Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Supplementary Information for:

Dehydrocoupling Routes to Element-Element Bonds Catalysed by Main Group Compounds

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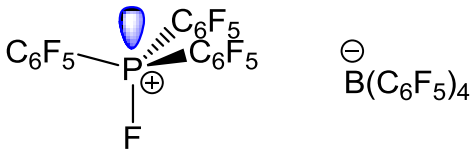
1. Tables and Figures

Table S1. Si-O dehydrocoupling reactions catalysed by $B(C_6F_5)_3$.[1]

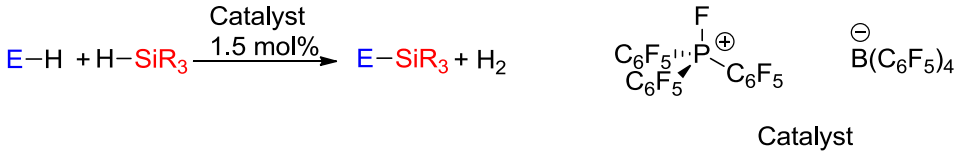
Alcohol	Silane	Product	Catalyst Loading	Time /h	Yield*
CyOH	Ph_3Si-H	Cy**O-Si**Ph_3	2 mol%	1	95
$^{i}Pr_2C(H)OH$	Ph_3Si-H	$^{i}Pr_2C(H)$**O-Si**Ph_3	2 mol%	2	95
1-AdOH	Et_3SiH	1-Ad**O-Si**Et_3	1 mol%	<1	79
H_2C=C(H)CH_2OH	Ph_3Si-H	H_2C=C(H)CH_2**O-Si**Ph_3	2 mol%	4	95
HC≡CCH_2OH	Ph_3Si-H	HC≡CCH_2**O-Si**Ph_3	8 mol%	2	95
$BrCH_2CH_2OH$	Ph_3Si-H	$BrCH_2CH_2$**O-Si**Ph_3	2 mol%	1	93
(*p*-OMe)C_6H_4OH	Ph_3Si-H	(*p*-OMe)C_6H_4**O-Si**Ph_3	5 mol%	20	95
(*p*-OBn)C_6H_4OH	Ph_3Si-H	(*p*-OBn)C_6H_4**O-Si**Ph_3	5 mol%	20	92
(*p*-CO_2Me)C_6H_4OH	Ph_3Si-H	(*p*-CO_2Me)C_6H_4**O-Si**Ph_3	5 mol%	20	87
MesOH	Ph_3Si-H	Mes**O-Si**Ph_3	2 mol%	2	72
MesOH	Et_3Si-H	Mes**O-Si**Et_3	2 mol%	2	95
MesOH	$Me_2{}^{t}BuSi$-H	Mes**O-Si**$Me_2{}^{t}Bu$	2 mol%	12	95
MesOH	Me_2PhSi-H	Mes**O-Si**Me_2Ph	2 mol%	1	80
MesOH	Me_2ClSi-H	Mes**O-Si**Me_2Cl	2 mol%	2	79
MesOH	Me_2HSi-H	Mes**O-Si**Me_2H	2 mol%	<1	95



Phosphonium

Figure S1 The highly electrophilic phosphonium ion in $[(C_6F_5)_3PF][B(C_6F_5)_4]$.[2]

Table S2 Dehydrocoupling of alcohols and silanes using a phosphonium ion catalyst.[3]

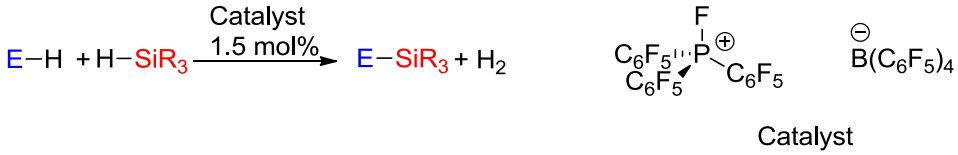


Catalyst

E-H	Silane	Product	Time /h	Yield*
PhOH	Et_3SiH	PhO-$SiEt_3$	2	>99
$(o\text{-}Me)_2(C_6H_3)OH$	Et_3SiH	$(o\text{-}Me)_2(C_6H_3)O\text{-}SiEt_3$	2	>99
$p\text{-}OMe(C_6H_4)OH$	Et_3SiH	$p\text{-}OMe(C_6H_4)O\text{-}SiEt_3$	18	>99
$p\text{-}Me(C_6H_4)OH$	Et_3SiH	$p\text{-}Me(C_6H_4)O\text{-}SiEt_3$	3	>99
C_6F_5OH	Et_3SiH	$C_6F_5O\text{-}SiEt_3$	24	>99
$p\text{-}C_8H_{17}(C_6H_4)CO_2H$†	Et_3SiH	$p\text{-}C_8H_{17}(C_6H_4)CO_2\text{-}SiEt_3$	1	>99

Conditions: 1 mol% catalyst, silane (1.1 eq.) and alcohol (1 eq.) in C_6D_5Br or CD_2Cl_2 (1.0 mL) at 25°C.*Yields measured by ^{1}H-NMR spectroscopy. †1.5 mol% catalyst was used.

Table S3 Dehydrocoupling of thiols and silanes using a phosphonium ion catalyst.[3]

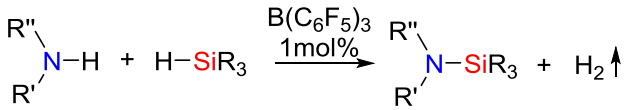


Catalyst

E-H	Silane	Product	Time /h	Yield*
PhSH	Et_3SiH	PhS-$SiEt_3$	<1	>99
$p\text{-}Me(C_6H_4)SH$	Et_3SiH	$p\text{-}Me(C_6H_4)S\text{-}SiEt_3$	<1	>99
$p\text{-}Cl(C_6H_4)SH$	Et_3SiH	$p\text{-}Cl(C_6H_4)S\text{-}SiEt_3$	<1	>99
$p\text{-}F(C_6H_4)SH$	Et_3SiH	$p\text{-}F(C_6H_4)S\text{-}SiEt_3$	<1	>99
C_6F_5SH	Et_3SiH	$C_6F_5S\text{-}SiEt_3$	168	>99

Conditions: 1.5 mol% catalyst, silane (1.1 eq.) and thiol (1 eq.) in C_6D_5Br or CD_2Cl_2 (1.0 mL) at 25°C.
*Yields measured by ^{1}H-NMR spectroscopy.

Table S4 Dehydrocoupling between silanes and carbazoles, anilines, diamines or indoles.[4]



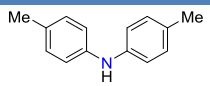
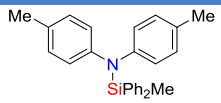
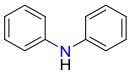
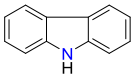
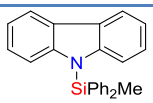
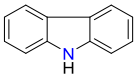
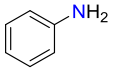
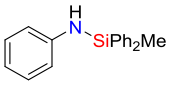
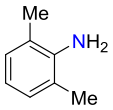
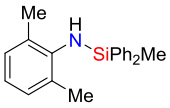
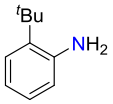
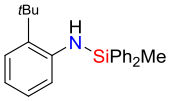
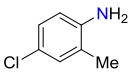
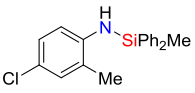
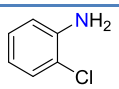
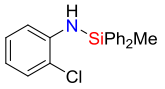
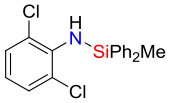
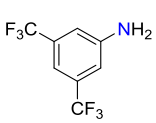
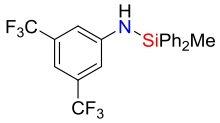
Amine	Silane	Product	Conditions	Time /h	Yield /%
	Ph_2MeSiH		25°C 1 mol% $B(C_6F_5)_3$	1	73
	Ph_2MeSiH		25°C 1 mol% $B(C_6F_5)_3$	1	91
	Ph_2MeSiH		25°C 1 mol% $B(C_6F_5)_3$	1	97
	Et_3SiH		25°C 10 mol% $B(C_6F_5)_3$	1	95
	$(Me_2HSi)_2O$		25°C 1 mol% $B(C_6F_5)_3$	1	97
	Ph_2MeSiH		70°C 5 mol% $B(C_6F_5)_3$	72	90
	Ph_2MeSiH		70°C 1 mol% $B(C_6F_5)_3$	48	90
	Ph_2MeSiH		70°C 1 mol% $B(C_6F_5)_3$	48	93
	Ph_2MeSiH		60°C 1 mol% $B(C_6F_5)_3$	36	97
	Ph_2MeSiH		60°C 1 mol% $B(C_6F_5)_3$	24	91
	Ph_2MeSiH		25°C 1 mol% $B(C_6F_5)_3$	36	88
	Ph_2MeSiH		25°C 1 mol% $B(C_6F_5)_3$	24	97

Table S4 continued…

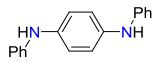
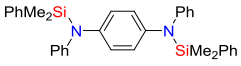
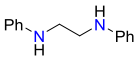
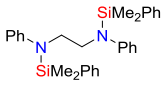
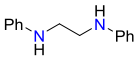
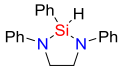
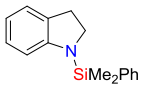
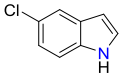
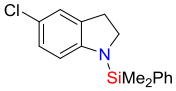
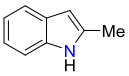
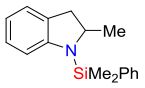
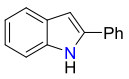
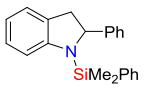
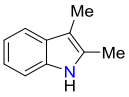
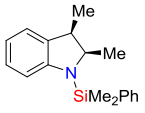
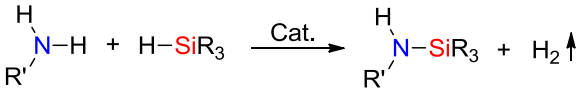
Amine	Silane	Product	Conditions	Time /h	Yield /%
	Ph_2MeSiH		25°C 2 mol% $B(C_6F_5)_3$	24	26
	Ph_2MeSiH		70°C 5 mol% $B(C_6F_5)_3$	24	92
	$PhSiH_3$		60°C 1 mol% $B(C_6F_5)_3$	24	83
	Ph_2MeSiH		70°C 10 mol% $B(C_6F_5)_3$	144	50
	Ph_2MeSiH		70°C 1 mol% $B(C_6F_5)_3$	24	81
	Ph_2MeSiH		70°C 1 mol% $B(C_6F_5)_3$	24	96
	Ph_2MeSiH		70°C 1 mol% $B(C_6F_5)_3$	24	97
	Ph_2MeSiH		70°C 1 mol% $B(C_6F_5)_3$	24	92

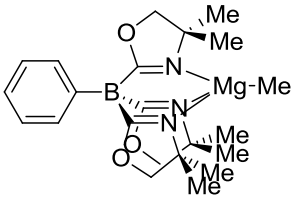
Table S5 Si-N bond formation using the fluorophosphonium catalyst $[(C_6F_5)_3PF][B(C_6F_5)_4]$.[3]

E-H	Silane	Product	Time /h	Yield*
Ph_2NH	Et_3SiH	$Ph_2N\text{-}SiEt_3$	10	>99
Ph_2NH	$ClMe_2SiH$	$Ph_2N\text{-}Si(Me)_2Cl$	1	>99
Ph_2NH	Ph_3SiH	$Ph_2N\text{-}SiPh_3$	20	>99
Ph_2NH	$PhMe_2SiH$	$Ph_2N\text{-}Si(Me)_2Ph$	48	>99
Ph_2NH	$^{i}Pr_3SiH$	-	96	0
$(p\text{-}MeC_6H_4)_2NH$	Et_3SiH	$(p\text{-}MeC_6H_4)_2N\text{-}SiEt_3$	30	>99
$(p\text{-}MeC_6H_4)_2NH$	$ClMe_2SiH$	$(p\text{-}MeC_6H_4)_2N\text{-}Si(Me)_2Cl$	16	>99
$(p\text{-}MeC_6H_4)_2NH$	Ph_3SiH	$(p\text{-}MeC_6H_4)_2N\text{-}SiPh_3$	36	40
$^{i}Pr_2NH$	Et_3SiH	-	48	0
$PhNH_2$	Et_3SiH	-	48	0

Conditions: 1.5 mol% catalyst, silane (1.1 eq.) and amine (1 eq.) in C_6D_5Br or CD_2Cl_2 (1.0 mL) at 25°C.
*Yields measured by ^{1}H-NMR.

Table S6 Group 2 catalysed Si-N coupling.[5]





Catalyst: TO^{M}Mg-Me

amine (equiv)	silane	Product	% yield (isolated)
$^{n}PrNH_2$ (3.5)	$PhSiH_3$	$(^{n}PrHN)_3SiPh$	99 (99)
$^{n}PrNH_2$ (3)	$PhMeSiH_2$	$(^{n}PrHN)_2SiMePh$	99 (90)
$^{n}PrNH_2$ (0.5)	$PhMeSiH_2$	$^{n}PrHN\text{-}SiHMePh$	99 (78)
$^{n}PrNH_2$ (3)	Ph_2SiH_2	$(^{n}PrHN)_2SiPh_2$	99 (99)
$^{n}PrNH_2$ (0.5)	Ph_2SiH_2	$^{n}PrHN\text{-}SiHPh_2$	99 (96)
$^{i}PrNH_2$ (2.5)	$PhSiH_3$	$(^{i}PrHN)_2SiHPh$	99 (99)
$^{i}PrNH_2$ (0.5)	$PhSiH_3$	$^{i}PrHN\text{-}SiH_2Ph$	99 (45)
$^{i}PrNH_2$ (2)	$PhMeSiH_2$	$^{i}PrHN\text{-}SiHMePh$	89 (67)
$^{i}PrNH_2$ (2)	Ph_2SiH_2	$^{i}PrHN\text{-}SiHPh_2$	99 (97)
$^{t}BuNH_2$ (2.5)	$PhSiH_3$	$^{t}BuHN\text{-}SiH_2Ph$	99 (90)
$^{t}BuNH_2$ (2)	$PhMeSiH_2$	$^{t}BuHN\text{-}SiHMePh$	90 (60)
$^{t}BuNH_2$ (2)	Ph_2SiH_2	$^{t}BuHN\text{-}SiHPh_2$	99 (81)
$PhNH_2$ (2.5)	$PhSiH_3$	$(PhHN)_2SiHPh$	99 (97)

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