Chemical Science

Cite this: *Chem. Sci.*, 2012, **3**, 72

www.rsc.org/chemicalscience

EDGE ARTICLE

C(sp^3)–F reductive elimination from alkylgold(III) fluoride complexes†

Neal P. Mankad and F. Dean Toste*

Received 29th July 2011, Accepted 30th September 2011
DOI: 10.1039/c1sc00515d

Rare examples of C(sp^3)–F reductive elimination were observed from several *cis*-F_2Au(R)(IPr) intermediates generated by oxidation of (IPr)AuR complexes with XeF_2. For R groups bearing β-hydrogens, β-hydride elimination was competitive with C(sp^3)–F reductive elimination. For strained cyclic R groups and most acyclic R groups lacking β-hydrogens, carbocation-like rearrangements occurred prior to C(sp^3)–F reductive elimination. Kinetics of the decay of one *cis*-F_2Au(R)(IPr) species, stereochemical analysis of reductive elimination with a chiral R group, and DFT analysis collectively suggest C(sp^3)–F reductive elimination proceeding through transient cationic $[(IPr)Au(F)(R)]^+$ intermediates with significant ionization of the Au–alkyl bonds.

Introduction

Installation of C–F bonds by transition metal catalysis is particularly fascinating both because of significant interest in fluorocarbon products for important applications,[1] but also because of the fundamental challenges posed by designing C–F bond-forming catalytic cycles.[2] One main difficulty involves mediating C–F reductive elimination, which is likely to be the key turnover step in many such catalytic cycles. C–F reductive elimination remains rare compared to other types of C–X reductive elimination (X = *e.g.* C, N, O, Cl, Br, I) despite the large thermodynamic driving force provided by formation of strong C–F bonds (H_3C–F BDE = 110 kcal mol^{-1}).[3] Key advances in stoichiometric C(sp^2)–F reductive elimination[4] as well as fluorination of transition metal π-complexes[5] have led directly to recent discoveries of corresponding C(sp^2)–F and C(allyl)–F bond-forming catalysts.[2,4d,5,6] On the other hand, stoichiometric C(sp^3)–F reductive elimination from discrete σ-organometallic intermediates has not been extensively studied[7] despite a number of reports of stable, high-valent alkyl–metal fluoride complexes.[8] Moreover, the reverse process, C(sp^3)–F oxidative addition, has only been observed directly in a single recent report.[9] Identification of systems that allow for C(sp^3)–F reductive elimination and careful study of the principles that govern this process promise to guide the design of future C(sp^3)–F bond-forming catalysts.[10]

Department of Chemistry, University of California-Berkeley, Berkeley, CA, 94720, USA. E-mail: fdtoste@berkeley.edu; Fax: +1 510-666-2504; Tel: +1 510-642-2850

† Electronic supplementary information (ESI) available: Synthetic, spectroscopic, kinetic, crystallographic, and computational details. CCDC reference numbers 837541. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1sc00515d

Results and discussion

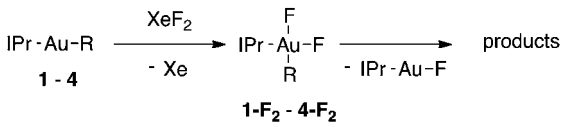
Fluorination of Au–C(sp^3) bonds

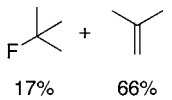
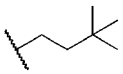
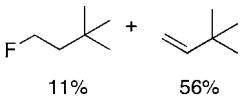
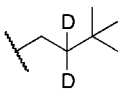
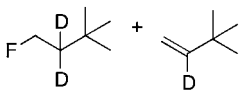
Alkylgold(III) intermediates are well known to undergo facile C–X reductive elimination (X = O, Cl, Br, or I). Recently a mechanistic study was conducted on carbon–halogen reductive elimination from X_2Au(Me)(IPr) complexes (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; X = Cl, Br, or I), which produce CH_3X even at low temperature.[11] In contrast, we recently reported the oxidation of (IPr)AuMe (**1**) with XeF_2 to yield the difluoride analogue *cis*-F_2Au(Me)(IPr) (**1-F$_2$**), which is remarkably robust towards thermal decomposition by CH_3F elimination.[12]

We reasoned that ground-state destabilization of F_2Au(R)(IPr) complexes might lead to successful C(sp^3)–F bond formation. It is well known that steric pressure facilitates reductive elimination processes in this way.[13] Indeed, during the course of our ongoing studies on the role of gold(III) fluorides in catalysis,[12,14] we sought to oxidize the more hindered complexes (IPr)Au(*t*Bu) (**2**) and (IPr)AuCH_2CH_2tBu (**3**) with XeF_2 in order to study the reactivity of the intermediates *cis*-F_2Au(*t*Bu)(IPr) (**2-F$_2$**) and *cis*-F_2Au(CH_2CH_2tBu)(IPr) (**3-F$_2$**) with arylboronic acid coupling partners. During those studies we found that, if starved of coupling partners, these intermediates decomposed to yield product mixtures containing the gold(I) fluoride complex (IPr)AuF, as well as alkenes resulting from formal β-H elimination and fluoroalkanes presumably derived from C(sp^3)–F reductive elimination (Table 1).[15] Reaction of (IPr)AuCH_2CD_2tBu (**4**), in which the β position is perdeuterated, with XeF_2 led to a product mixture only slightly perturbed from that of **3** (Table 1) and in which β-H(D) elimination still outcompeted C–F elimination.

We next examined complexes bearing cyclic alkyl groups in order to disfavor β-H elimination (Table 2). For cyclohexyl derivative **5**, C–F reductive elimination indeed outcompeted β-H

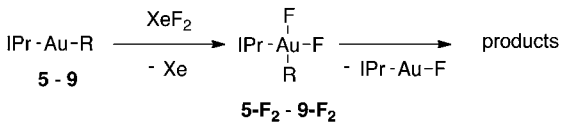
Table 1 Fluorination of selected alkylgold(I) complexes[a]

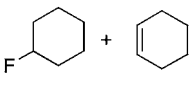
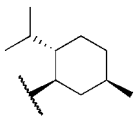
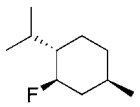
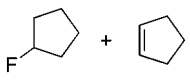
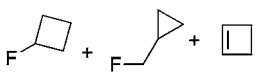
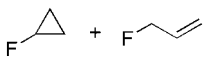


Number	R	Product mixture[b]
1[c]		None
2		 17% 66%
3[c]		 11% 56%
4[c]		 15% 33%

[a] 30 mM (IPr)AuR, 1.1 equiv XeF_2, $CDCl_3$ solvent, room temp. [b] Determined by ^1H and ^{19}F NMR. Several NMR yields should be considered lower limits due to product volatility. [c] *cis*-$F_2Au(R)(IPr)$ intermediate observed by ^{19}F NMR.

Table 2 Fluorination of cycloalkylgold(I) complexes[a]



Number	R	Product mixture[b]
5		 60% 24%
6		 95%
7		 30% 49%
8		 49% 28% 7%
9[c]		 44% 18%

[a] 30 mM (IPr)AuR, 1.1 equiv XeF_2, $CDCl_3$ solvent, room temp. [b] Determined by ^1H and ^{19}F NMR. Several NMR yields should be considered lower limits due to product volatility. [c] *cis*-$F_2Au(R)(IPr)$ intermediate observed by ^{19}F NMR.

elimination by a ratio of ~5 : 2. The bulkier (−)-menthyl derivative **6** produced (−)-menthyl fluoride as the exclusive product with perfect stereoretention and with no evidence of alkene products.[16] Surprisingly, β-H elimination outcompeted C–F reductive elimination for cyclopentyl derivative **7**. For the more strained cycloalkyl derivatives **8** and **9**, β-H elimination pathways were marginalized but carbocation-like rearrangement processes were observed as minor pathways relative to direct C–F reductive elimination. Specifically, cyclopropylmethyl fluoride was observed as a minor product from fluorination of cyclobutyl derivative **8**, and allyl fluoride was observed as a minor product from fluorination of cyclopropyl derivative **9** (Table 2).

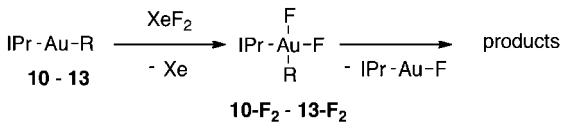
We next studied complexes lacking β-hydrogens (Table 3). Reaction of the *neo*-pentyl complex **10** with XeF_2 also led to carbocation-like behavior, with the rearranged tertiary alkyl fluoride product (*tert*-pentyl fluoride) dominating over the expected primary alkyl fluoride product (*neo*-pentyl fluoride). This apparent methyl migration was also observed for the trimethylsilylmethyl derivative **11**, with the rearrangement pathway outcompeting the direct C–F reductive elimination pathway to yield ethylfluorodimethylsilane as the major product (Table 3). Alkyl migration even occurred for the 1-adamantylmethyl complex **12** upon reaction with XeF_2, further highlighting the preference for Au^{III}-mediated $C(sp^3)$–F reductive elimination to produce tertiary rather than primary fluoroalkanes when possible. By contrast, reaction of (IPr)AuCH_2Ph (**13**) with XeF_2 yielded FCH_2Ph in good yield (Table 3).

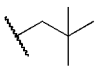
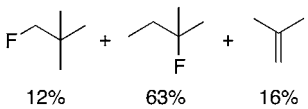
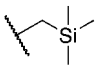
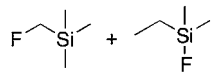
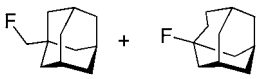
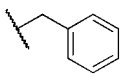
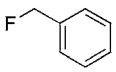
The (IPr)AuF byproduct of these reductive elimination processes was accessed on preparative scale by reaction of **13** with XeF_2 and studied by X-ray crystallography. The solid-state structure of (IPr)AuF·$2CH_2Cl_2$ revealed an extended hydrogen-bonding network, with the CH_2Cl_2 solvent molecules acting as hydrogen bond donors towards the terminal Au–F moiety (Fig. 1). Similar hydrogen bonding interactions exist for (SIPr)AuF·$2CH_2Cl_2$ (SIPr = 1,3-bis(2,6-diisopropylphenyl) imidazolin-2-ylidene).[17] The Au–F distance in (IPr)AuF (2.071 (2) Å) is slightly shorter than that in (SIPr)AuF (2.082(2) Å).

Kinetics of the decay of an alkylgold(III) difluoride intermediate

For several of the fluorination reactions the *cis*-$F_2Au(R)(IPr)$ intermediates were easily identified by their characteristic ^{19}F NMR properties (Table S1†),[12] and it was thus established that (IPr)AuF and the organic products depicted in Tables 1–3 appeared over time as these *cis*-$F_2Au(R)(IPr)$ complexes disappeared. One such intermediate, **11-F_2**, was chosen for kinetics studies. The disappearance of intermediate **11-F_2** obeyed first-order kinetics (Figure S1†). An Eyring plot (Figure S2†) revealed activation parameters of $\Delta H^{\ddagger} = 12.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30$ e.u., and thus an activation free energy of $\Delta G^{\ddagger} = 21.7$ kcal mol^{-1} at 298 K. When samples were spiked with various concentrations of added tetrabutylammonium fluoride (TBAF), the decay of **11-F_2** exhibited an approximately inverse first-order relationship with fluoride concentration (Fig. 2 and S3†).

Table 3 Fluorination of alkylgold(I) complexes lacking β-hydrogens[a]



Number	R	Product mixture[b]
10[c]		 12% 63% 16%
11[c]		 11% 75%
12		 11% 73%
13		 85%

[a] 30 mM (IPr)AuR, 1.1 equiv XeF_2, $CDCl_3$ solvent, room temp. [b] Determined by ^1H and ^{19}F NMR. Several NMR yields should be considered lower limits due to product volatility. [c] *cis*-$F_2Au(R)(IPr)$ intermediate observed by ^{19}F NMR.

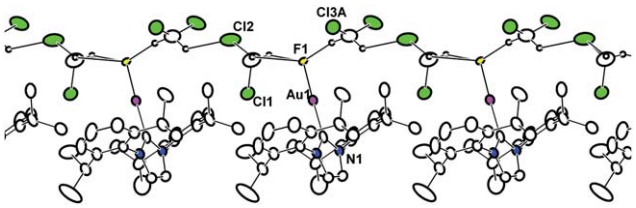


Fig. 1 Extended solid-state structure of $(IPr)AuF\cdot 2CH_2Cl_2$, as 50% ellipsoids. Only solvent hydrogen atoms (in calculated positions) are shown. Selected bond lengths (Å) and angles (°): Au–F, 2.071(2); Au–C, 1.954(5); C–Au–F, 177.65(15).

A proposed mechanistic scheme accounting for the various observed reaction pathways is shown in Scheme 1. Consistent with the inverse rate dependence on fluoride concentration, we propose initial fluoride dissociation from an alkylgold(III) difluoride complex to reveal an activated, 3-coordinate complex of the type $[(IPr)Au(F)(R)]^+$. Such a complex with R = Me has been characterized crystallographically in dimeric form.[12] This key intermediate can then mediate R–F reductive elimination *via* a classical 3-centered transition state, consistent with the observed retention of stereochemistry observed for **6**, followed by trapping of the $[(IPr)Au]^+$ fragment with the dissociated fluoride. The coordinatively unsaturated nature of a $[(IPr)Au(F)(R)]^+$ species would also allow for β-H elimination either by a traditional Au-mediated mechanism[18] or by deprotonation of the β position by F^-. We further propose that such a 3-coordinate, cationic species places a significant degree of positive charge character in the Au^{III}–R bond, resulting in the alkyl migrations and other carbocation-like rearrangements described herein *in lieu* of direct C–F reductive elimination. The large and negative $\Delta S^{\ddagger}$ for the decay of **11-F$_2$** is unusual for a dissociative process and could be indicative of a highly ordered transition state necessary for tandem methyl migration/reductive elimination. It is also possible that solvent reorganization is necessary for solvation of F^- and contributes to this entropic term.[19]

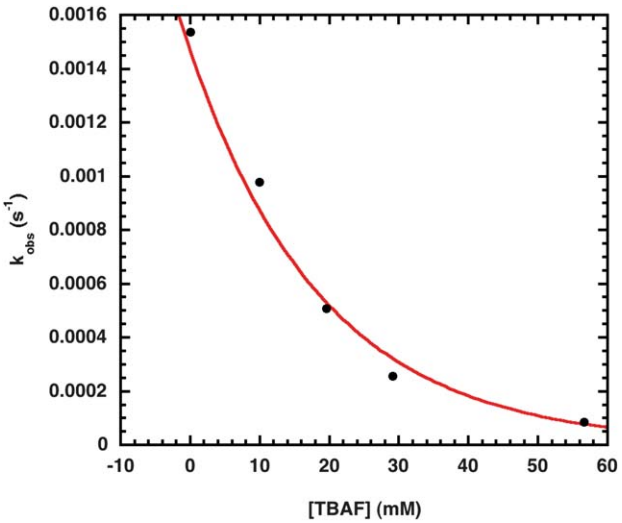
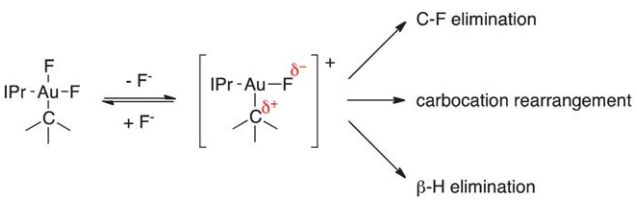


Fig. 2 Dependence of the rate of decay of *cis*-$F_2Au(CH_2SiMe_3)(IPr)$ (**11-F$_2$**) on F^- concentration, as determined by the method of initial rates. $k_{obs} = (\Delta[\mathbf{11\text{-}F_2}]/\Delta t)/[\mathbf{11\text{-}F_2}]_0$, $[\mathbf{11\text{-}F_2}]_0 = 32.4$ mM, TBAF = tetrabutylammonium fluoride. The red line is a smoothed-curve guide.

Iodination of Au–C(sp^3) bonds

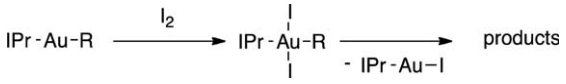
It has been established previously[11] that CH_3I reductive elimination from *trans*-$I_2Au(Me)(IPr)$ similarly proceeds through transient $[(IPr)Au(Me)(I)]^+$. We thus chose to examine the degree of carbocation-like character possessed by such cationic alkylgold(III) iodide intermediates relative to their alkylgold(III) fluoride analogues.

Product mixtures derived from halogenation of selected (IPr)AuR complexes with I_2 are shown in Table 4. First it is worth reiterating that though C–F reductive elimination was not observed even at elevated temperatures for R = Me, clean C–I reductive elimination was observed at room temperature.[11,12] While β-H elimination and cyclobutyl ring contraction/opening did occur to some extent for the bulkier iodide complexes, certain carbocation-like rearrangement such as methyl migration and cyclopropyl ring-opening which occurred readily for the fluoro complexes did not occur to any detectable extent for the iodo complexes. For example, the *neo*-pentyl and trimethylsilylmethyl



Scheme 1 Proposed mechanistic scenario.

Table 4 Iodination of selected alkylgold(I) complexes[a]



R	Product mixture[b]
CH_3	$I-CH_3$, quant.[c]
	55% + 18%
	60% + 31% + 5%
	93%
	84%
Si	Si, 95%

[a] 30 mM (IPr)AuR, 1.1 equiv I_2, $CDCl_3$ solvent. [b] Determined by ^1H NMR. Several NMR yields should be considered lower limits due to product volatility. [c] Taken from ref. 11.

derivatives produced the primary rather than tertiary iodoalkane products exclusively (Table 4). It follows that the carbocationic character of alkylgold(III) complexes is accentuated by fluoride ligands. Lastly, we note that, like C–F reductive elimination, C–I reductive elimination from gold(III) complexes has been shown previously to proceed with stereoretention.[14] For no case other than (IPr)AuMe was the alkylgold(III) diiodide intermediate observable by NMR spectroscopy prior to iodoalkane extrusion.[11]

DFT analysis of relevant alkylgold(III) intermediates

In order to examine the nature of the cationic $[(IPr)Au(F)(R)]^+$ intermediates, we initiated a preliminary DFT study. The optimized structure of *cis*-$F_2Au(CH_2tBu)(IPr)$ (**10-F$_2$**) exhibited the expected square planar geometry with a Au–CH_2 distance of 2.110 Å and Au–F distances of 2.014 and 2.112 Å (*cis* and *trans* to the alkyl group, respectively). Minimization of $[(IPr)Au(CH_2tBu)(F)]^+$ (**10-F$^+$**) from various starting geometries converged to an optimized T-shaped geometry, with the vacant coordination site occurring *trans* to the alkyl ligand. The Au–CH_2 distance in **10-F$^+$** was elongated to 2.180 Å despite dissociation of the *trans* ligand and onset of positive molecular charge. The calculated LUMO (LUMO = lowest unoccupied molecular orbital) of **10-F$^+$**, shown in Fig. 3, was σ*(Au–alkyl) in character and exhibited a through-space antibonding overlap between the σ*(Au–alkyl) contribution and that from an

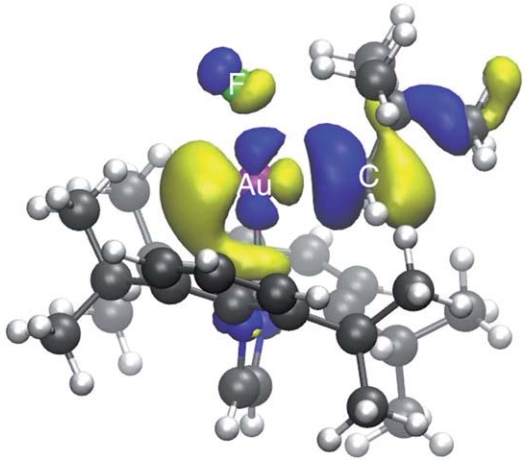
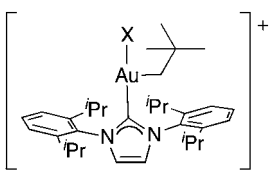


Fig. 3 Calculated LUMO (BPV86/LANL2DZ/6-311G++**, implicit CH_2Cl_2 solvation, 0.04 isocontour) of $[(IPr)Au(CH_2tBu)(F)]^+$ (**10-F$^+$**).

adjacent σ(C–CH_3) bond, suggesting an electronic mechanism for methyl migration. Mülliken population analysis indicated that the LUMO of **10-F$^+$** had larger %C contribution (43%) and smaller %Au contribution (20%) than the LUMO of **10-F$_2$** (26% C, 31%Au).

In order to understand the special carbocation-like behavior of $[(IPr)Au(F)(R)]^+$ intermediates, we analyzed the entire halide series $[(IPr)Au(X)(CH_2tBu)]^+$ (**10-X$^+$**, X = F, Cl, Br, and I) by analogous DFT methods. The entire series of complexes was predicted to have roughly similar Au–C_{alkyl} distances, electrostatic charges on CH_2, and LUMO compositions (Table S4†). A striking relationship was observed, however, between the identity of the halide ligand X and the natural charge on Au (Table 5). According to natural population analysis, the electrostatic charge on Au ranged from 0.48e in **10-I$^+$** to 0.86e in **10-F$^+$**. Because the natural charge on the alkyl CH_2 unit remained roughly constant (0.14e for **10-I$^+$** to 0.11e for **10-F$^+$**) across the series, this translated to a particularly polarized Au–C_{alkyl} bond for **10-F$^+$**, as measured by the difference in charge between Au and CH_2 (Table 5). In other words, the fluoro ligand imparts a build-up of positive charge on Au, thereby partially ionizing the Au–C_{alkyl} bond and making (IPr)AuF a particularly effective

Table 5 Charge distribution of **10-X$^+$** as a function of X[a]



X	q(Au)[b]	q(X)[b]	q(CH_2)[b]	Δq(Au–CH_2)[c]
F	0.86	−0.62	0.11	0.75
Cl	0.69	−0.53	0.14	0.55
Br	0.61	−0.42	0.14	0.47
I	0.48	−0.29	0.14	0.34

[a] Natural charge based on NBO analysis (BPV86/LANL2DZ/6-311G++**, implicit CH_2Cl_2 solvation). [b] q = charge. [c] Δq = difference in charge between Au and CH_2.

leaving group. These factors are likely contributors to the unusual carbocation-like behaviour observed in Au-mediated C(sp^3)–F reductive elimination reactions.

Conclusions

Alkylgold(III) fluoride complexes are proposed as the active electrophiles in many Au(I)/Au(III) catalytic cycles involving nucleophilic coupling partners.[20] For such reactions it has been proposed[12,14,21] that:

1) C–C coupling is enabled by the relatively long lifetime of alkylgold(III) fluoride intermediates towards C–F reductive elimination

2) C–C coupling occurs by direct attack of nucleophiles on the alkyl group rather than by transmetalation to Au followed by reductive elimination

3) the presence of fluoride ligands enhances the reactivity of alkylgold(III) intermediates towards cross-coupling.

The results communicated herein are fully consistent with these assertions. Gold(III)-mediated C(sp^3)–F reductive elimination clearly is less facile than, for example, gold(III)-mediated C(sp^3)–I reductive elimination, based both on the differing reactivity of F_2Au(Me)(IPr) and I_2Au(Me)(IPr) as well as the longer lifetimes of F_2Au(R)(IPr) intermediates relative to the corresponding I_2Au(R)(IPr) intermediates. The predominantly C_{alkyl}-centric nature of the LUMO in complexes like **10-F$^+$** provides an electronic basis for direct attack of nucleophiles onto C_{alkyl} rather than Au. Apparently one role of fluoride in such cross-coupling reactions, in addition to forming strong B–F or Si–F bonds, is to accentuate carbocation-like character by having a highly ionic interaction with Au^{III} relative to other, more covalent Au^{III}–X bonds (such as X = I). This discrepancy is evident both in the differing electronic structures of **10-F$^+$** and **10-I$^+$** as well as in their distinct reductive elimination reactivity patterns (Tables 1–4). We therefore suspect that Au^{III}–F bonds will continue to play an important role in Au(I)/Au(III) catalysis development, and attempts to incorporate C–F reductive elimination into such cycles are currently underway.

Acknowledgements

This work was supported by NIHGMS (RO1 GM073932). N.P.M. was supported by a NIH Kirchstein-NRSA postdoctoral fellowship. The UC Berkeley Molecular Graphics and Computational Facility is supported by the NSF (CHE-0840505). Prof. Robert Bergman provided helpful suggestions.

Notes and references

1 K. Müller, C. Faeh and F. Diederich, *Science*, 2007, **317**, 1881.
2 T. Furuya, A. S. Hamlet and T. Ritter, *Nature*, 2011, **473**, 470.
3 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.
4 Selected examples: (*a*) V. V. Grushin, *Acc. Chem. Res.*, 2010, **43**, 160; (*b*) N. D. Ball and M. S. Sanford, *J. Am. Chem. Soc.*, 2009, **131**, 3796; (*c*) T. Furuya, D. Benitez, E. Tkatchouk, A. Strom, P. Tang, W. A. Goddard III and T. Ritter, *J. Am. Chem. Soc.*, 2010, **132**, 3793; (*d*) D. A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. Garcia-Fortanet, T. Kinzel and S. L. Buchwald, *Science*, 2009, **325**, 1661.
5 Selected examples: (*a*) J. A. Akana, K. X. Bhattacharyya, P. Müller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2007, **129**, 7736; (*b*) M. H. Katcher and A. G. Doyle, *J. Am. Chem. Soc.*, 2010, **132**, 17402; (*c*) C. Hollingworth, A. Hazari, M. N. Hopkinson, M. Tredwell, E. Benedetto, M. Huiban, A. D. Gee, J. M. Brown and V. Gouverneur, *Angew. Chem., Int. Ed.*, 2011, **50**, 2613.
6 For example: (*a*) T. Furuya and T. Ritter, *Org. Lett.*, 2009, **11**, 2860; (*b*) K. L. Hull, W. Q. Anani and M. S. Sanford, *J. Am. Chem. Soc.*, 2006, **128**, 7134; (*c*) X. Wang, T.-S. Mei and J.-Q. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7520.
7 (*a*) S.-B. Zhao, J. J. Becker and M. R. Gagné, *Organometallics*, 2011, **30**, 3926; (*b*) A. W. Kaspi, I. Goldberg and A. Vigalok, *J. Am. Chem. Soc.*, 2010, **132**, 10626.
8 Selected examples: (*a*) C. M. Anderson, M. Crespo, G. Ferguson, A. J. Lough and R. J. Puddephatt, *Organometallics*, 1992, **11**, 1177; (*b*) R. P. Hughes, R. B. Laritchev, L. N. Zakharov and A. L. Rheingold, *Organometallics*, 2005, **24**, 4845.
9 (*a*) J. Choi, D. Y. Wang, S. Kundu, Y. Choliy, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *Science*, 2011, **332**, 1545. See also: (*b*) J. Terao, H. Todo, H. Watabe, A. Ikumi, Y. Shinohara and N. Kambe, *Pure Appl. Chem.*, 2008, **80**, 941 and references therein.
10 C(sp^3)–F reductive elimination can be hypothesized to occur for certain existing catalytic cycles. For example: T. Wu, G. Yin and G. Liu, *J. Am. Chem. Soc.*, 2009, **131**, 16354.
11 V. J. Scott, J. A. Labinger and J. E. Bercaw, *Organometallics*, 2010, **29**, 4090.
12 N. P. Mankad and F. D. Toste, *J. Am. Chem. Soc.*, 2010, **132**, 12859.
13 J. F. Hartwig, *Inorg. Chem.*, 2007, **46**, 1936.
14 E. Tkatchouk, N. P. Mankad, D. Benitez, W. A. Goddard, III and F. D. Toste, *J. Am. Chem. Soc.*, 2011, **133**, 14293.
15 C–C homocoupling rather than C–F coupling occurs when similar reactions are carried out with R_3PAuR' complexes: (*a*) A. S. K. Hashmi, T. D. Ramamurthi and F. Rominger, *J. Organomet. Chem.*, 2009, **694**, 592; (*b*) ref. 12.
16 A. A. Zuzek, S. C. Reynolds, D. S. Glueck, J. A. Golen and A. L. Rheingold, *Organometallics*, 2011, **30**, 1812.
17 D. S. Laitar, P. Müller, T. G. Gray and J. P. Sadighi, *Organometallics*, 2005, **24**, 4503.
18 A. Tamaki, S. A. Magennis and J. K. Kochi, *J. Am. Chem. Soc.*, 1974, **96**, 6140.
19 Selected examples of reductive elimination with large and negative $\Delta S^{\ddagger}$: (*a*) D. L. Packett and W. C. Trogler, *Inorg. Chem.*, 1988, **27**, 1768; (*b*) M. P. Brown, R. J. Puddephatt and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.*, 1974, 2457.
20 Recent reviews: (*a*) K. M. Engle, T.-S. Mei, X. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2011, **50**, 1478; (*b*) M. N. Hopkinson, A. D. Gee and V. Gouverneur, *Chem.–Eur. J.*, 2011, **17**, 8248.
21 (*a*) W. E. Brenzovich Jr., D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard III and F. D. Toste, *Angew. Chem., Int. Ed.*, 2010, **49**, 5519; (*b*) W. E. Brenzovich Jr., J.-F. Brazeau and F. D. Toste, *Org. Lett.*, 2010, **12**, 4728; (*c*) A. D. Melhado, W. E. Brenzovich Jr., A. D. Lackner and F. D. Toste, *J. Am. Chem. Soc.*, 2010, **132**, 8885.

