ORGANOMETALLICS

Phosphorus Coordination Chemistry in Catalysis: Air Stable P(III)-Dications as Lewis Acid Catalysts for the Allylation of C-F Bonds

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Supporting Information

ABSTRACT: Modification of C-F bonds with main-group catalysts has typically employed electron-deficient Lewis superacids in high oxidation states, and the challenges of preparing and handling such species have prevented broader adoption of metal-free reduction protocols. Here, we show that a hemilabile ligand coordinated to an easily accessed P(III) center imparts air stability without sacrificing the ability to activate C-F bonds. Catalytic C-C coupling of benzyl fluorides with allylsilanes was achieved using a P(III) complex under benchtop conditions. This application of coordination chemistry principles to main-group Lewis acids reveals a new strategy for controlling catalysis.



he evolution of p-block-based catalysts has most commonly involved variations of the substituents or molecular charge on the main-group element. For example, neutral compounds such as BF₃ and AlCl₃¹ or cationic species such as [CPh₃]⁺ and [SiEt₃]²⁺ are classic main-group Lewis acids that derive their Lewis acidity from a vacant p orbital on the central atom. Such species have found widespread applications in synthetic chemistry. Similarly, modifications of the substituents on the main-group elements to alkyl or aryl substituents have broadened the range of utility. Among the numerous variations, the electrophilic borane $B(C_6F_5)_3$ has been widely used as a catalyst activator in olefin polymerizations, as a Lewis acid catalyst for hydrosilylations, and as the quintessential Lewis acid in frustrated Lewis pair (FLP) chemistry.³ More recently, we have focused attention on electrophilic phosphonium cations (EPCs), which derive their Lewis acidity from vacant σ^* orbitals. Such P(V) species are highly reactive^{2c,4} and have been shown to catalyze hydrodefluorination,^{4d} hydroarylation,⁵ hydrogenation,⁶ dehydrocoupling, polymerization,⁷ hydrosilylation,⁷ and $C(sp^3)-C$ -(sp³) cross-coupling.⁸

Targeting a broader synthetic strategy to p-block Lewis acid catalysts, we noted the innumerable developments of homogeneous transition-metal catalyst systems that have emerged from the concepts of coordination chemistry. Using judicious ligand design and ligand libraries, families of catalysts are readily synthesized and are tunable for specific reactivity. In contrast, these principles have had limited application in the development of p-block-element-based catalysts. Notable exception are catalysts derived from group 13 complexes, where the modular design of O/N-based salen or porphyrin ligands has been exploited for polymerization catalysts. We also noted the seminal work of Burford⁹ and others,¹⁰ who have prepared a broad array of electrophilic polycations by replacing

anionic substituents at P(III) with neutral donors.¹¹ On the basis of these developments, we envisioned families of catalysts derived from P(III) coordination compounds. Herein, we begin by targeting P(III)-based Lewis acid catalysts derived from the coordination of bi- and tridentate N-based ligands to a dicationic P(III) center. These species effect catalytic $C(sp^3)-C(sp^3)$ cross-coupling of C-F bonds with allylsilanes, illustrating the potential of main-group coordination compounds to provide reactivity complementary to transitionmetal systems.

We have recently described P(III) dications stabilized by bipyridine and terpyridine: namely, [(bipy)PPh][B(C₆F₅)₄]₂ (1) and $[(terpy)PPh][B(C_6F_5)_4]_2$ (2) (Figure 1).¹² In a similar fashion, the diimino-pyridine complexes $[(C_5H_3N)(C_7)]$ $(Me)=NR_{2}PPh][X]_{2}$ (X = O₃SCF₃, R = Mes (3), Dipp (4); $X = B(C_6F_5)_4$, R = Mes (5), Dipp (6)) (Figure 1) were prepared from a one-pot reaction combining PhPCl₂, Na[B- $(C_6F_5)_4$], or Me₃SiOSO₂CF₃ and the appropriate tridentate ligand in DCM. The cations of 3/5 and 4/6 exhibit ³¹P NMR chemical shifts at 33.5 and 61.2 ppm, respectively, consistent with the dicationic charge. X-ray structures of 3 and 5 unambiguously confirmed these formulations (Figure 2). The $P-N_{imine}$ distances in 3 were found to be 1.960(3) and 1.994(3) Å, while the P–N $_{\rm Py}$ distance is 1.787(3) Å. While the tridentate ligands are essentially planar, the phenyl ring is approximately orthogonal to this plane, with C-P-N angles of 93.4(1), 88.7(1), and 106.3(2)°. The corresponding P-C distance is 1.815(4) Å. Similar metrics were observed for 5, although disorder in the aryl-N groups precludes a detailed

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Figure 1. Phosphorus dication complexes 1-6.



Figure 2. POV-ray depiction of the dications of (a) **3** and (b) **5**. Color scheme: P, orange; C, black, N, blue. Hydrogen atoms and the triflate anions have been omitted for clarity.

comparison; nonetheless, the metrics are comparable to those in the molecular structures of the cations in 1 and 2.

The established ability of 1 and 2 to activate C–F bonds for hydrodefluorination prompted an examination of the potential for catalytic C–C coupling reactions. To this end, preliminary experiments were performed, generating 2 mol % of species 1, 2, 5, and 6 in situ with the subsequent addition of the benzyl fluoride and the allylsilane. These screenings were consistent with the generation of silyl fluoride and the formation of the C–C coupling product $C_6H_5CH_2CH_2C(R)=CH_2$, albeit in unoptimized yields.

To elaborate these catalytic C–C bond formations, the preparations of the dicationic species were done on a larger scale. These syntheses of compounds 5 and 6 proved challenging, while compounds 1 and 2 were readily prepared and purified on a gram scale. Using $0.5-2 \mod \%$ of the species 1 as a Lewis acid catalyst in the reactions of the benzyl fluorides 4-RC₆H₄CH₂F (R = Ph, *t*Bu, F) and 2-PhC₆H₄CH₂F, adamantyl fluoride, or C₅H₁₁F with the allylsilanes CH₂=

C(R)CH₂SiMe₃ (R = Me, H, Br, CH₂Cl) furnished the corresponding C–C coupled allylated benzyl derivatives of the general form $RC_6H_4CH_2CH_2C(R)=CH_2$ (R = Ph, tBu, F) or $RCH_2C(R)=CH_2$ (R = Ad, Cy) and Me₃SiF (Table 1 entries 1–16). In general, good to excellent conversions to the C–C coupling product were observed for nearly all substrates at room temperature in DCM. Although 1 does function as a highly efficient catalyst (TON up to 500) for these C–C coupling reactions, it does require anhydrous and O₂-free conditions, as it decomposes rapidly in air.

In marked contrast, the hypervalent P(III) terpy complex 2 (Gutmann-Beckett acceptor number 27) is a substantially weaker electrophile in comparison to 1 (acceptor number 93) but is more user-friendly from a practical perspective. It is airstable in the solid state, and solutions of 2 show only 7% decomposition in air over 24 h. Gratifyingly, 2 also catalyzes the C–C coupling of benzyl fluorides $4-RC_6H_4CH_2F$ (R = Ph, tBu, F), 2-PhC₆H₄CH₂F, and 3,4-C₆F₂H₃CH₂F with the allylsilanes $CH_2 = C(R)CH_2SiMe_3$ (R = Me, H, Br, CH_2Cl , 4-PhC₆H₄) to give $C(sp^3)-C(sp^3)$ coupled products of the general form $RC_6H_4CH_2CH_2C(R) = CH_2$ and Me_3SiF (Table 1, entries 19-37). While these reactions are slower than those mediated by 1 and require the elevation of temperature to 35-100 °C, the yields are excellent even when reactions were performed in air using wet DCM as the solvent (Table 1, entries 21, 22, 26, 29, 32). Furthermore, the scope was extended to effect addition of allylsilanes to 1-fluoroadamantane, 1-fluoropentane, difluorotoluene, and trifluoromethyltoluene (Scheme 1). In the last two cases, the di- and triallylated products were detected by mass spectroscopy, but additional decomposition, presumably via Lewis acid catalyzed polymerization, was also observed. Efforts to intercept the mono- or diallylated intermediates by adjusting the stoichiometry were unsuccessful.

Mechanistically, this catalytic activity is thought to involve the activation of C-F bonds by the Lewis acidic phosphorus dications. While compound 1 is coordinatively unsaturated, dissociation of one arm of the tridentate ligand is required to generate such Lewis acidity in compounds 2, 5, and 6. The possibility of such hemilability was probed computationally for 2 and 5. In the case of 2, dissociation of a ligand arm yields a species resembling 1 and is 16.6 kcal/mol uphill with an activation barrier of 18.9 kcal/mol. Dissociation of one of the imine arms in 5 proceeds over an activation barrier of 23.0 kcal/mol to give an intermediate that is 21.7 kcal/mol higher in energy than the coordinatively saturated species. These observations are consistent with the air stability of the 10valence-electron phosphorus centers, yet they also account for the reactivity that is thermally accessible in solution. Further evidence of the role of coordinative unsaturation in the initiation of the C-F bond activation was derived from the combination of 1 or 2 with a stoichiometric amount of pphenylbenzyl fluoride. This led to an immediate reaction, with the ³¹P and ¹⁹F NMR spectra indicating formation of P-F bonds and ultimately PhPF₂ (Figures S76-S80), along with poly(methylenebiphenylene) via Friedel-Crafts oligomerization. It is noteworthy that equimolar combinations of 1 or 2with methallyltrimethylsilane showed no reaction at room temperature. For 2, even heating to 55 °C for 2 days showed no reaction. ³¹P NMR spectroscopy showed the persistence of the P(III) cations at the end of the catalytic reactions (Figures S81 and S82). Silyl cation catalysis seem unlikely, as such species have short lifetimes in DCM¹³ at 55 °C and are highly

Table 1. Catalytic $C(sp^3)-C(sp^3)$ Coupling of C-F Bonds with Allylsilanes by 1 or 2^a

 \mathbb{R}^1 Ι.

		R^F +	R' Si< _[℃	cat.] → R			
	Augraelliana	n ¹	-IVI	e ₃ SIF	$T(^{\circ}C)$	riald 0/	n no d
	пиогоакане	K	Cat. (%)	ι (Π)	I (C)	yield, 70	prou.
			Catalyst	1		h	
1	$4-PhC_6H_4CH_2F$	Me	0.8	2	25	>998	A
2	$4-PhC_6H_4CH_2F$	H	1.0	2	25	>990	В
3	$4-PhC_6H_4CH_2F$	Br	2.4	1	25	98 ^b	С
4	$4-PhC_6H_4CH_2F$	CH ₂ CI	1.5	1	25	86 ⁰	D
5	$4-tBuC_6H_4CH_2F$	Me	0.4	2	25	72^{b}	E
6	$4-tBuC_6H_4CH_2F$	Н	0.7	1	25	47 ⁰	F
7	$4-tBuC_6H_4CH_2F$	Br	1.5	2	25	>990	G
8	$4-tBuC_6H_4CH_2F$	CH_2Cl	1.2	1	25	860	Н
9	$4-FC_6H_4CH_2F$	Me	0.3	2	25	>99%	I
10	$4-FC_6H_4CH_2F$	Н	0.2	1	25	61 ^b	J
11	$4-FC_6H_4CH_2F$	Br	1.3	1	25	67 ⁶	K
12	$4-FC_6H_4CH_2F$	CH_2Cl	1.9	1	25	70^{b} (55)	L
13	2-PhC ₆ H ₄ CH ₂ F	Me	0.2	4	25	>99 ⁶	Μ
14	2-PhC ₆ H ₄ CH ₂ F	Н	0.4	4	25	>99 ^b (91)	Ν
15	2-PhC ₆ H ₄ CH ₂ F	Br	2.0	1	25	>99 ⁶	0
16	2-PhC ₆ H ₄ CH ₂ F	CH_2Cl	1.7	1	25	83 ⁶	Р
17	Ad-F	Н	0.3	0.5	25	82 ^b	Q
18	$C_5H_{11}F$	Н	0.2	22	25	25 ^b	S
			Catalyst	2			
19	4-PhC ₆ H ₄ CH ₂ F	Me	1.4	20	35	89 ^b	Α
20	4-PhC ₆ H ₄ CH ₂ F	Me	2.9	30	55	80 ^c	Α
21	4-PhC ₆ H ₄ CH ₂ F	Me	2.9	30	55	83 ^d	Α
22	4-PhC ₆ H ₄ CH ₂ F	Н	3.3	24	25	88^{d} (58)	В
23	4-PhC ₆ H ₄ CH ₂ F	CH ₂ Cl	4.8	30	55	91 ^b	D
25	$4-tBuC_6H_4CH_2F$	Me	1.5	20	25	91 ^c	Е
26	$4-tBuC_6H_4CH_2F$	Н	2.9	24	55	95 ^d	F
27	4-FC ₆ H ₄ CH ₂ F	Me	1.2	20	35	89 ^b	Ι
28	2-PhC ₆ H ₄ CH ₂ F	Me	1.2	20	35	96 ^c	Μ
29	2-PhC ₆ H ₄ CH ₂ F	Me	5.1	30	25	88 ^d	Μ
30	2-PhC ₆ H ₄ CH ₂ F	Н	5.3	40	55	95 ^b	Ν
31	2-PhC ₆ H ₄ CH ₂ F	Br	4.1	30	55	85 ^b	0
34	Ad-F	Me	7	0.25	25	86 ^c	R
35	$C_5H_{11}F$	Н	8	24	55	83 ^b	S
24	4-PhC ₆ H ₄ CH ₂ F	$4-FC_6H_4$	3.7	20	55	86 ^b	Т
32	3,4-C ₆ F ₂ H ₃ CH ₂ F	Me	3.7	20	55	79^d	U
33	3,4-C ₆ F ₂ H ₃ CH ₂ F	Br	3.4	64	55	67 ^c	v
36	PhCF ₂ H	Me	3.7	24	55	b,e	W
37	PhCF ₃	Me	2.7	20	100	b,e	Х

 R^1

"Reactions were performed with 0.1 mmol of alkyl fluoride and 0.3 mmol of allylsilane. "Performed under an N2 atmosphere using dry DCM. ^cPerformed in air using dry DCM. ^dPerformed in air using undried DCM. ^eComplete consumption of starting material was observed, but accurate yields could not be determined due to purification issues. Isolated yields for reactions done on a 1 mmol scale are given in parentheses. Yields were determined by NMR spectroscopy using mesitylene as internal standard.

moisture sensitive. Brønsted acid catalysis¹⁴ was discounted, as reactions in wet DCM required higher catalyst loadings and temperatures and longer reaction times to reach completion. Collectively, these data suggest that 1 and 2 are catalysts rather than stoichiometric initiators forming silyl cations from allylsilanes. We propose a mechanism involving C-F bond activation by coordination of the benzyl fluoride to the P(III) Lewis acid and subsequent nucleophilic attack by the allylsilane, affording C-C bond formation and fluoride transfer to the silvl group, regenerating the P(III) dications (Scheme 2). It is noteworthy that the reaction of pentyl fluoride provides a mixture of C-C coupling products; thus, a

mechanism involving carbocationic intermediates is also possible.

A preliminary assessment of functional group tolerance of the catalysts 1 and 2 was obtained by performing catalytic couplings of allylsilanes $CH_2 = C(R)CH_2SiMe_3$ (R = Me, H) with 4-PhC₆H₄CH₂F in the presence of 1 equiv of a functionalized additive (see the Supporting Information). The reactions mediated by 1 were significantly inhibited by addition of donors such as p-FC₆H₄CN, OBn₂, PhOH, DMF, pyridine, and Ph₂NH and were only moderately effective in the presence of Ph₂CO and Ph₂O. Complex 2 exhibited better tolerance, affording 50-84% yields of the C-C coupling product in the presence of *p*-FC₆H₄CN, OBn₂, PhOH, Ph₂NH,

Scheme 1. C-C Coupling Products Using 1 and 2 as Catalysts







and Ph_2CO , but showed no activity in the presence of DMF or pyridine. These data illustrate that donors inhibit the reactivity of **1**, whereas for **2**, the hemilability of the tridentate ligand, which generates the active site, also provides intramolecular competition for external donors.

The ability to activate C-F σ -bonds, known for their strength and kinetic inertness, is interesting, as this transforms a fragment generally perceived as inert into a functional group for C-C bond formation. This aspect was furthered by the chemoselectivity of these P(III) catalysts for C-F bonds. The reactivity of benzyl chlorides and bromides revealed no allylation at room temperature. However, heating the reaction mixture of 4-PhC₆H₄CH₂Br and CH₂=C(H)CH₂SiMe₃ to 55 °C resulted in a yield of B in 24% using 1 as the catalyst and 19% using 2 (see the Supporting Information). The high selectivity for reactions of C-F bonds stands in contrast to metal-mediated cross coupling reactions, where alkyl bromide and chloride species are highly reactive whereas alkyl fluorides are not. Thus, the present main-group catalysts provide chemistry that is orthogonal to the plethora of transitionmetal-based C-C coupling protocols.

In conclusion, we have reported the first application of P(III) Lewis acids in a catalytic C–C coupling reaction using alkyl fluorides and allylsilanes. Notably, the hypervalent catalyst 2 strikes a balance between activity and stability, allowing C–F bond activation to proceed under ambient benchtop conditions due to the presence of a hemilabile

ligand. This strategy contrasts with the previous use of highly reactive low-coordinate main-group Lewis superacids (e.g., silylium, alumenium, fluorophosphonium cations). While these findings foreshadow a more general adoption of main-group catalysts in C–F bond functionalization, the present report reveals the potential of easily accessible P(III) coordination compounds in catalysis. Ongoing efforts are targeting new catalytic applications of such main-group coordination complexes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00686.

Experimental and crystallographic data (PDF)

Accession Codes

CCDC 1869010–1869011 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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