1** catalyzed the addition of Et_3SiH to the olefin but also resulted in the replacement of the *O*-methyl group by Et_3Si. Phosphonium cation catalyst **1** was tolerant of the silyl ether functionality, affording **3i** in excellent yield after 12 h. Internal olefins also underwent hydrosilylation, as heating *trans*-2-hexene to 60 °C with Et_3SiH in the presence of **1** gave selective conversion to **3j**, whereas cyclohexene reacted with this silane to produce **3k** in good yield at room temperature. Finally, the alkynes dec-1-yne and diphenylacetylene were hydrosilylated with Et_3SiH, producing selectively the *cis*-olefinic products **4a** and **4b**, respectively, in high yields.

Efforts to garner some mechanistic insights were undertaken. To this end, the ^1H NMR spectrum of Et_3SiH with 5 mol % **1** in CD_2Cl_2 at ambient temperature shows a dramatically broadened SiH signal with no observable $^3J_{HH}$ to the CH_2 units, consistent with a Si···H···P interaction. This feature is consistent with previously reported data[11] and is reminiscent of observations made by Piers and co-workers who described hydrosilylation catalysis by $B(C_6F_5)_3$, which serves to activate the silane.[16−21] Thus, the phosphonium cation catalysts appear to activate both olefin and silane in independent experiments, bringing into question the pathway for hydrosilylation. It is noteworthy that during hydrosilylation catalysis, no evidence for olefin isomerization or polymerization was observed.

Calculations at the wB97XD/def2-TZV level of theory[22,23] were conducted by modeling interactions of the phosphonium ion with silane and olefin. Computations have previously shown that the LUMO of the phosphonium cation contains the σ^* orbital oriented opposite the P−F bond. It is this orbital that was found to be the acceptor, prompting interaction of hydrosilane with **1**. The calculations also reveal that this interaction results in a ΔH of -15.2 kcal mol^{-1} This stabilization was found to be greater than the corresponding interaction of **1** with olefin ($\Delta H = -8.1$ kcal mol^{-1}; see Supporting Information). These data are, thus, consistent with a mechanism in which phosphonium activates hydrosilane. This view is further supported by the observation that attempts to effect hydrosilylation with the sterically encumbered silane iPr_3SiH shows no reaction over a 24 h period. Experimental data for the hydrosilylation of methylcyclohexene (Scheme 2) using Et_3SiH afforded the product **3l** using either $B(C_6F_5)_3$[24−26] or **1** as the catalyst. In the case of borane-catalyzed hydrosilylation, previous studies by the groups of Gervorgyan[26] and Oestreich[27] have unambiguously established an *anti* 1,2-addition of Si−H to olefin. A similar mechanism has been demonstrated by Oestrich for ketone and imine hydrosilylation.[24,25] Thus, in the present case, a similar route is proposed in which addition of olefin to phosphonium-activated silane generates a carbocation[24,25] to which the hydride is delivered in an *anti*-fashion. The stability of the fluorophosphonium cations throughout the catalysis support the view that free silylium cation is not generated as silylium ions would be expected to degrade the fluorophosphonium cation to yield the notoriously strong Si−F bond.[10,11]

Scheme 2. Proposed Mechanism of Hydrosilylation



Olefin hydrosilylation reactions are important catalytic processes employed industrially to produce a variety of silicon-containing materials.[28−33] Hydrosilylation catalysts based on platinum group metals such as Pt, Pd, Ru, and Rh are commonly employed,[34−38] and despite their high costs, Pt compounds represent the most common catalysts for this purpose.[39−42] In 2012, Chirik et al. reported reactive Fe compounds as interesting alternatives to Pt.[43] To date, known metal-free catalysts for hydrosilylation are based on Lewis acidic B and Al species.[26,29] The present results provide a new avenue to this reaction and are the first to employ electrophilic fluorophosphonium cation catalysts for hydrosilylation.

To summarize, it has been shown that the σ^* orbital of phosphonium cations with suitable substituents is sufficiently low in energy to result in strong Lewis acidity. This feature is evidenced by the ability of theses cations to effect olefin isomerization, initiate cationic polymerizations, and catalyze the hydrosilylation of olefins and acetylenes. This approach affords a new avenue to Lewis acid catalysis and further expands the applications of metal-free catalysts into reactivity traditionally achieved by transition metal catalysts. We are continuing to probe the reactivity of these and related electrophilic phosphonium cations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparations of compounds, reaction procedures, NMR spectra, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of NSERC of Canada. D.W.S. is grateful for the award of a Canada Research Chair. C.B.C. gratefully acknowledges the receipt of an NSERC of Canada CGS-D and a Walter C. Sumner Fellowship.

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