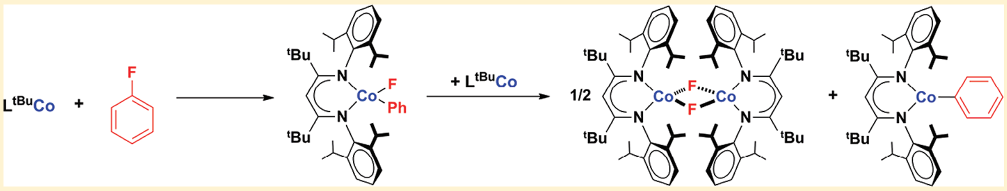
ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

Low-Coordinate Cobalt Fluoride Complexes: Synthesis, Reactions, and Production from C−F Activation Reactions

Thomas R. Dugan, Jonathan M. Goldberg, William W. Brennessel, and Patrick L. Holland*

Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

Supporting Information



ABSTRACT: A cobalt(II) fluoride complex, $[L^{tBu}Co(\mu\text{-}F)]_2$ [L^{tBu} = 2,2,6,6-tetramethyl-3,5-bis(2,6-diisopropylphenylimido)-hept-4-yl], was synthesized from $L^{tBu}Co$ using Me_3SnF via homolytic cleavage of the Sn−F bond. $L^{tBu}Co$ also performed the overall binuclear oxidative addition of fluorinated arenes to give $[L^{tBu}Co(\mu\text{-}F)]_2$ and a cobalt(II) aryl complex of the corresponding fluorobenzene substrate in a 1:2 molar ratio. The C−F activation reaction has a first-order rate dependence on both cobalt and fluorobenzene concentrations. The rate is increased by *meta*-fluoride substituents, and slowed by *ortho*-fluoride substituents, suggesting electronic and steric influences on the transition state, respectively. The data are most consistent with a mechanism beginning with rate-limiting oxidative addition of the aryl fluoride to cobalt(I), followed by rapid reduction of the cobalt(III) aryl fluoride intermediate by a second molecule of $L^{tBu}Co$. $[L^{tBu}Co(\mu\text{-}F)]_2$ also reacts with Et_3SiH to give the hydride complex $[L^{tBu}Co(\mu\text{-}H)]_2$. This hydride complex has low reactivity toward alkenes and N_2, in contrast to an earlier report.

INTRODUCTION

The C−F bond is one of the strongest bonds encountered in organic compounds.[1] C−F bonds are significantly stronger than analogous C−H bonds.[2] For example, the bond dissociation energy (BDE) of $F{-}CH_3$ is 5 kcal/mol stronger than that of the C−H bond in methane, and the BDE of $F{-}C_6H_5$ is 13 kcal/mol stronger than that of the C−H bond in benzene.[3] The increased bond strength makes fluorocarbons more resistant to degradation than analogous hydrocarbons. Therefore, molecules containing C−F bonds are useful for applications where resistance to oxidation or metabolism is beneficial.[4] As a result, nearly 20% of all pharmaceuticals and 40% of all agrochemicals incorporate at least one C−F bond.[5] In pharmaceuticals, the strength of the C−F bond improves the metabolic stability, the lipophilicity, and binding to drug interaction sites.[6−8]

The resistance of fluorocarbons to oxidation makes them persist in the environment.[9] For example, perfluorocyclopentane and perfluorocyclohexane have half-lives of >3000 years in the atmosphere.[10] Therefore, the removal of fluorines from fluorocarbon compounds ("C−F activation") is an important goal, in order to convert them into more biodegradable fluorine-free analogues.[11] The cleavage of C−F bonds often uses transition-metal complexes.[1a,12] The products of C−F activation reactions are metal−fluoride complexes[13] that are also of interest because of their potentially reactive M−F bonds.[12m]

The metal-mediated cleavage of a C−F bond can occur by different pathways, depending on the type of C−F bond and the metal.[12m] These pathways include oxidative addition;[14] metal−carbon bond formation via elimination of HF,[15] Si−F,[11a,16] B−F,[17] and Al−F bonds;[18] metal−fluorine bond formation via hydrodefluorination[19] or defluorination;[20] and nucleophilic attack by an electron-rich metal.[21] However, in complexes of precious metals, C−H activation is often kinetically preferred over C−F activation.[16a,22] Recently, the oxidative addition of aryl C−F bonds to low-valent cobalt phosphine complexes was described.[23] These reports with cobalt inspired us to investigate aryl C−F activation with $L^{tBu}Co$, a masked two-coordinate cobalt(I) complex [L^{tBu} = 2,2,6,6-tetramethyl-3,5-bis(2,6-diisopropylphenylimido)hept-4-yl]. In a recent communication, we disclosed that $L^{tBu}Co$ reacts with fluorobenzene to give a cobalt(II) fluoride complex, $[L^{tBu}Co(\mu\text{-}F)]_2$, and a cobalt(II) phenyl complex, $L^{tBu}CoPh$.[24] In the work described in this report, the scope of the reaction between $L^{tBu}Co$ and fluorobenzenes was explored. Kinetic studies show the rate law and substituent effects and elucidate the mechanism of C−F activation. Although $[L^{tBu}Co(\mu\text{-}F)]_2$ was previously reported, a new synthetic route to $[L^{tBu}Co(\mu\text{-}F)]_2$ from a tin reagent is provided here. This synthetic route has now permitted $[L^{tBu}Co(\mu\text{-}F)]_2$ to be isolated in high yield free from impurities for the first time. The fluoride complex, in turn, led to a low-coordinate cobalt hydride complex that is compared to the literature.

Special Issue: Fluorine in Organometallic Chemistry

Received: October 16, 2011
Published: January 19, 2012

dx.doi.org/10.1021/om200991k | *Organometallics* 2012, 31, 1349−1360

RESULTS

Reduction of Me$_3$SnF by L$^{t\mathrm{Bu}}$Co gives [L$^{t\mathrm{Bu}}$Co(μ-F)]$_2$ (1). The synthesis of **1** was previously reported from C−F activation of fluorobenzene by L$^{t\mathrm{Bu}}$Co;[24] however, because this synthesis always gave **1** as part of a mixture with L$^{t\mathrm{Bu}}$CoPh, an alternative synthesis of **1** was desired. We have reported that the cobalt(II) methyl complex L$^{t\mathrm{Bu}}$CoCH$_3$ reacts with trimethyltin fluoride (Me$_3$SnF) to give a cobalt fluoride complex, but this product retained the tin in an unusual trimetallic Co−Sn−Co core.[25] Interestingly, L$^{t\mathrm{Bu}}$Co reacted with Me$_3$SnF overnight in THF at 70 °C to give **1** in 73% yield. In a modification that requires one less isolation step, it is possible to reduce L$^{t\mathrm{Bu}}$CoCl with KC$_8$ in THF to give a solution of L$^{t\mathrm{Bu}}$Co(THF), which was then treated with Me$_3$SnF in THF to give **1** in a comparable yield. The characterization of [L$^{t\mathrm{Bu}}$Co(μ-F)]$_2$ has been confirmed by several physical methods (see the Experimental Section). Addition of pyridine gave quantitative conversion to the previously characterized L$^{t\mathrm{Bu}}$CoF(py),[25] as judged by ^{1}H NMR spectroscopy (see the Supporting Information).

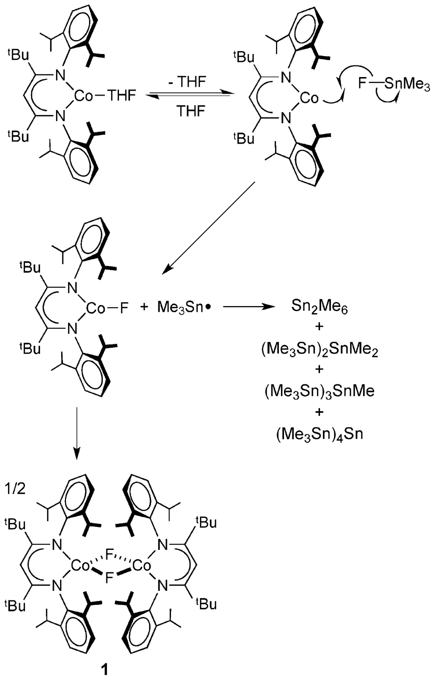
Compound **1** is formally a dicobalt(II) complex. The room-temperature magnetic moment of **1** at 26 °C was 6.4 ± 0.2 μ_B in C$_6$D$_6$ and 6.1 ± 0.1 μ_B in THF-d_8. This was slightly higher than the spin-only magnetic moment for two uncoupled S = 3/2 centers of 5.5 μ_B, suggesting a contribution from spin−orbit coupling, as in other high-spin diketiminate-cobalt(II) complexes.[26] The signals in the ^{1}H NMR spectrum of **1** in C$_6$D$_6$ and THF-d_8 were not assigned to specific protons on account of several broad and overlapped resonances. The broadness was the result of a fluxional process with a coalescence temperature near 0 °C (see the Supporting Information).

The ability of Me$_3$SnF to act as a net "F$^\bullet$" source suggested that the tin fragment was reduced in the reaction. ^{119}Sn{^{1}H} NMR spectroscopy was used to identify the tin product in the crude product from the reaction of L$^{t\mathrm{Bu}}$Co and Me$_3$SnF. The ^{119}Sn{^{1}H} NMR spectrum showed a resonance at δ −108.82 ppm, which matched the literature chemical shift for Sn$_2$Me$_6$.[27] Five additional resonances at δ −80.5, −89.9, −99.5, −261.7, and −489.8 ppm in the ^{119}Sn{^{1}H} NMR spectrum were assigned to (Me$_3$Sn)$_2$SnMe$_2$, (Me$_3$Sn)$_3$SnMe, and (Me$_3$Sn)$_4$Sn.[28] The relative amounts of these four tin products were not definitively quantified from the experiment, but their formation is consistent with previous reports on the decomposition of free Me$_3$Sn$^\bullet$ radicals through the intermediacy of the carbenoid SnMe$_2$.[28] Thus, our data support the reaction stoichiometry shown in Scheme 1.

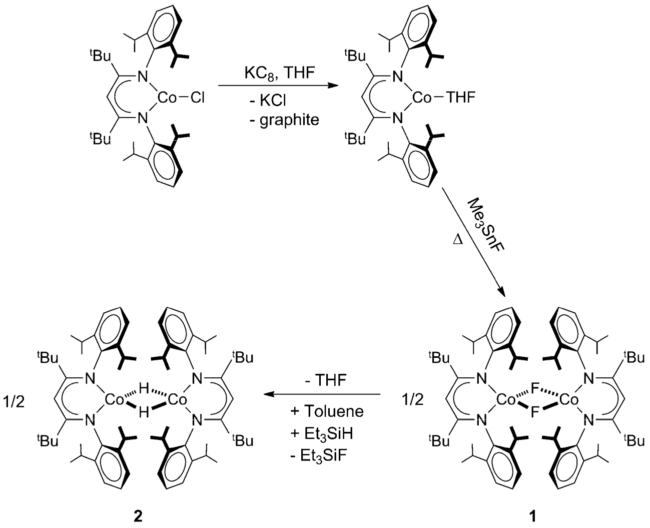
Reaction of 1 with Et$_3$SiH produces [L$^{t\mathrm{Bu}}$Co(μ-H)]$_2$ (2). [L$^{t\mathrm{Bu}}$Co(μ-H)]$_2$ was previously synthesized from L$^{t\mathrm{Bu}}$CoCl and KBEt$_3$H, but this route did not give a pure hydride product.[29] We hypothesized that compound **1** could give the cobalt hydride complex, based on the previously reported reaction of L$^{t\mathrm{Bu}}$FeF with triethylsilane (Et$_3$SiH) to give [L$^{t\mathrm{Bu}}$Fe(μ-H)]$_2$.[16b,30] Addition of a slight excess of Et$_3$SiH to a solution of **1** in benzene-d_6 resulted in the immediate darkening of the solution to give a brown color. The ^{1}H NMR spectrum showed complete conversion of **1** to a new product. Compound **2** was isolated in 61% yield from in situ generation of **1** from L$^{t\mathrm{Bu}}$CoCl (Scheme 2).

The molecular structure of **2** is shown in Figure 1. The structure was solved in the space group $P\bar{1}$ and contained cocrystallized benzene-d_6. The previously reported structure of

Scheme 1. Proposed Mechanism for the Production of 1 and Various Tin Products from a Cobalt(I) Source and Me$_3$SnF



Scheme 2



2 was also solved in $P\bar{1}$, but was a different crystal form.[29] The positions of the bridging hydrides were located in the difference Fourier map and refined. Because all four positions had similar electron densities, the 50:50 ratio of disorder occupancies was fixed in the refinement. The backbones of the two β-diketiminate ligands are nearly perpendicular, with the angle between the N11−Co1−N21 and N14−Co2−N24 planes being 87.79(6)°. The distance between the Co atoms is 2.4763(4) Å, and the cobalt hydride distances are between 1.56 and 1.67 Å. All of these values are similar to the previous lower-quality crystal structure of this molecule.[29]

Though the crystal for the crystal structure had incorporated C$_6$D$_6$, bulk samples of compound **2** crystallized with two Et$_2$O molecules, as judged by the ^{1}H NMR spectrum and combustion analysis. The molecule has C_1 symmetry in the solid state, but the ^{1}H NMR spectrum of **2** indicated C_2 symmetry with a C_2

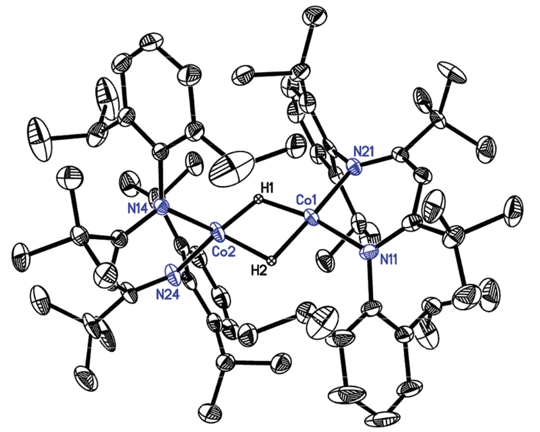


Figure 1. Molecular structure of $[L^{tBu}Co(\mu\text{-}H)]_2$ (**2**) using 50% probability thermal ellipsoids. All carbon-bound hydrogen atoms and cocrystallized solvent have been omitted for clarity. Only one set of hydride positions is shown for clarity. Selected bond distances [Å] and bond angles [deg] for **2**: Co1−Co2, 2.4763(4); Co−N, 1.961(2)−1.977(2); N11−Co1−N21, 96.02(6); N14−Co−N24, 95.60(6).

axis through the cobalt centers. The ^{1}H NMR spectrum was similar in C_6D_6 and in THF-d_8, indicating that the dimeric structure is maintained in THF. The solution magnetic moment of **2** at 27 °C was 6.1 ± 0.1 μ_B in C_6D_6 and 6.0 ± 0.1 μ_B in THF-d_8, which indicated little magnetic coupling between the cobalt(II) ions despite the short Co−Co distance.

Previous ^{1}H NMR studies of the iron analogue of **2**, $[L^{tBu}Fe(\mu\text{-}H)]_2$, showed that it was in equilibrium with a three-coordinate monomer in solution.[31] To evaluate the potential splitting of dimeric **2** into a C_{2v} symmetry monomer, its ^{1}H NMR spectra in C_6D_6 were collected between 26 and 80 °C (Figure 2). The only changes were in the chemical shift due to the Curie Law, and the magnetic moment of **2** was the same within error at all temperatures. Therefore, all of our evidence suggests that compound **2** exists as a dimer in both the solid state and in solution.

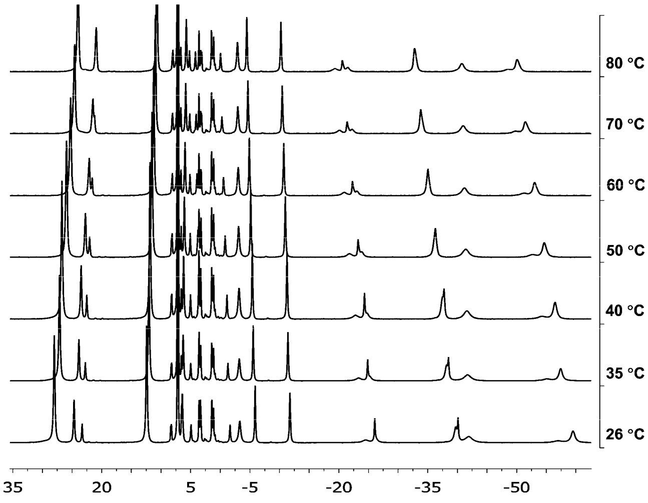
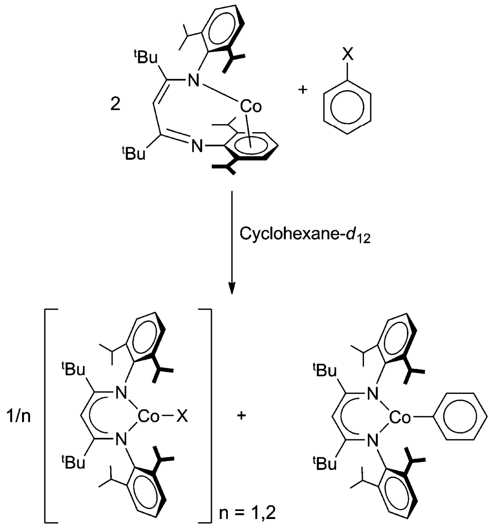


Figure 2. Variable-temperature ^{1}H NMR spectra of **2** recorded between 26 and 80 °C in C_6D_6.

The reactivity of **2** was probed in order to compare it with the analogous iron hydride complex.[32] Heating excess cyclohexene or 1-hexene with **2** in C_6D_6 overnight at 70 °C yielded only trace amounts of the [1,2]-addition products (L^{tBu}CoCy or L^{tBu}Co(*n*-hexyl), respectively), and most of the **2** remained unchanged. L^{tBu}Co(*n*-hexyl) was identified and characterized by its independent synthesis from L^{tBu}CoCl and hexylMgBr (see the Experimental Section). Excess pyridine was added to a solution of **2** in C_6D_6 in an attempt to reductively eliminate H_2 to form L^{tBu}Co(pyridine);[25] however, no reaction was observed after several hours at room temperature. Heating the solution at 80 °C overnight gave L^{tBu}Co(pyridine) in 52% yield via the ^{1}H NMR integration standard. Heating **2** in C_6D_6 at 80 °C overnight with a slight excess of *tert*-butylpyridine gave the L^{tBu}Co(*tert*-butylpyridine) complex in an improved 68% yield via the ^{1}H NMR integration standard. A quantitative yield of H_2 was observed by GC when the reaction with *tert*-butylpyridine was performed in a test tube. Overall, compound **2** was not very reactive toward alkenes or Lewis bases.

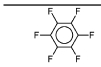
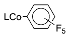
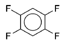
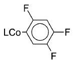
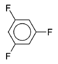
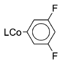
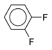
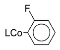
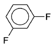
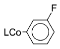
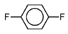
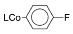
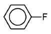
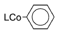
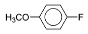
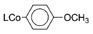
Products from L^{tBu}Co and Aryl Halides. We recently reported that fluorobenzene reacted with L^{tBu}Co at 60 °C for 18 h in cyclohexane-d_{12} to give L^{tBu}CoPh and $[L^{tBu}Co(\mu\text{-}F)]_2$ (**1**).[24] The concentration of L^{tBu}CoPh in the product mixture had been determined by ^{1}H NMR spectroscopy, but the concentration of **1** in solution had not been determined directly due to its broad ^{1}H NMR spectrum. We now report that it is possible to quantify the production of **1** indirectly, by taking advantage of its quantitative reaction with triethylsilane (Et_3SiH) to give $[L^{tBu}Co(\mu\text{-}H)]_2$ (**2**). (Note that L^{tBu}Co does not react with Et_3SiH under any conditions.) Thus, at the end of the reaction, a slight excess of Et_3SiH was added to produce **2**, and the concentration could be determined relative to a Cp_2Ni integration standard. The ratio of [L^{tBu}CoPh] to [**2**] was 2:1. Assuming quantitative production of **2** from **1**, the ratio of [L^{tBu}CoPh] to [**1**] was therefore also 2:1, as illustrated in Scheme 3.

Scheme 3. Net Binuclear Oxidative Addition of Aryl Halides to L^{tBu}Co Produces the Corresponding L^{tBu}CoX and L^{tBu}CoPh Complexes (X = F, Cl, Br)



The reaction of L^{tBu}Co with other fluorobenzenes was explored to discover the scope of the C−F activation reaction (Table 1). In these reactions, excess (5−15 equiv) of the fluorinated arene substrate was added to a solution of L^{tBu}Co in cyclohexane-d_{12}. The reaction mixture was heated at 60 °C from 1 to 18 h depending on the substrate. The ^{1}H NMR spectra showed that all L^{tBu}Co disappeared over time. The ^{1}H

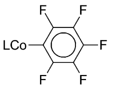
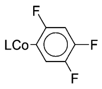
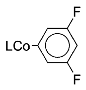
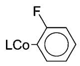
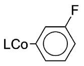
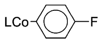
Table 1. Products from $\mathrm{L}^{tBu}\mathrm{Co}$ and Fluorobenzenes[a]

Substrate	Intial $[\mathrm{L}^{tBu}\mathrm{Co}]$ mM	Product 1	[Product 1] mM	Product 2	[Product 2] mM
	27.6 ± 3.0		14.8 ± 0.6	$[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$	6.7 ± 0.2
	40.2 ± 2.6		19.6 ± 2.7	$[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$	8.1 ± 0.5
	34.7 ± 3.5		17.2 ± 0.7	$[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$	7.8 ± 0.4
	31.3 ± 4.3		14.9 ± 0.6	$[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$	6.5 ± 0.2
	35.3 ± 4		16.7 ± 1.7	$[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$	8.5 ± 0.6
	27.3 ± 2.0		10.6 ± 0.9	$[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$	4.5 ± 0.2
	29.1 ± 3.0		15.6 ± 0.8	$[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$	8.0 ± 0.3
	33.6 ± 3.9		19.3 ± 0.7	$[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$	8.5 ± 0.5

[a] All reactions were performed in cyclohexane-d_{12}. All reactions were heated at 60 °C except for the reaction with hexafluorobenzene, which was performed at room temperature.

NMR spectrum of the product mixture showed resonances for $[\mathrm{L}^{tBu}\mathrm{Co}(\mu\text{-F})]_2$ and for a species that was consistent with the expected aryl complex. The cobalt aryl products were identified by $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR spectroscopy (Table 2); *meta*- and *para*-fluorine signals were always observed, but *ortho*-fluorine signals were sometimes absent due to proximity to the paramagnetic metal. The ratios of the cobalt aryl complexes to **1** were determined to be roughly 2:1 using the same strategy described above for fluorobenzene (addition of $\mathrm{Et_3SiH}$ after completion of the reaction to form easily quantified **2** from **1**), and the derived concentrations are given in Table 1.

Table 2. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR Chemical Shifts (ppm) and Assignments of Cobalt Aryl Complexes

Cobalt aryl complex	δ, (assignment)
	28.9, (2F, *m*-F) 74.8, (1F, *p*-F)
	978, (*o*-F) -30.4 -62.8
	113.5
	647
	108.3
	-19.9

Alkyl fluorides did not react with $\mathrm{L}^{tBu}\mathrm{Co}$: heating excess α,α,α-trifluorotoluene or perfluorocyclohexane (10 equiv) with $\mathrm{L}^{tBu}\mathrm{Co}$ at 90 °C in cyclohexane-d_{12} yielded only slow decomposition. However, $\mathrm{L}^{tBu}\mathrm{Co}$ did react with 1 equiv of chlorobenzene or bromobenzene at room temperature in less than 1 h to give a mixture of $\mathrm{L}^{tBu}\mathrm{CoPh}$ and $\mathrm{L}^{tBu}\mathrm{CoX}$ (X = Cl, Br) via ^{1}H NMR spectroscopy. A $\mathrm{Cp_2Ni}$ internal integration standard showed that $\mathrm{L}^{tBu}\mathrm{CoPh}$ and $\mathrm{L}^{tBu}\mathrm{CoX}$ were formed in a 1:1 ratio with quantitative yield. $\mathrm{L}^{tBu}\mathrm{CoBr}$ was identified based on the similarity of its ^{1}H NMR spectra to that of literature $\mathrm{L}^{tBu}\mathrm{CoCl}$.[33] Thus, the reaction of $\mathrm{L}^{tBu}\mathrm{Co}$ with each aryl halide results in an overall binuclear oxidative addition,[34] as shown in Scheme 3.

Kinetic Studies of Aryl C−F Bond Cleavage by $\mathrm{L}^{tBu}\mathrm{Co}$. The novel C−F activation reaction and the quantitative formation of products encouraged us to elucidate the mechanism of the reaction of $\mathrm{L}^{tBu}\mathrm{Co}$ with fluorobenzenes through kinetic studies. We used UV−vis spectrophotometry to monitor the disappearance of a characteristic absorption band of $\mathrm{L}^{tBu}\mathrm{Co}$ at 412 nm during reactions of $\mathrm{L}^{tBu}\mathrm{Co}$ with an excess of fluorinated arene in hexane at 60 °C. The kinetic traces fit to a single exponential equation with $R \geq 0.999$ in each case; the fits yielded pseudo-first-order rate constants (k_{obs}). Plots of $\ln(A - A_\infty)$ versus time were linear over 4−6 half-lives, and the appropriate plots for half-order, three-halves-order, and second-order dependences deviated significantly from linearity (see the Supporting Information). The second-order rate constants (k) were obtained by plotting the pseudo-first-order k_{obs} versus substrate concentration, which was corrected for the change in density of hexane at 60 °C (see Figure 4 and the Supporting Information).[35]

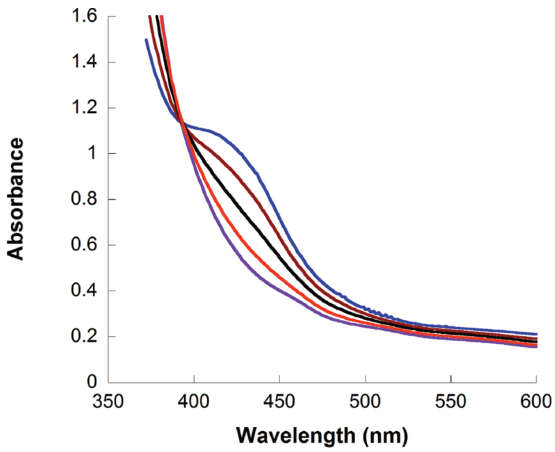


Figure 3. Spectral changes observed upon heating solutions of $\mathrm{L}^{tBu}\mathrm{Co}$ (0.26 mM) and fluorobenzene (64 mM) at 60 °C. Concentrations are reported after mixing.

The spectral changes of the fluorobenzene reaction with respect to time are shown in Figure 3. An isosbestic point at 390 nm suggested that no intermediates build up in the course of the reaction (consistent with observations from ^{1}H NMR spectroscopy). The fluoroarene concentrations were varied

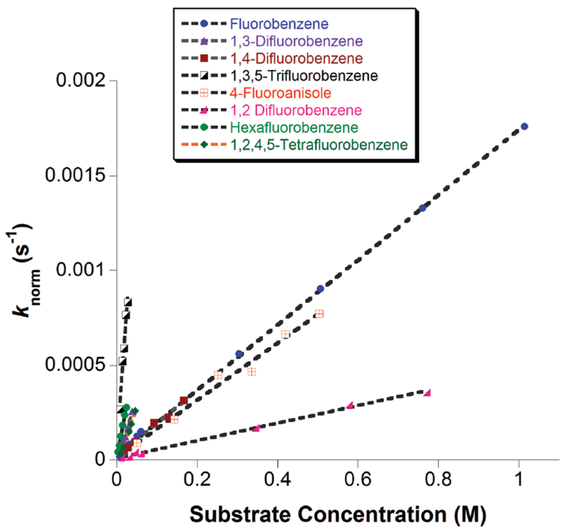


Figure 4. Linear dependences of k_{norm} on the concentration of aryl fluorides at 60 °C are shown. A plot detailing the low-concentration region is in the Supporting Information.

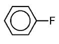
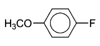
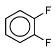
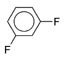
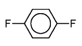
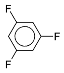
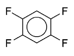
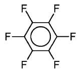
through concentrations up to approximately 1 M. As shown in Figure 4, k_{obs} increased linearly with increasing substrate concentration, and the intercepts of the best-fit lines were close to zero. These observations indicate the rate law

$$\text{rate} = k[\text{L}^{t\text{Bu}}\text{Co}][\text{fluorobenzene}] \quad (1)$$

These results show that C−F bond cleavage by $L^{tBu}Co$ was the rate-determining step of the reaction.

Table 3 provides the second-order rate constant for each substrate, the rate constant normalized for the number of C−F bonds (k_{norm}, which represents the reactivity of *each* C−F bond), and the normalized rate constant relative to fluorobenzene for easier comparison. Several trends are evident when comparing the normalized rates for different difluorobenzene substrates: a *para*-fluorine substituent has no effect on the rate constant, a *meta*-fluorine substituent speeds the rate by a factor of 4, and an ortho substituent slows the rate by a factor of 4. Though the effects of multiple fluorines were not precisely additive, these general trends held throughout the series. Thus, 1,3,5-trifluorobenzene, which contained all *meta* C−F bonds, was ~2.5 times faster than hexafluorobenzene, which is impeded by *ortho*-F substituents. Finally, to define inductive versus resonance contributions, we tested 4-fluoroanisole, which has a methoxy substituent para to the fluorine. As in 1,4-difluorobenzene, the effect of the substituent was minimal: this result indicates that the electronic influence of fluorines is primarily an inductive rather than a resonance effect. This also explains why the *meta*-fluoride substituent is more influential than the *para*-fluoride substituent. The *ortho*-fluorine effect is opposite and is attributed to a steric effect.

Table 3. Rate Constants for Fluorobenzene Substrates at 60 °C in Hexane

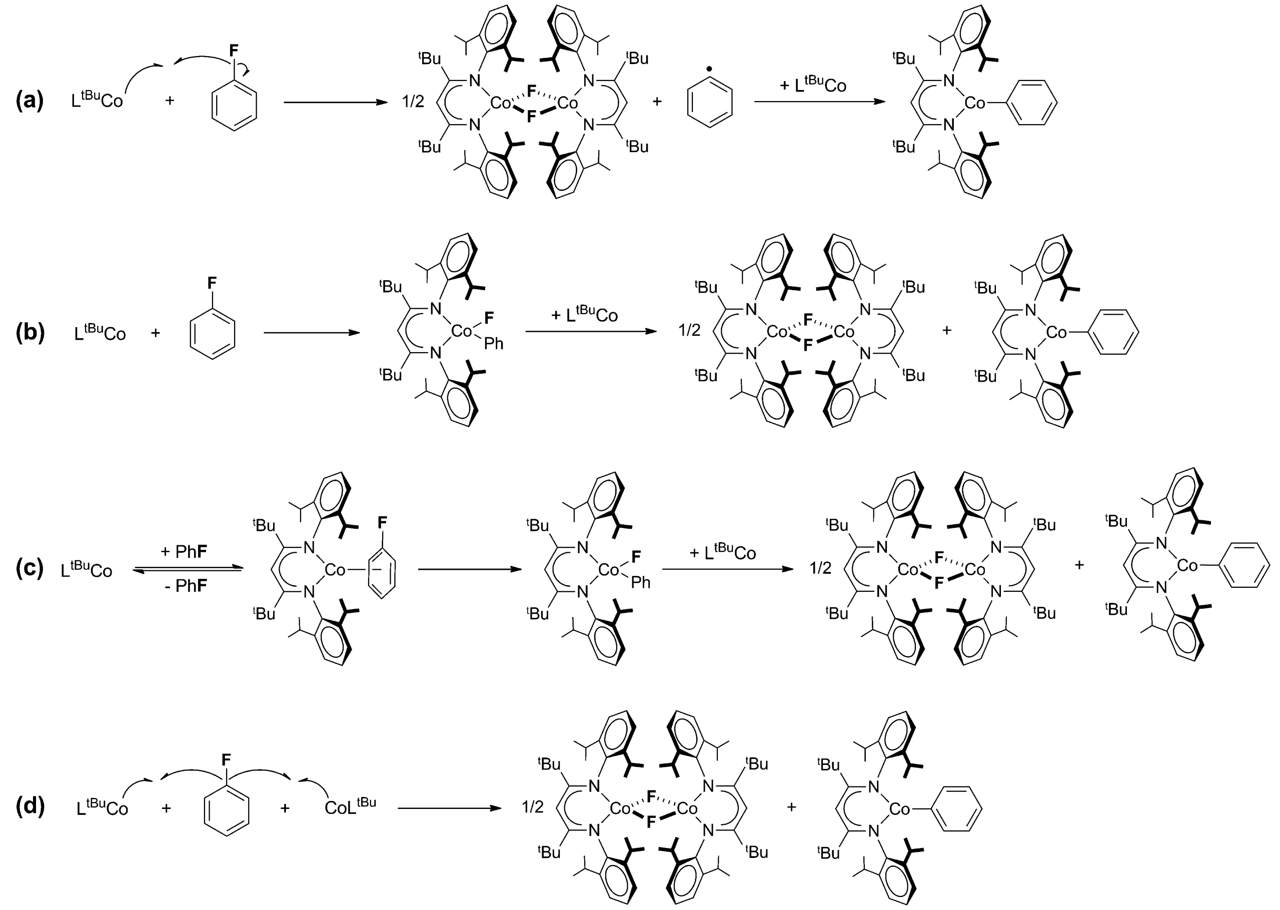
Substrate	k ($M^{-1}s^{-1}$)	k/# of C-F bonds (k_{norm})	relative k_{norm}
	$1.72(1) \times 10^{-3}$	$1.72(1) \times 10^{-3}$	1.0
	$1.5(1) \times 10^{-3}$	$1.5(1) \times 10^{-3}$	0.9
	$9.3(3) \times 10^{-4}$	$4.7(3) \times 10^{-4}$	0.27
	$1.31(9) \times 10^{-2}$	$6.5(4) \times 10^{-3}$	3.8
	$3.5(2) \times 10^{-3}$	$1.7(2) \times 10^{-3}$	1.0
	$8.6(9) \times 10^{-2}$	$2.9(3) \times 10^{-2}$	17.1
	$2.5(1) \times 10^{-2}$	$6.1(1) \times 10^{-3}$	3.6
	$6.81(3) \times 10^{-2}$	$1.14(3) \times 10^{-2}$	6.6

■ DISCUSSION

Formation of $[L^{tBu}Co(\mu\text{-}F)]_2$. Transition-metal fluoride complexes have not been reported as frequently as other transition-metal halide complexes because of obstacles to their preparation.[13a] Most cobalt fluoride complexes have been formed via fluoride abstraction from BF_4^- and PF_6^- salts.[36] Other fluoride sources for cobalt fluoride complexes are KF[37] and organofluorine compounds.[23] This paper demonstrates a new method for the synthesis of transition-metal fluorides, the use of Me_3SnF as a source of formal $F^\bullet$. The balanced reaction is shown in Schemes 1 and 3 above. The one-electron reduction of the Sn−F reagent by cobalt(I) produces the cobalt(II) fluoride complex and an unstable trimethyltin radical. Trimethyltin radicals dimerize to give hexamethylditin[38] and also form dimethylstannylene and methyl radicals under heating or photolytic conditions.[39] These known byproducts from $Me_3Sn^\bullet$ account for the species that we observed by $^{119}Sn\{^1H\}$ NMR spectroscopy (Scheme 1 above). To our knowledge, this is the first report of the formation of a simple transition-metal fluoride complex by the one-electron reduction of the Sn−F bond in Me_3SnF. Me_3SnF has been used as a F^- source in the synthesis of main group and transition-metal fluorides.[40] The new synthetic method shown here may be useful more generally for making transition-metal fluoride complexes from a low-valent metal precursor.

Reactivity of $[L^{tBu}Co(\mu\text{-}H)]_2$ Compared to Other Late Transition-Metal β-Diketiminate Hydride Complexes. The reaction of **1** with silanes yielded pure samples of **2** that were suitable for reactivity studies. Compound **2** showed limited reactivity toward small-molecule substrates, such as alkenes, N_2, and pyridines. This behavior was distinctly different than the closely related iron analogues $[L^{tBu}Fe(\mu\text{-}H)]_2$ and $[L^{Me}Fe(\mu\text{-}H)]_2$, which were very reactive toward a variety of small molecules. The iron hydride complexes exhibited three general types of reactivity: first, they reacted as Brønsted bases with Brønsted acids to release H_2 and to give an Fe complex of the conjugate base; second, the Fe−H bond added across multiple bonds to give a [1,2]-addition product; third, the complexes underwent reductive elimination of H_2, followed by coordination of the donor ligand, to give an Fe^I product.[32] $[L^{Me}Ni(\mu\text{-}H)]_2$ was not as reactive as the Fe hydride complexes as it only exhibited the third reactivity trend.[41] Hydride complexes of $[L^{tBu}FeH]_2$ did not react thermally with

Scheme 4. Potential Pathways for the Activation of Aryl C−F Bonds by 2: (a) Radical Pathway, (b) Oxidative Addition, Followed by Reduction, (c) Coordination of Aryl Fluoride, Followed by Bond Cleavage, and (d) Termolecular Pathway



N$_2$.[42] We show here that the [L^{tBu}CoH]$_2$ analogue **2** also does not react with N$_2$. Interestingly, **2** also failed to show the reactivity trends exhibited by the other hydride complexes. The reaction of alkenes with **2** only gave a trace amount of the expected Co alkyl complex after prolonged heating. Displacement of H$_2$ by pyridine required heating for the reaction to proceed, whereas the iron analogue eliminated H$_2$ at room temperature.

What is the reason for the reduced reactivity of [L^{tBu}Co(μ-H)]$_2$ relative to its iron analogue? Kinetic studies on [L^{tBu}Fe(μ-H)]$_2$ with alkynes indicated that the dimer must break into monomers in order to react.[31] With [L^{Me}Fe(μ-H)]$_2$, kinetic studies on its reaction with boranes suggested that the Fe$_2$(μ-H)$_2$ core must partially dissociate into an intermediate with one bridging hydride ligand and one terminal hydride ligand.[43] Thus, our working model is that the reactivity of iron hydride complexes is dependent on the ability to dissociate bridging hydrides in the dimeric core. This model can also explain why the cobalt hydrides are less reactive than the iron analogues, since the more electronegative cobalt binds its ligands more tightly.[44] We thus suggest that breaking up the Co$_2$(μ-H)$_2$ core has a significantly higher barrier with Co than with Fe, which accounts for its reduced reactivity.

Comparison of 2 to Previously Reported [L^{tBu}Co(μ-H)]$_2$. A previous report described the reaction of L^{tBu}CoCl with KBEt$_3$H, which was proposed to give [L^{tBu}Co(μ-H)]$_2$;[29] however, measurements on this species indicated a mixture. For example, the reported ^{1}H NMR spectrum contained many resonances, with no simple correspondence to the crystallographically determined structure.[29] This mixture will be subsequently designated as "**2**". Subsequent work indicated that the products of this reaction did not reliably give the same crude ^{1}H NMR spectrum. In the present work, analytically pure **2** was obtained through an alternative route, by reacting Et$_3$SiH with [L^{tBu}Co(μ-F)]$_2$. The new technique gave pure **2** that allowed us to re-evaluate the properties of impure "**2**".

Surprisingly, the ^{1}H NMR spectrum of analytically pure **2** did not have any peaks in common with the reported spectrum of "**2**".[29] This indicates that very little (if any) **2** was present in the samples of "**2**" used in the previous study. This observation brought into question the reported reactivity of the cobalt(II) hydride complex.[29] Compound "**2**" was reported to react with N$_2$ thermally to give L^{tBu}CoNNCoL^{tBu} and H$_2$. However, purified **2** did not react with N$_2$ in C$_6$D$_6$ under any conditions to give L^{tBu}CoNNCoL^{tBu}. In the previous paper, "**2**" was reported to react with cyclohexene at room temperature to give L^{tBu}CoCy. However, the addition of cyclohexene to pure **2** yielded only traces of L^{tBu}CoCy after heating overnight at 70 °C. Similarly, no [1,2]-addition was observed in the reaction of purified **2** with 1-hexene. K$_2$[L^{tBu}CoH]$_2$ was previously reported from the addition of 2 equiv of KBEt$_3$H to L^{tBu}CoCl;[29] however, K$_2$[L^{tBu}CoH]$_2$[29] was not observed when **2** was mixed with KBEt$_3$H or with KC$_8$. However, L^{tBu}Co did react with KBEt$_3$H to give K$_2$[L^{tBu}CoH]$_2$ in quantitative yield by the ^{1}H NMR integration standard. Also, pure **2** reacted with pyridine or *tert*-butylpyridine to give the corresponding cobalt(I) pyridine complex[25] and H_2 upon heating to 80 °C. This was the same product previously reported, but a higher temperature was required with the purified **2**.

Thus, *the current studies show the earlier description*[29] *of the preparation of "2" from hydride reagents, and the description of its reactivity with cyclohexene, pyridine, and* N_2*, to be in error.* It should be noted that the preparation and reactivity of the cobalt(I) hydride complex $K_2[L^{tBu}CoH]_2$, also reported in that paper, has proven reliable in continued studies on its properties. Thus, the cobalt(I) hydride complex $K_2[L^{tBu}CoH]_2$ indeed reacts with N_2, and the mechanistic studies reported on the N_2 reaction using this material[29] are reliable. An alternative synthesis of $K_2[L^{tBu}CoH]_2$ is reported here, from the reaction of $L^{tBu}Co$ with $KBEt_3H$; a related transformation is probably involved in the previous isolation of the cobalt(I) hydride compound $K_2[L^{tBu}CoH]_2$.

What factors can account for the differences between **2** and the previously reported "**2**"? Closer inspection of the reported ^1H NMR spectrum of "**2**" in C_6D_6 (aided by the subsequent identification of key $L^{tBu}Co$ compounds) reveals that "**2**" was a crude mixture of $L^{tBu}Co$ and $L^{tBu}Co$(benzene). Thus, $KBEt_3H$ acted as a reducing agent rather than a hydride donor in the production of "**2**". In addition, the reverse reaction of $L^{tBu}Co$ and H_2 did not produce **2** under any conditions, including high temperature, high pressure, and long reaction times. This contrasts with the iron analogues, where reduction of $L^{tBu}FeCl$ under an atmosphere of H_2 rapidly produced $[L^{tBu}Fe(\mu\text{-}H)]_2$.[30] These observations point toward either $L^{tBu}Co$ being lower in energy than **2** + H_2 or $L^{tBu}Co$ having a much higher barrier to oxidative addition of H_2 than Fe. In addition, the prevalence of $L^{tBu}Co$ in previously reported samples of "**2**" explains its reactivity with N_2. It was recently demonstrated that $L^{tBu}Co$ reacts with N_2 to give $L^{tBu}CoNNCoL^{tBu}$ in high yield.[24] Thus, the resonances that disappeared upon addition of N_2 to "**2**" were not $[L^{tBu}Co(\mu\text{-}H)]_2$, but rather this reaction consumed $L^{tBu}Co$.

Aryl C−F Activation by L^{tBu}Co. The activation of C−F bonds by cobalt complexes is rare.[1a,23,45] Recent reports utilized Co^0 and Co^I phosphine complexes to perform the activation of aryl C−F bonds.[23] These complexes often required a directing group, such as a ketone or an imine, ortho to the C−F bond for reactivity, though in one case, no directing group was required.[23c] Also, some substrates were observed to give C−H activation instead of C−F activation in competition experiments.[23b,d] The overall binuclear oxidative addition of aryl C−F bonds by $L^{tBu}Co$ reported here exhibited none of these limitations. $L^{tBu}Co$ does not attack C−H bonds in arenes, in contrast to complexes of Rh, Pt, and Pd, where the activation of aryl C−H bonds is preferred kinetically to the activation of aryl C−F bonds.[22] As a result, $L^{tBu}Co$ is useful for understanding the selectivity of aryl C−F bond cleavage in partially fluorinated substrates.

Zhu and Budzelaar recently reported a Co system that accomplishes the overall binuclear oxidative addition of aryl chlorides.[46] In their system, aryl C−X bond cleavage resulted from the hydrogenolysis of a bis(imino)pyridine Co alkyl complex in the presence of the substrate. This resulted in the formation of a Co−X complex and the corresponding Co−aryl complex. The product ratio varied greatly depending on the substrate, suggesting a pathway that involves aryl radicals. The complex did not react with C−F bonds.

$L^{tBu}Co$ undergoes the overall binuclear oxidative addition of aryl fluorides to give two Co^{II} products: a Co^{II} fluoride complex (**1**) and a Co^{II} aryl complex of the corresponding aryl fluoride. Four plausible pathways to the observed products are shown in Scheme 4. The first is a radical pathway (Scheme 4a), where $L^{tBu}Co$ reduces the aryl C−F bond by one electron to form the Co−F bond in $L^{tBu}CoF$ and to produce a phenyl radical. The second molecule of $L^{tBu}Co$ could then react with $Ph^\bullet$ to form the Co−C bond in $L^{tBu}CoPh$. In the second pathway (Scheme 4b), $L^{tBu}Co$ oxidatively adds the aryl C−F bond to give a Co^{III} complex $L^{tBu}Co(F)(Ph)$. The Co^{III} complex then oxidizes a second molecule of $L^{tBu}Co$ in a rapid step to give the two Co^{II} products. The third pathway (Scheme 4c) starts with coordination of the fluorobenzene to $L^{tBu}Co$ to give a cobalt arene complex. The cobalt arene complex oxidatively adds the aryl C−F bond to give a Co^{III} complex, which proceeds to the products like Scheme 4b. The fourth pathway (Scheme 4d) has two molecules of $L^{tBu}Co$ simultaneously attacking fluorobenzene, and the Co centers reduce the aryl C−F bond by one electron each. This forms the Co−F and Co−aryl bonds in one concerted step. These pathways are similar to those that were proposed for the formation of $[L^{tBu}Fe(\mu\text{-}H)]_2$ in an overall binuclear oxidative addition of H_2 to an Fe^I intermediate.[30]

Can the pathway be distinguished based on our experimental results? One important piece of evidence is that the Co aryl complexes accounted for 50% of the Co in the product, and the amount of **1** accounted for the other 50% of the Co. No biphenyl or benzene was detected in the product mixture by ^1H NMR spectroscopy or GC-MS. These results argue against the radical pathway (a), which would be expected to give some biphenyl, benzene, other coupled side products, and/or a nonstatistical product ratio, as in the literature results on aryl chlorides described above.[46]

The observed experimental rate law, expressed in eq 1, is first-order in both cobalt concentration and fluorobenzene concentration. Pathway (d) is expected to have a rate law that is second-order with respect to cobalt concentration and first-order in fluorobenzene concentration. This does not agree with the experimental rate law, so pathway (d) may be eliminated from consideration.

The rate law for mechanism (b) with the first step rate-limiting is shown in eq 2.

$$-\frac{d[L^{tBu}Co]}{dt} = k_1[L^{tBu}Co][PhF] \tag{2}$$

The steady-state approximation was used to derive the rate law for mechanism (c), as no intermediates were observed during the reaction. The rate law predicted for mechanism (c) is shown (eq 3).

$$-\frac{d[L^{tBu}Co]}{dt} = \frac{2k_1k_2[L^{tBu}Co]^2[PhF]}{k_{-1}[PhF] + k_2[L^{tBu}Co]} \tag{3}$$

The rate is expected to saturate in [PhF]. When $k_{-1}[PhF] \ll k_2[L^{tBu}Co]$, it reduces to the rate law observed in eq 4, and when $k_{-1}[PhF] \gg k_2[L^{tBu}Co]$, it gives the rate law observed in eq 5.

$$-\frac{d[L^{tBu}Co]}{dt} = 2k_1[L^{tBu}Co][PhF] \tag{4}$$

$$-\frac{d[L^{tBu}Co]}{dt} = \frac{2k_1k_2}{k_{-1}}[L^{tBu}Co]^2 \tag{5}$$

Equation 4 agrees with the experimental rate law, and no curvature of the plot of k_{obs} versus [PhF] was observed up to 1 M.

Thus, the kinetic data admit mechanism (c) only if k_{-1}[PhF] ≪ k_2[L^{tBu}Co], conditions where eq 4 holds. In a relevant observation, we recently described the binding of other arenes (benzene, toluene) to L^{tBu}Co.[24] The binding equilibria were established very rapidly, within a minute at room temperature, and the equilibrium constants were near unity. In contrast, L^{tBu}Co was *not* observed to bind fluorobenzenes by ^{1}H NMR spectroscopy (no changes in the chemical shifts of the resonances, or appearance of new signals up to [PhF] = 2 M). Thus, considering the high concentration of [PhF] and higher temperature used in the reaction with fluoroarenes, and the analogy to rapid coordination/decoordination of other unreactive arenes, the term k_{-1}[PhF] must be large. As a result, it is very unlikely that the rate of PhF coordination/decoordination could be slow enough to fulfill the requirement that k_{-1}[PhF] ≪ k_2[L^{tBu}Co]. A final argument against arene precoordination with a slow k_{-1} comes in the substituent effects: mechanism (c) would not predict 1,3,5-trifluorobenzene to be faster than the better π-acceptor hexafluorobenzene. Therefore, our data argue against mechanism (c) in multiple ways.

By process of elimination, *our data are most consistent with mechanism (b)* in Scheme 4. To agree with our data, the oxidative addition of PhF to a single cobalt center must be the rate-limiting step. (We cannot exclude *irreversible* precoordination of the PhF in the rate-limiting step, nor can our kinetic data resolve the details of the mechanism after the rate-limiting step.) Mechanism (b) is further supported by its ability to explain the relative rates of C−F activation for a variety of fluorobenzene substrates using steric and electronic effects. A *meta*-fluorine substituent has a σ_m value of +0.34, whereas a *para*-fluorine substituent has a σ_p value of +0.06.[47] Therefore, a *meta*-fluorine substituent has a greater electron-withdrawing effect than a para substituent, as observed in the kinetic results. The normalized rate constants for fluorobenzene and 1,4-difluorobenzene were the same within error, whereas the normalized rate constant of 1,3-difluorobenzene is 3.8 times greater than that of fluorobenzene. The inductive effect was most clearly visible in 1,3,5-trifluorobenzene, which was the fastest substrate. Finally, an electron-donating *para*-methoxy substituent (σ_p = −0.27)[47] gave a rate that is only slightly slower than fluorobenzene, and the small impact implies that the resonance contribution is minor. This suggests a transition-state structure as shown in Figure 5, with negative charge density on the carbon of the C−F bond. Increased rates from an inductive effect have been observed in the oxidative additions of aryl halides to other metal complexes.[48]

The addition of fluorine ortho to the cleaved C−F significantly slowed the rate of C−F activation due to steric effects; for example, the addition of *ortho*-fluorines in hexafluorobenzene retarded the rate when compared with 1,3,5-trifluorobenzene. This observation is inconsistent with a mechanism that begins with rate-limiting electron transfer from the metal complex to the fluoroarene, as observed in rhodium systems.[11a] An interesting test case is 1,2,4,5-tetrafluorobenzene, in which all C−F bonds are equivalent, and each has one *ortho*-, one *meta*-, and one *para*-fluorine. The C−F activation rate for 1,2,4,5-tetrafluorobenzene was greater than that for fluorobenzene and nearly the same as that for 1,3-difluorobenzene, indicating that the electronic meta influence is dominant over the steric ortho influence.

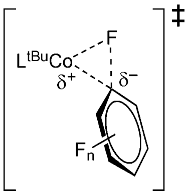


Figure 5. Proposed transition state for C−F cleavage. This model is consistent with the rate law, the steric and electronic substituent effects, and the lack of radical products. The binding mode of L^{tBu} to cobalt in the transition state is purposely unspecified: it may be $\kappa N,\eta^6$-arene[24] or κ^2.

■ CONCLUSIONS

Diketiminate-bound cobalt(I) complexes homolytically cleaved the strong Sn−F bond in Me$_3$SnF to give a cobalt(II) fluoride complex, [L^{tBu}Co(μ-F)]$_2$. The availability of [L^{tBu}Co(μ-F)]$_2$ led to the synthesis of pure [L^{tBu}Co(μ-H)]$_2$. [L^{tBu}Co(μ-H)]$_2$ was shown to be relatively unreactive, which is potentially due to a kinetic barrier to cleavage of the dimer core. The reactivity of this hydride complex contradicts previously published work, showing that the previously reported synthesis and reactivity of "[L^{tBu}Co(μ-H)]$_2$" was incorrect and that the previous samples were primarily composed of L^{tBu}Co and unknown impurities.

Cobalt(I) sources L^{tBu}Co and L^{tBu}Co(THF) reacted with aryl fluorides in a net binuclear oxidative addition reaction, to give cobalt(II) fluoride and cobalt(II) aryl complexes. Kinetic and other mechanistic studies showed that the aryl C−F activation occurred via oxidative addition of the aryl fluoride to L^{tBu}Co, followed by rapid reduction with a second molecule of L^{tBu}Co. Overall, these results demonstrate that low-coordinate cobalt systems have great promise for breaking strong bonds through well-defined mechanisms.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an argon atmosphere (or nitrogen atmosphere where specified) by Schlenk techniques or in an M. Braun glovebox maintained at or below 1 ppm of O$_2$ and H$_2$O. Glassware was dried at 150 °C overnight, and Celite was dried overnight at 200 °C under vacuum. Pentane, hexane, benzene, diethyl ether, and toluene were purified by passage through activated alumina and Q5 columns from Glass Contour Co. (Laguna Beach, CA). THF was distilled under N$_2$ from a potassium benzophenone ketyl solution. All solvents were degassed to remove N$_2$ before bringing them into the glovebox. All solvents were stored over 3 Å molecular sieves. Benzene-d_6 was dried and stored over flame-activated alumina. Toluene-d_8, cyclohexane-d_{12}, THF-d_8, and hexamethyldisiloxane were vacuum-transferred from sodium benzophenone ketyl solutions and were stored over 3 Å molecular sieves. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Triethylsilane was degassed and was stored over 3 Å molecular sieves. BEt$_3$ (1.0 M in hexanes) and hexylmagnesium bromide (2.0 M in Et$_2$O) were purchased from Aldrich and were used as received. KH was purchased from Aldrich as a suspension in mineral oil; it was washed with hexane and dried prior to use. Hexafluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,3,5-trifluorobenzene, 1,2-difluorobenzene, 1,3-difluorobenzene, 1,4-difluorobenzene, fluorobenzene, 4-fluoroanisole, chlorobenzene, bromobenzene, α,α,α-trifluorotoluene, pyridine, and *tert*-butylpyridine were dried by distillation from calcium hydride and were stored over 3 Å molecular sieves. Potassium triethylborohydride,[49] potassium graphite,[42a] trimethyltin fluoride,[16b] L^{tBu}CoCl,[33] and L^{tBu}Co[24] were prepared by published procedures.

^{1}H and ^{119}Sn{^{1}H} NMR data were recorded on a Bruker Avance 500 spectrometer (500 and 186.50 MHz, respectively). ^{19}F{^{1}H} NMR data were recorded on a Bruker Avance 400 spectrometer or a Bruker DRX-300 spectrometer (376 and 282.40 MHz, respectively). All resonances in the ^{1}H NMR spectra are referenced to residual protiated solvents: benzene (δ 7.16 ppm), toluene (δ 2.09 ppm), THF (δ 3.58 or 1.73 ppm), cyclohexane (δ 1.38 ppm). All resonances in the ^{119}Sn{^{1}H} NMR spectra were referenced to an internal standard of tetramethyltin (δ 0 ppm). Resonances in the ^{19}F{^{1}H} NMR spectra were referenced to hexafluorobenzene (δ −164.9 ppm) and were reported against $CFCl_3$ (δ 0 ppm). Resonances were singlets unless otherwise noted. The NMR probe temperature was calibrated using either ethylene glycol or methanol.[50] IR data were recorded on a Shimadzu FTIR spectrophotometer (FTIR-8400S) using a KBr pellet. UV−vis spectra were recorded on a Cary 50 spectrophotometer using Schlenk-adapted quartz cuvettes with a 1 mm optical path length. Solution magnetic susceptibilities were determined by the Evans method.[51] Elemental analyses were determined by the CENTC Elemental Analysis Facility at the University of Rochester. Microanalysis samples were weighed with a PerkinElmer model AD-6 Autobalance, and their compositions were determined with a PerkinElemer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox under argon.

Synthesis of [L^{tBu}Co(μ-F)]$_2$ (1). L^{tBu}Co (162 mg, 0.289 mmol) and Me_3SnF (52.7 mg, 0.288 mmol) were added to a resealable flask. THF (10 mL) and toluene (15 mL) were added to produce a dark green mixture. The mixture was mixed and heated at 70 °C for 21 h, which gave an apple-green mixture. The volatile components were removed under reduced pressure to give a red residue. The residue was dissolved in 3 mL of toluene/pentane (1:1 v/v) and was filtered through Celite. Cooling the solution to −45 °C gave 53 mg of a cherry-red crystalline solid. Three subsequent crystallizations from the mother liquor produced an additional 70 mg of product. The total yield was 73.2%.

Alternative synthesis: L^{tBu}CoCl (227 mg, 0.381 mmol) was dissolved in THF (15 mL) to give an olive-green solution. KC_8 (56.0 mg, 0.414 mmol) was added, giving L^{tBu}Co(THF)[24] as a green mixture, which was stirred for 1.5 h. The precipitate was allowed to settle, and the solution was filtered through Celite. The resulting green solution was transferred to a resealable flask. Trimethyltin fluoride, Me_3SnF (70.9 mg, 0.388 mmol), was added to the flask. Additional THF was used to rinse in the tin reagent, which brought the total volume to 30 mL. The mixture was heated at 70 °C for 18 h to give an apple-green solution. The volatile components were removed under reduced pressure to give a red residue. The product was extracted with toluene (15 mL) and was filtered through Celite to give a red solution. The product was crystallized by the method in the first preparation to give the product (164 mg, 74.2% yield). ^{1}H NMR (C_6D_6, 25 °C): δ 71.1, 39.6, 38.4, 29.4, 23.3, 8.8 8.2, 8.1, 6.3, 3.2, 1.4, −16.0, −20.3, −27.5, −39.5, −88.8, −138 ppm. Many of the resonances were broad and overlapping, which prevented reliable integration and assignment (see the Supporting Information). ^{119}Sn{^{1}H} (THF-d_8): δ −80.5 ($(Me_3Sn)_4Sn$), −89.9 ($(Me_3Sn)_3SnMe$), −99.5 ($(Me_3Sn)_2SnMe_2$), −108.82 ($Me_3SnSnMe_3$), −261.7 ($(Me_3Sn)_2SnMe_2$), −489.8 ($(Me_3Sn)_3SnMe$) ppm (spectra in the Supporting Information). μ_{eff} (C_6D_6, 26 °C) 6.4(2) μ_B. IR (KBr): 3053 (w), 2961 (s), 2927 (m), 2907 (m), 2868 (s), 1539 (m), 1491 (s), 1465 (m), 1433 (m), 1384 (s), 1361 (s), 1310 (s), 1274 (w), 1253 (m), 1215 (m), 1183 (w), 1156 (w), 1122 (w), 1100 (m), 1056 (w), 1023 (w), 934 (w), 782 (m), 757 (m), 712 (w) cm^{-1}. UV−vis (toluene): 350 (29.9 mM^{-1} cm^{-1}), 550 (sh, ∼0.5 mM^{-1} cm^{-1}) nm. Anal. Calcd for $C_{70}H_{106}N_4F_2Co$: C, 72.51; H, 9.23; N, 4.83. Found: C, 72.58; H, 9.35; N, 4.96.

Synthesis of [L^{tBu}Co(μ-H)]$_2$ (2). L^{tBu}CoCl (250 mg, 0.419 mmol) was dissolved in THF (12 mL) to give a dark olive solution. KC_8 (61.9 mg, 0.458 mmol) was added, giving L^{tBu}Co(THF) as a green mixture that was stirred for 3 h. The mixture was allowed to settle and was filtered through Celite. The resulting green solution was transferred to a resealable flask. Me_3SnF (78.0 mg, 0.427 mmol) was added to the flask. Additional THF was used to rinse in the tin reagent, which brought the total volume to 25 mL. The mixture was heated at 70 °C for 20 h to give an apple-green solution. The volatile components were removed under reduced pressure to give a red residue. The residue was extracted with toluene (25 mL) and filtered through Celite into a small Schlenk flask. Triethylsilane (200 μL, 1.25 mmol) was added. The solution slowly turned color from red to brown-red over 15 min. The volatile components were removed under reduced pressure after 3.5 h to give a brown residue. The residue was extracted with THF (7 mL) and filtered through Celite to give a brown solution. The solution was concentrated to 2 mL, and Et_2O (6 mL) was added. The solution was cooled to −45 °C, which produced 131 mg of a semicrystalline brown solid. A second crop of product was collected by concentrating the mother liquor to 1 mL, adding more Et_2O, and cooling to −45 °C. This gave an additional 30 mg of product for a total yield of 60.5%. Single crystals for X-ray crystallography were grown from a saturated solution in benzene-d_6. ^{1}H NMR (C_6D_6, 25 °C): δ 93.3 (2H), 28.0 (18H, ^{t}Bu), 24.7 (6H), 23.3 (2H), 12.4 (18H, ^{t}Bu), 6.4 (6H), 4.9 (2H), 3.2 (8H, Et_2O CH_2), 1.1 (12H, Et_2O CH_3), −1.7 (2H), −3.3 (6H), −5.9 (6H), −11.8 (6H), −24.6, −26.1, −39.8, −40.1, −42.0, −57.1, −59.6 ppm. A few of the resonances were broad and overlapping, which prevented reliable integrations for identification (see the Supporting Information). μ_{eff} (C_6D_6, 27 °C) 6.0(1) μ_B. IR (KBr): 3060 (w), 3025 (w), 2962 (s), 2932 (m), 2870 (m), 1535 (m), 1484 (s), 1466 (m), 1430 (m), 1381 (s), 1358 (s), 1312 (s), 1271 (w), 1255 (m), 1214 (w), 1180 (w), 1159 (w), 1125 (w), 1100 (w), 1022 (w), 782 (s), 769 (w), 759 (w), 712 (s) cm^{-1}. UV−vis (THF): 315 (22.5 mM^{-1} cm^{-1}), 351 (21.5 mM^{-1} cm^{-1}), 480 (br sh, ∼4 mM^{-1} cm^{-1}), 560 (br sh, ∼1 mM^{-1} cm^{-1}), 690 (sh, ∼0.5 mM^{-1} cm^{-1}), 760 (0.56 mM^{-1} cm^{-1}) nm. Anal. Calcd for $C_{70}H_{108}N_4Co\cdot 2C_4H_{10}O_2$: C, 73.66; H, 10.17; N, 4.41. Found: C, 74.06; H, 9.95; N, 4.56.

Synthesis of L^{tBu}Co(*n*-hexyl). L^{tBu}CoCl (508 mg, 0.852 mmol) was dissolved in toluene (50 mL) to give a brown solution. HexylMgBr (0.43 mL, 0.86 mmol) was added to the solution, which immediately produced a red-orange mixture. After 1 h, the volatile components were removed under reduced pressure to give an orange residue. The residue was extracted with pentane (50 mL) and was filtered through Celite to remove the insoluble material. The resulting orange solution was concentrated to 3 mL, and hexamethyldisiloxane (3 mL) was added. This solution was concentrated to ∼3 mL and was stored at −45 °C, which produced a crystalline red product (330 mg, 60% yield). ^{1}H NMR (C_6D_6, 25 °C): δ 242 (2H), 73.3 (4H), 27.0 (18H, ^{t}Bu), 18.0 (2H), 11.3 (2H), 9.8 (2H), 4.2 (2H), 3.8 (12H, ^{i}Pr-CH_3), −28.3 (2H), −50.9 (4H), −52.9 (1H,), −120 (12H, ^{i}Pr-CH_3) ppm. μ_{eff} (C_6D_6, 26 °C) 4.9(1) μ_B. IR (KBr): 2959 (s), 2925 (m), 2868 (m), 1508 (m), 1460 (m), 1431 (m), 1384 (s), 1363 (s), 1317 (s), 1253 (w), 1220 (m), 1197 (m), 1154 (m), 1129 (w), 1098 (m), 1055 (w), 1030 (w), 933 (w), 893 (w), 845 (w), 803 (w), 777 (m), 756 (m) cm^{-1}. UV−vis (pentane): 278 (14.6 mM^{-1} cm^{-1}), 332 (12.9 mM^{-1} cm^{-1}), 370 (sh, ∼9 mM^{-1} cm^{-1}), 468 (1.21 mM^{-1} cm^{-1}), 560 (sh, ∼0.1 mM^{-1} cm^{-1}), 736 (0.12 mM^{-1} cm^{-1}) nm. Anal. Calcd for $C_{41}H_{66}N_2Co$: C, 76.24; H, 10.32; N, 4.34. Found: C, 76.07; H, 10.52; N, 4.13.

X-ray Crystallography. The crystal structure of [L^{tBu}Co(μ-F)]$_2$ was previously reported.[24] A crystal structure of [L^{tBu}Co(μ-H)]$_2$ has also been previously reported;[29] however, a higher-quality structure is reported here, with different packing.

Crystals were placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer[52] for a data collection at 100.0(1) K using Mo Kα radiation and a graphite monochromator. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50° steps in ω at six different φ settings and a detector position of −38° in 2θ. The intensity data were corrected for absorption.[53] Final cell constants were calculated from the *xyz* centroids of >3700 strong reflections from the actual data collection after integration.[54]

Structure **2** was solved using SIR97[55] and refined using SHELXL-97.[56] The space group $P\bar{1}$ was determined based on intensity statistics. A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference

Fourier cycles were performed, which located the remaining non-hydrogen atoms. The bridging hydride positions were located in the difference Fourier map at low resolution (~1.2 Å). Their positions, once established, were refined relative to those of atom Co2. Their isotropic displacement parameters were also refined relative to those of Co2: $U_{iso}[H] = 2U_{eq}[Co]$. The 50:50 ratio of disorder occupancies was fixed once it was observed that all four positions had very similar peak heights. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Also, two diketiminate ligand arms, two isopropyl groups, and one *tert*-butyl group are modeled as disordered over two positions each. All except the latter required 50:50 ratios of disorder components due to nearby crystallographic inversion centers. The *tert*-butyl group is rotationally disordered, with a refined component ratio of 82:18. Per dicobalt molecule are two cocrystallized half-occupancy deuterated benzene solvent molecules, which lie on crystallographic inversion centers. The final full-matrix least-squares refinement converged to $R1 = 0.0621$ (F^2, $I > 2I$) and $wR2 = 0.1576$ (F^2, all data).

The structure of $L^{tBu}Co(n\text{-hexyl})$ was solved using SHELXS-97[56] and refined using SHELXL-97.[56] The space group *Pbca* was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated, which provided all non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full-matrix least-squares refinement converged to $R1 = 0.0546$ (F2, $I > 2I$) and $wR2 = 0.1433$ (F^2, all data).

UV–vis Kinetics. A Cary 50 spectrophotometer, equipped with a Cary single-cell Peltier accessory to maintain the temperature within ±0.1 °C, was used for all kinetics experiments. All measurements were performed in Schlenk-adapted cuvettes with a 1 cm optical path length. The standard procedure for sample preparation in the glovebox is described below. A 5 mM stock solution of $L^{tBu}Co$ in hexane (0.25 mL) was added to a 5 mL volumetric flask. The desired amount of fluorinated substrate was added to the flask, which was then diluted to 5 mL with hexane. The yellow solution was transferred to a Schlenk cuvette, which was sealed with a glass stopper. The cuvette was taken from the glovebox and was placed in the UV–vis apparatus. UV–vis spectra were recorded between 900 and 300 nm with a 600 nm/min scan rate at 3 min intervals. The interval time was varied depending on the substrate concentration. The first 1–2 points were typically discarded as the temperature had not equilibrated.

A kinetic trace for each reaction was generated by plotting absorbance (y) versus reaction time (t), which was analyzed using Kaleidagraph v. 3.51.[57] These data were fit to the general first-order integrated kinetic equation, $\text{Abs} = a + [b\exp(-k_{obs}t)]$, where a and b are constants and k_{obs} is the pseudo-first-order rate constant. The R values for fitting the kinetic traces were at least 0.999.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional kinetic, spectroscopic, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: holland@chem.rochester.edu.

■ ACKNOWLEDGMENTS

Funding was provided by the U.S. Department of Energy, Office of Basic Energy Sciences, Grant No. DE-FG02-09ER16089. The authors thank Dr. Ryan Cowley and Prof. Daniel Weix for helpful discussions.

■ REFERENCES

(1) (a) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373. (b) Barthazy, P.; Hintermann, L.; Stoop, R. M.; Worle, M.; Mezzetti, A.; Togni, A. *Helv. Chim. Acta* **1999**, *82*, 2448. (c) Smart, B. E. *J. Fluorine Chem.* **2001**, *109*, 3. (d) O'Hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308.

(2) Clot, E.; Eisenstein, O.; Jasim, N.; MacGregor, S. A.; McGrady, J. E.; Perutz, R. N. *Acc. Chem. Res.* **2011**, *44*, 333.

(3) Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007.

(4) Begue, J.-P.; Bonnet-Delpon, D. *J. Fluorine Chem.* **2006**, *127*, 992.

(5) (a) Thayer, A. M. *Chem. Eng. News* **2006**, *84*, 15. (b) Isanbor, C.; O'Hagan, D. *J. Fluorine Chem.* **2006**, *127*, 303.

(6) Kirk, K. L. *J. Fluorine Chem.* **2006**, *127*, 1013.

(7) Park, B. K.; Kitteringham, N. R.; O'Neill, P. M. *Annu. Rev. Pharmacol. Toxicol.* **2001**, *41*, 443.

(8) Ojima, I., Ed. *Fluorine In Medicinal Chemistry and Chemical Biology*; Wiley: Chichester, U.K., 2009.

(9) McCulloch, A. *J. Fluorine Chem.* **2003**, *123*, 21.

(10) Ravishankara, A. R.; Solomon, S.; Turnipseed, A. A.; Warren, R. F. *Science* **1993**, *259*, 194.

(11) Selected examples of hydrodefluorination: (a) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359. (b) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674. (c) Burch, R. R.; Calabrese, J. C.; Ittel, S. D. *Organometallics* **1988**, *7*, 1642. (d) Clot, E.; Mégret, C.; Kraft, B. M.; Eisenstein, O.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 5647. (e) Douvris, C.; Nagaraja, C. M.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2010**, *132*, 4946. (f) Edelbach, B. L.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 7734. (g) Young, R. J.; Grushin, V. V. *Organometallics* **1999**, *18*, 294. (h) Fuchibe, K.; Ohshima, Y.; Mitomi, K.; Akiyama, T. *J. Fluorine Chem.* **2007**, *128*, 1158. (i) Amii, H.; Uneyama, K. *Chem. Rev.* **2009**, *109*, 2119.

(12) (a) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293. (b) Hughes, R. P. *Adv. Organomet. Chem.* **1990**, *31*, 183. (c) Morrison, J. A. *Adv. Organomet. Chem.* **1993**, *35*, 211. (d) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber.* **1997**, *130*, 145. (e) Richmond, T. G. *Top. Organomet. Chem.* **1999**, *3*, 243. (f) Richmond, T. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3241. (g) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2002**, *102*, 4009. (h) Braun, T.; Perutz, R. N. *Chem. Commun.* **2002**, 2749. (i) Mazurek, U.; Schwarz, H. *Chem. Commun.* **2003**, 1321. (j) Jones, W. D. *Dalton Trans.* **2003**, 3991. (k) Torrens, H. *Coord. Chem. Rev.* **2005**, *249*, 1957. (l) Braun, T.; Wehmeier, F. *Eur. J. Inorg. Chem.* **2011**, 613. (m) Braun, T.; Perutz, R. N. Transition-Metal Mediated C–F Bond Activation. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Amsterdam, 2006.

(13) (a) Doherty, N. M.; Hoffmann, N. W. *Chem. Rev.* **1991**, *91*, 553. (b) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425. (c) Plenio, H. *Chem. Rev.* **1997**, *97*, 3363.

(14) Osterberg, C. E.; Richmond, T. G. Activation of Carbon–Fluorine Bonds by Oxidative Addition to Low-Valent Transition Metals. In *Inorganic Fluorine Chemistry*; Oxford University Press: London, 1994.

(15) (a) Amii, H.; Uneyama, K. *Chem. Rev.* **2009**, *109*, 2119. (b) Meier, G.; Braun, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 1546. (c) Hughes, R. P. *Eur. J. Inorg. Chem.* **2009**, 4591. (d) Driver, T. G. *Angew. Chem., Int. Ed.* **2009**, *48*, 7974. (e) Sun, A. D.; Love, J. A. *Dalton Trans.* **2010**, *39*, 10362. (f) Richmond, T. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3241.

(16) (a) Vela, J.; Smith, J. M.; Yu, Y.; Ketterer, N. A.; Flaschenriem, C. J.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2005**, *127*, 7857. (b) Noveski, D.; Braun, T.; Schulte, M.; Neumann, B.; Stammler, H.-G. *Dalton Trans.* **2003**, 4075. (c) Braun, T.; Wehmeier, F.; Altenhöner, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5321. (d) Lindup, R. J.; Marder, T. B.; Perutz, R. N.; Whitwood, A. C. *Chem. Commun.* **2007**, 3664. (e) Yang, J.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 12656. (f) Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 1847.

(17) (a) Braun, T.; Ahijado-Salomon, M.; Altenhöner, K.; Teltewskoi, M.; Hinze, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 1818. (b) Teltewskoi, M.; Panetier, J. A.; Macgregor, S. A.; Braun, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 3947.

(18) (a) Jäger-Fiedler, U.; Klahn, M.; Arndt, P.; Baumann, W.; Spannenberg, A.; Burlakov, V. V.; Rosenthal, U. *J. Mol. Catal. A* **2007**, *261*, 184. (b) Ali, M.; Liu, L.-P.; Hammond, G. B.; Xu, B. *Tetrahedron Lett.* **2009**, *50*, 4078. (c) Klahn, M.; Fischer, C.; Spannenberg, A.; Rosenthal, U.; Krossing, I. *Tetrahedron Lett.* **2007**, *48*, 8900. (d) Terao, J.; Begum, S. A.; Shinohara, Y.; Tomita, M.; Naitoh, Y.; Kambe, N. *Chem. Commun.* **2007**, 855.

(19) (a) Douvris, C.; Ozerov, O. V. *Science* **2008**, *321*, 1188. (b) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2000**, *122*, 8559. (c) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10973. (d) Hughes, R. P.; Laritchev, R. B.; Williamson, A.; Incarvito, C. D.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2003**, *22*, 2134. (e) Edelbach, B. L.; Fazlur-Rahman, A. K.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 3170. (f) Maron, L.; Werkema, E. L.; Perrin, L.; Eisenstein, O.; Andersen, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 279. (g) Adonin, N. Y.; Starichenko, V. F. *Mendeleev Commun.* **2000**, *10*, 60. (h) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 727. (i) Johnson, S. A.; Taylor, E. T.; Cruise, S. J. *Organometallics* **2009**, *28*, 3842. (j) Prikhod'ko, S. A.; Adonin, N. Y.; Babushkin, D. E.; Parmon, V. N. *Mendeleev Commun.* **2008**, *18*, 211. (k) Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 1847. (l) Fout, A. R.; Scott, J.; Miller, D. L.; Bailey, B. C.; Pink, M.; Mindiola, D. J. *Organometallics* **2009**, *28*, 331. (m) Bailey, B. C.; Huffman, J. C.; Mindiola, D. H. *J. Am. Chem. Soc.* **2007**, *129*, 5302. (n) Krasnov, V. I.; Platonov, V. E.; Beregoyava, I. V.; Shohegolava, L. N. *Tetrahedron* **1997**, *53*, 1797. (o) Kühnel, M. F.; Lentz, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 2933. (p) Rieth, R. D.; Brennessel, W. W.; Jones, W. D. *Eur. J. Inorg. Chem.* **2007**, 2839. (q) Kraft, B. M.; Jones, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 8681. (r) Watson, L. A.; Yandulov, D. V.; Caulton, K. G. *J. Am. Chem. Soc.* **2001**, *123*, 603. (s) Deck, P. A.; Konaté, M. M.; Kelly, B. V.; Slebodnick, C. *Organometallics* **2004**, *23*, 1089. (t) Bouwkamp, M. W.; deWolf, J.; Morales, I. D. H.; Gercama, J.; Meetsma, A.; Troyanov, S. I.; Hessen, B.; Teuben, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 12956. (u) Santamaría, C.; Beckhaus, R.; Haase, D.; Saak, W.; Koch, R. *Chem Eur. J.* **2001**, *7*, 622. (v) Bareille, L.; Becht, S.; Cui, J. L.; Le Gendre, P.; Moïse, C. *Organometallics* **2005**, *24*, 5802.

(20) (a) Burdeniuc, J.; Chupka, W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 10119. (b) Burdeniuc, J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 2525. (c) Burdeniuc, J.; Crabtree, R. H. *Organometallics* **1998**, *17*, 1582.

(21) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 38. (b) Jolly, P. W.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 5830. (c) Edelbach, B. L.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 7734. (d) Doig, S. J.; Hughes, R. P.; Davis, R. E.; Gadol, S. M.; Holland, K. D. *Organometallics* **1984**, *3*, 1921. (e) Hughes, R. P.; Doig, S. J.; Hemond, R. C.; Smith, W. L.; Davis, R. E.; Gadol, S. M.; Holland, K. D. *Organometallics* **1990**, *9*, 2745. (f) Rausch, M.; Bruhn, C.; Steinborn, D. *J. Organomet. Chem.* **2001**, *622*, 172.

(22) (a) Bosque, R.; Clot, E.; Fantacci, S.; Maseras, F.; Eisenstein, O.; Perutz, R. N.; Renkema, K. B.; Caulton, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 12634. (b) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674.

(23) (a) Li, X.; Sun, H.; Yu, F.; Flörke, U.; Klein, H.-F. *Organometallics* **2006**, *25*, 4695. (b) Camadanli, S.; Beck, R.; Flörke, U.; Klein, H.-F. *Dalton Trans.* **2008**, 5701. (c) Zheng, T.; Sun, H.; Chen, Y.; Li, X.; Durr, S.; Radius, U.; Harms, K. *Organometallics* **2009**, *28*, 5771. (d) Zheng, T.; Sun, H.; Ding, J.; Zhang, Y.; Li, X. *J. Organomet. Chem.* **2010**, *695*, 1873. (e) Lian, X.; Xu, X.; Sun, H.; Chen, Y.; Zheng, T.; Li, X. *Dalton Trans.* **2010**, *39*, 9523.

(24) Dugan, T. R.; Sun, X.-R.; Rybak-Akimova, E. V.; Olatunji-Ojo, O.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 12418.

(25) Ding, K.; Dugan, T. R.; Brennessel, W. W.; Bill, E.; Holland, P. L. *Organometallics* **2009**, *28*, 6650.

(26) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416.

(27) Wakasa, M.; Kugita, T. *Organometallics* **1999**, *18*, 2941.

(28) Davies, A. G., Gielen, M., Pannell, K. H., Tiekink, E. R. T., Eds. *Tin Chemistry: Fundamentals, Frontiers, and Applications*; Wiley: New York, 2008; p 36.

(29) Ding, K.; Brennessel, W. W.; Holland, P. L. *J. Am. Chem. Soc.* **2009**, *131*, 10804.

(30) Dugan, T. R.; Holland, P. L. *J. Organomet. Chem.* **2009**, *694*, 2825.

(31) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752.

(32) Yu, Y.; Sadique, A. R.; Smith, J. M.; Dugan, T. R.; Cowley, R. E.; Brennessel, W. W.; Flaschenriem, C. J.; Bill, E.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2008**, *130*, 6624.

(33) Ding, K.; Dugan, T. R.; Holland, P. L.; Adhikari, D.; Mindiola, D. J. *Inorg. Synth.* **2010**, *35*, 43.

(34) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: Hoboken, NJ, 2005; p 161. (b) Hartwig, J. *Organotransition Metal Chemistry From Bonding to Catalysis*; University Science Books: Sausalito, CA, 2010; p 262.

(35) Beg, S. A.; Tukur, N. M.; Al-Harbi, D. K.; Hamad, E. Z. *J. Chem. Eng. Data* **1993**, *38*, 461.

(36) (a) van Driel, G. J.; Driessen, W. L.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 2919. (b) Rietmeijer, F. J.; van Albada, G. A.; De Graaff, R. A. G.; Hasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 3597. (c) Rietmeijer, F. J.; Haasnoot, J. G.; Den Hartog, A. J.; Reedijk, J. *Inorg. Chim. Acta* **1986**, *113*, 147. (d) Jansen, J. C.; van Koningsveld, H.; Reedijk, J. *Nature* **1977**, *269*, 318. (e) van Kralingen, C. G.; Reedijk, J. *Chem. Commun.* **1976**, 533. (f) Meyer, F.; Heinze, K.; Nuber, B.; Zsolnai, L. *J. Chem. Soc., Dalton Trans.* **1998**, 207. (g) Handley, D. A.; Hitchcock, P. B.; Leigh, G. J. *Inorg. Chim. Acta* **2001**, *314*, 1. (h) Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452. (i) Lee, S. C.; Holm, R. H. *Inorg. Chem.* **1993**, *32*, 4745.

(37) Chang, W.-K.; Chiang, R.-K.; Jiang, Y.-C.; Wang, S.-L.; Lee, S.-F.; Lii, K.-H. *Inorg. Chem.* **2004**, *43*, 2564.

(38) Dong, J.; Devi, P. S.; Mendoza, E.; Gafney, H. D. *Inorg. Chem.* **2002**, *41*, 11.

(39) (a) Omae, I. *Organotin Chemistry*; Elsevier: Dordrecht, The Netherlands, 1989; p 181. (b) Bowman, W. R.; Bridge, C. F.; Brookes, P.; Cloonan, M. O.; Leach, D. C. *J. Chem. Soc., Perkin Trans.* **2002**, *1*, 58.

(40) A few selected references that illustrate the reaction of Me_3SnF with metal chlorides: (a) Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. *Organometallics* **1994**, *13*, 1251. (b) Murphy, E. F.; Lübben, T.; Herzog, A.; Roesky, H. W.; Demsar, A.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **1996**, *35*, 23. (c) Liu, F.-Q.; Herzog, A.; Roesky, H. W.; Usón, I. *Inorg. Chem.* **1996**, *35*, 741. (d) Shah, S. A. A.; Dorn, H.; Voigt, A.; Roesky, H. W.; Parisini, E.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 3176. (e) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806. (f) Singh, S.; Ahn, H.-J.; Stasch, A.; Jancik, V.; Roesky, H. W.; Pal, A.; Biadene, M.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2006**, *45*, 1853. (g) Yang, Y.; Schulz, T.; John, M.; Ringe, A.; Roesky, H. W.; Stalke, D.; Magull, J.; Ye, H. *Inorg. Chem.* **2008**, *47*, 2585. (h) Eger, S.; Immel, T. A.; Claffey, J.; Müller-Bunz, H.; Tacke, M.; Groth, U.; Huhn, T. *Inorg. Chem.* **2010**, *49*, 1292.

(41) Pfirrmann, S.; Limberg, C.; Ziemer, B. *Dalton Trans.* **2008**, 6689.

(42) (a) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. *J. Am. Chem. Soc.* **2006**, *128*, 756. (b) The smaller $L^{Me}Ni$ hydride complex also does not react with N_2: Pfirrmann, S.; Yao, S.; Ziemer, B.; Stosser, R.; Driess, M.; Limberg, C. *Organometallics* **2009**, *28*, 6855.

(43) Yu, Y.; Brennessel, W. W.; Holland, P. L. *Organometallics* **2007**, *26*, 3217.

(44) Housecroft, C. E.; Sharpe, A. G. *Inorg. Chem.*, 2nd ed.; Pearson: London, 2001.
(45) Korn, T. J.; Schade, M. A.; Wirth, S.; Knochel, P. *Org. Lett.* **2006**, *8*, 725.
(46) Zhu, D.; Budzelaar, P. H. M. *Organometallics* **2010**, *29*, 5759.
(47) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
(48) (a) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665. (b) Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810. (c) Biscoe, M. R.; Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 6686. (d) Kleimark, J.; Hedström, A.; Larsson, P.-F.; Johansson, C.; Norrby, P.-O. *ChemCatChem* **2009**, *1*, 152. (e) Guijarro, A.; Rosenberg, D. M.; Rieke, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 4155. (f) Ahlquist, M.; Norrby, P.-O. *Organometallics* **2007**, *26*, 550. (g) Böhm, V. P. W; Herrmann, W. A. *Chem. Eur. J.* **2001**, *7*, 4191. (h) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.
(49) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 3804.
(50) (a) Kaplan, M. L.; Bovey, F. A.; Cheng, H. N. *Anal. Chem.* **1975**, *47*, 1703. (b) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.
(51) (a) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872. (b) Schubert, E. M. *J. Chem. Educ.* **1992**, *69*, 62.
(52) *APEX2*, version 2010.7-0; Bruker AXS: Madison, WI, 2010.
(53) Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.
(54) *SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009.
(55) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.
(56) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.
(57) *KaleidaGraph 3.51*; Synergy Software: Reading, PA, 2000.