Facile Reductive Elimination from Homogeneous Gold(III) complexes

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Dec. 9th 2014

1 Basic reactivity of gold

2 C-C, C-X formation by reductive elimination

3 Summary and Outlook

Characteristics of gold

Au

$[Xe]4f^{14}5d^{10}6s^{1}$

The most prominent characteristics of the electronic structure of Au are the consequence of strong relativistic effects.

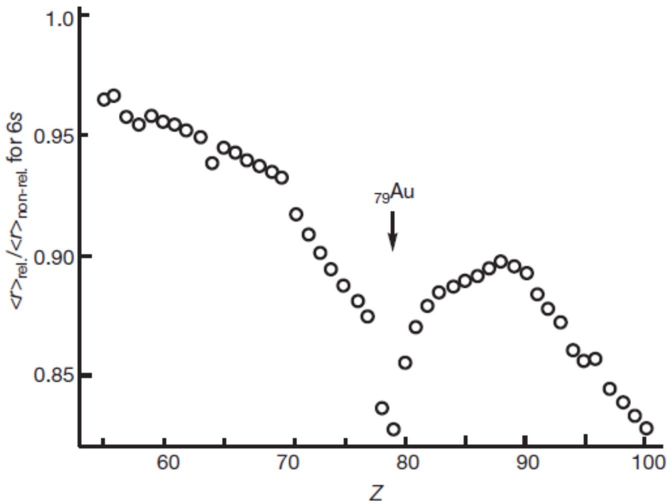
relativistic effects

$$m = m_0/\sqrt{[1-(v/c)^2]} \qquad \text{eq.(1)}$$

where *m* is the corrected mass, m_0 is non-relativistic (rest) mass, and *v* is velocity. The expression v/c can therefore be calculated as Z/137 (137 atomic units (a.u.) = c). For Au, v/c = 79/137.

- **m ↑, then Bohr radius ↓. That means the contraction of 6s and 6p orbital.**
- **electrons occupying the d and f orbitals are better shielded, therefore see a weaker nuclear attraction.**

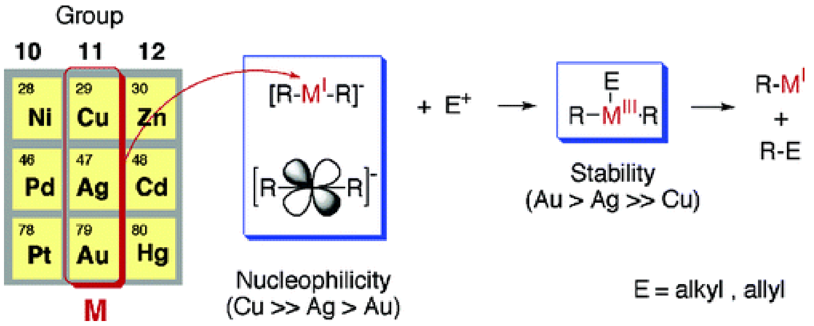
Gorin, D. J.; Toste, F. D. *Nature,* **2007**, 446, 395.

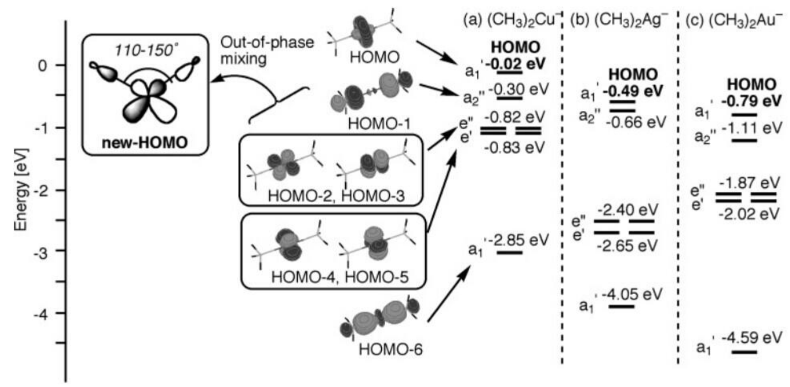


Box 1 Figure 1 | Calculated relativistic contraction of the 6s orbital. The relativistic and non-relativistic 6s orbital radii were determined computationally[100]. Notably, Pt, Au and Hg are markedly influenced. (Reprinted from ref. 4, with permission from the American Chemical Society.)

Oxidative additions and reductive eliminations reactivity

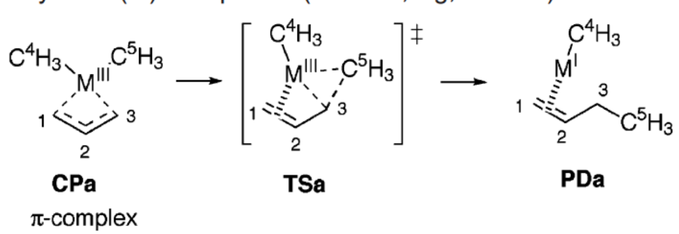
Slow oxidative additions





Slow reductive eliminations

Scheme 5. Chemical Models of Reductive Elimination of π-Allyl Dimethylmetal(III) Complexes (M = Cu, Ag, and Au)



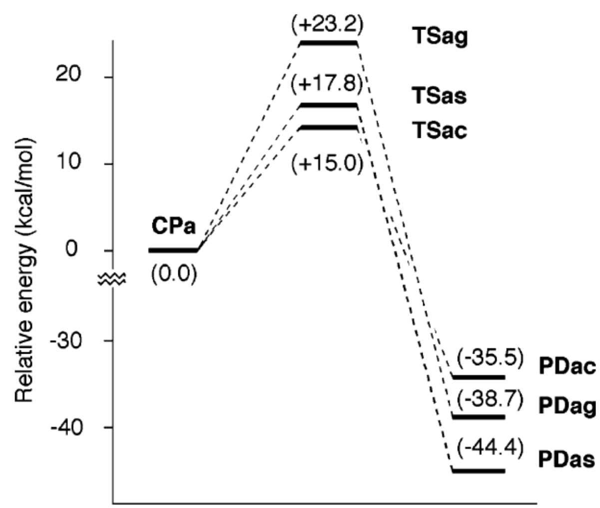
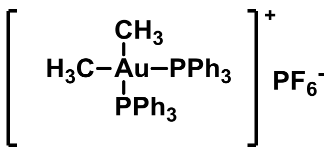


Figure 13. Potential energy profile of the reductive elimination of (CH_3)(allyl)M(III) (M = Cu, Ag, and Au) at the B3LYP/631SDD level.

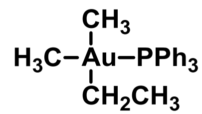
Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 1446.

Oxidative additions and reductive eliminations reactivity

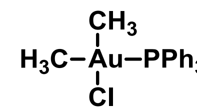
Thermodynamic alkylgold(III) stable coumpunds



stable at rt

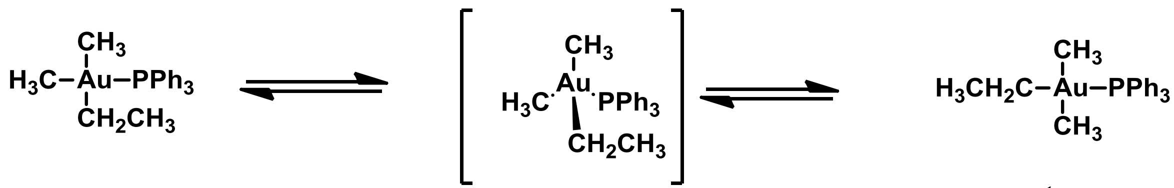


stable at rt



undergo alkyl-alkyl reductive elimination at 70 ^{o}C(k_{obs}= 10^{-5} – 10^{-3} s^{-1})

slow reductive elimination at 40 ^{o}C(k_{obs}= 10^{-7} s^{-1})



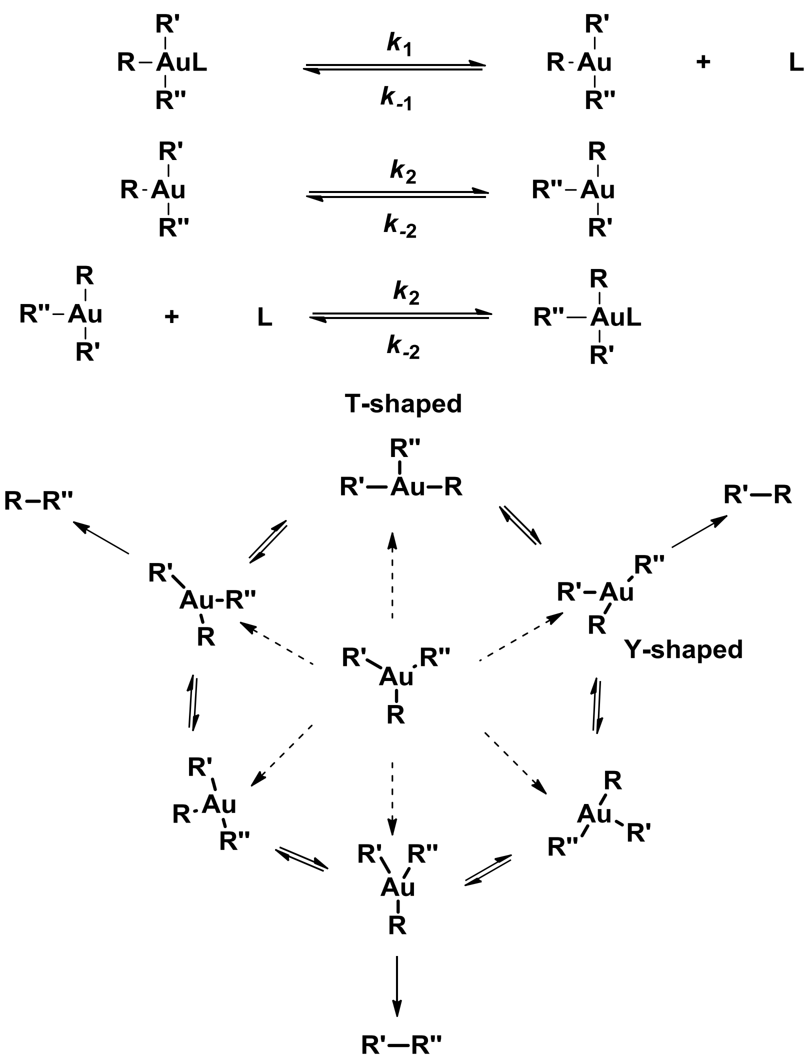
cis

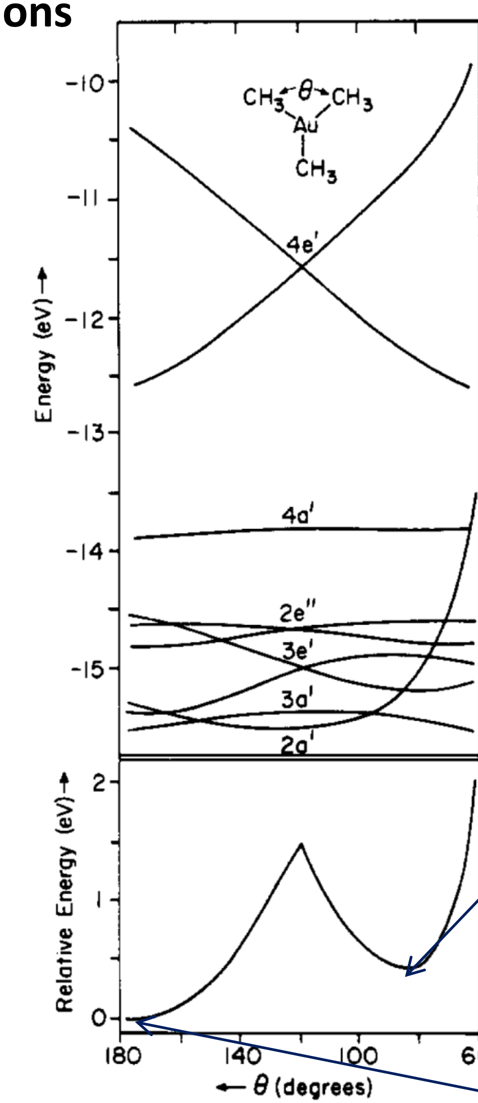
trans

Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140.
Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.
Komiya, S.; Kochi, J. K. *J. Am. Chem. Soc*. **1976**, *98*, 7599.
Kuch, P. L.; Tobias, R. S. *J. Organomet. Chem.* **1976**, *122*, 429.

Oxidative additions and reductive eliminations reactivity

Mechanism of isomerization and reductive eliminations





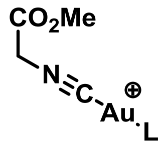
Y-shaped
Saddle point

T-shaped
energy minima

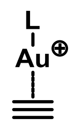
Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

Traditional manifolds of reactivity in gold catalysis

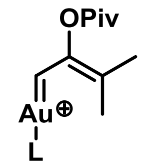
Au(I)



Lewis acid



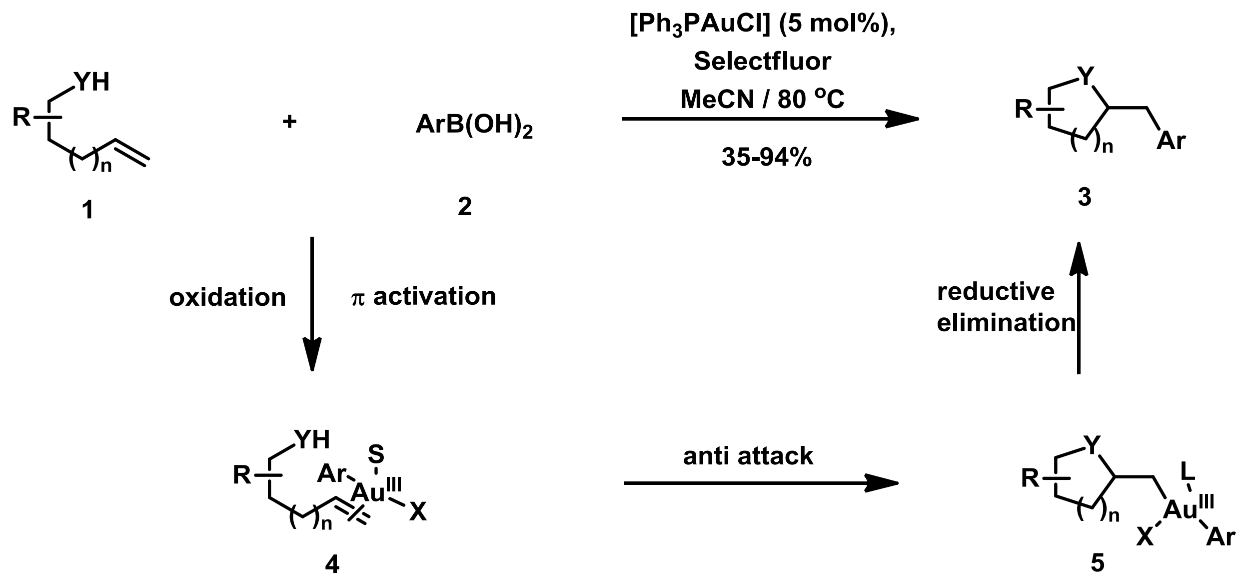
π-activation



carbeniod reactivity

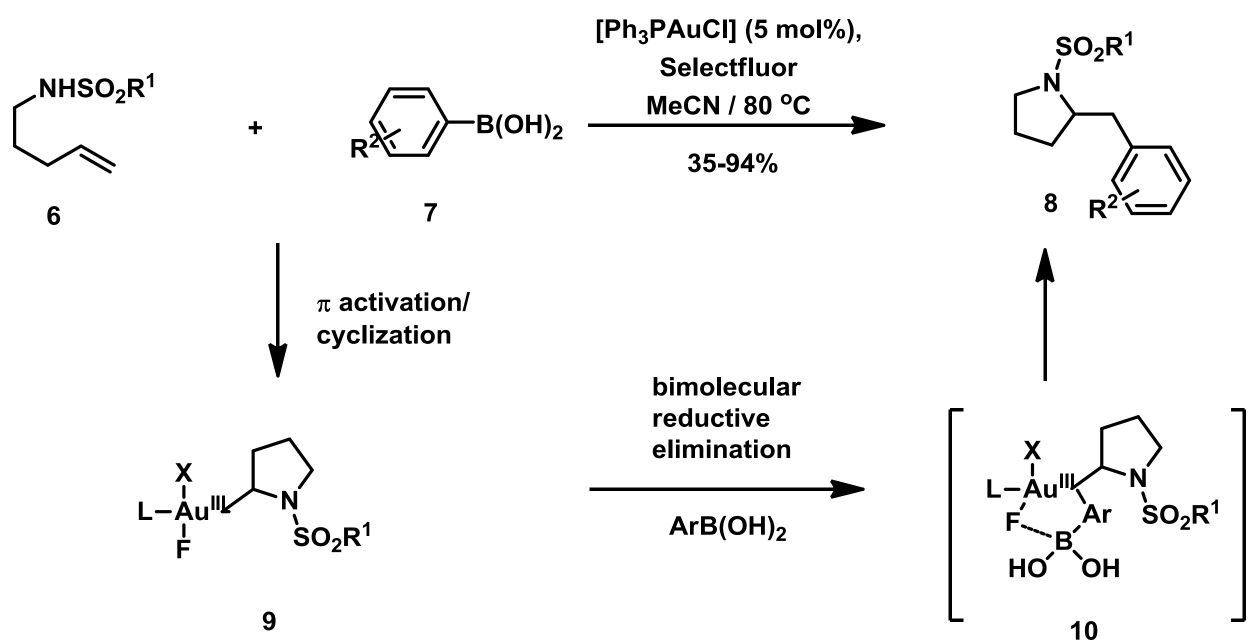
Levin, M. D.; Toste, F. D. *Angew. Chem., Int. Ed.* **2014**, *53*, 6211.

Au(III) with strong oxidant (F^+ or I^{3+})

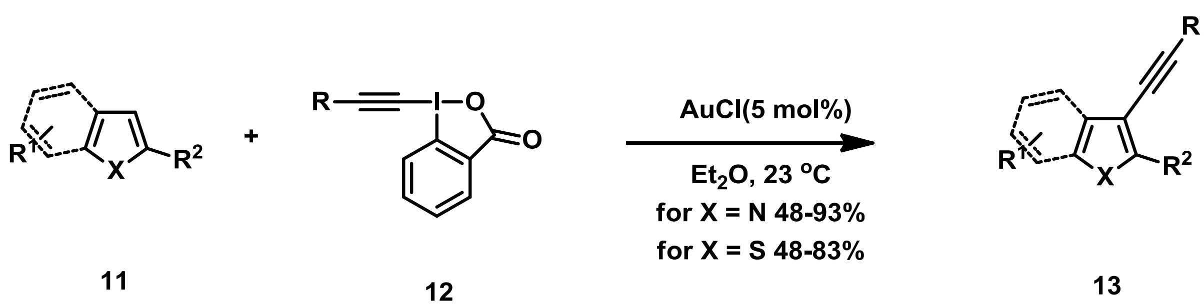


Zhang, G.; Cui, L.; Zhang, L. *J. Am. Chem. Soc.* **2010**,*132*, 1474.

Traditional manifolds of reactivity in gold catalysis



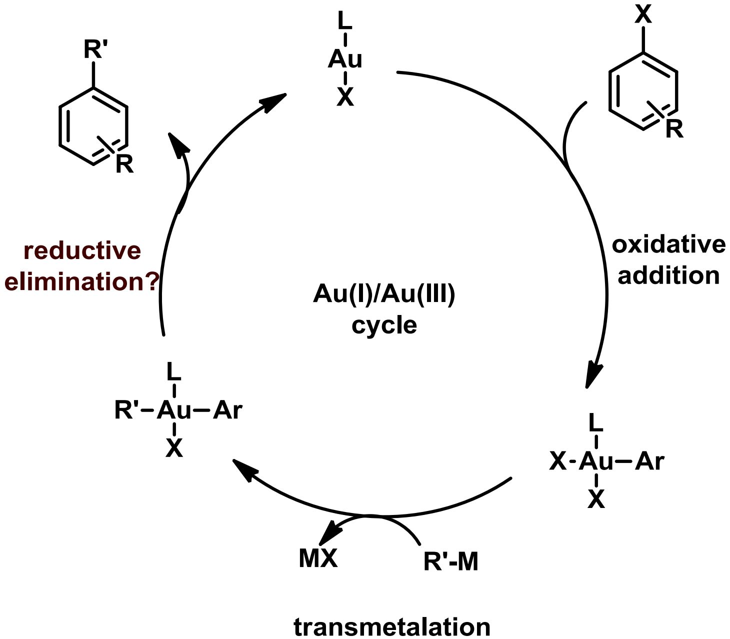
Toste, F. D. *Angew. Chem., Int. Ed.* **2010**, *49*, 5519.



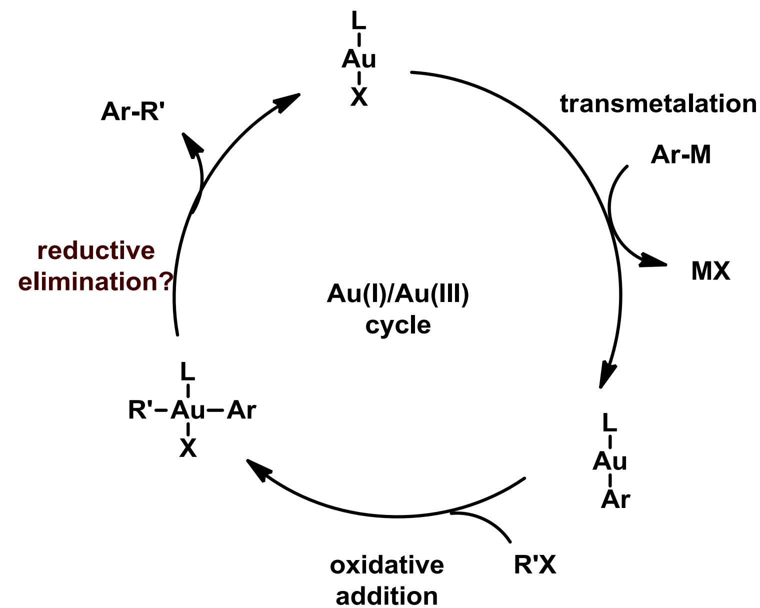
Brand, J. P.; Waser, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 9346.

Brand, J. P.; Waser, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 7304.

What ‘s the difficulty in Au(I)/Au(III) cycle?

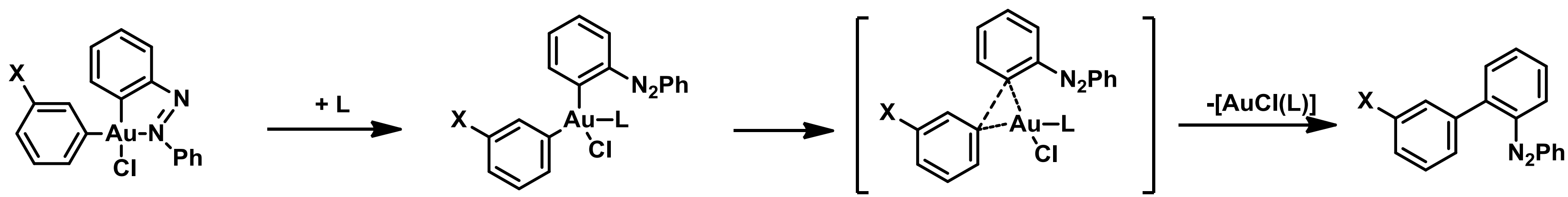


Vs



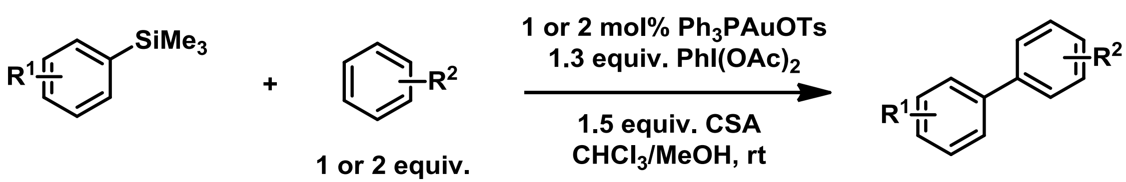
C(sp²)-C(sp²) facile reductive elimination

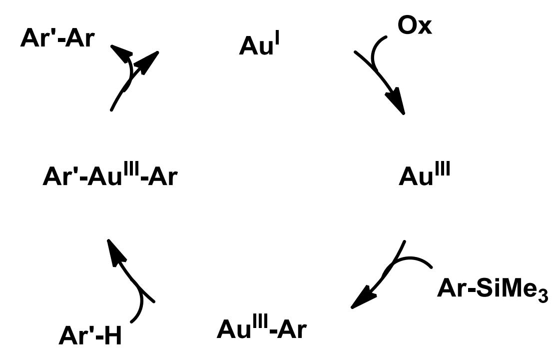
Room temperature



14 15 16 17

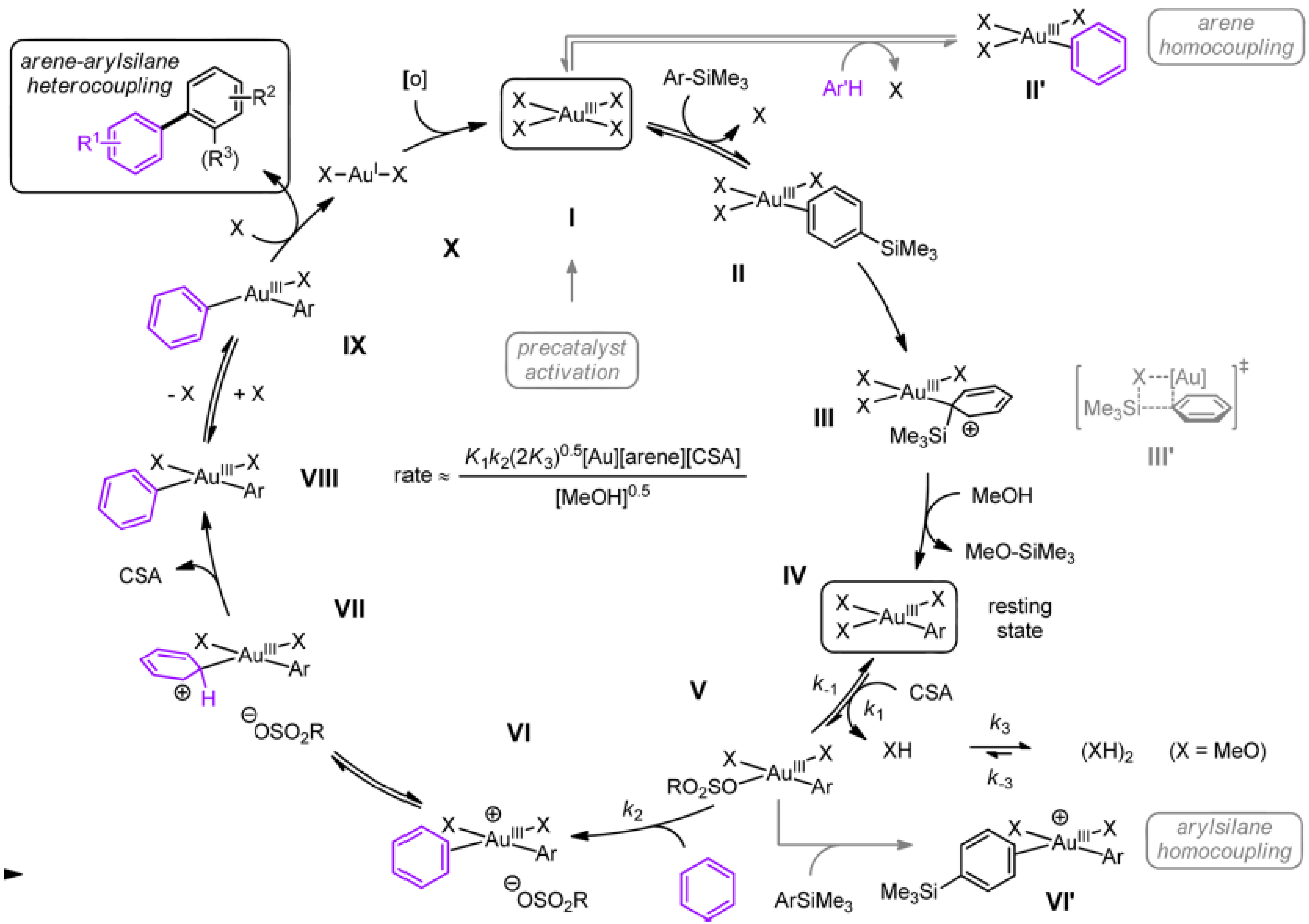
Vicente, J.; Bermudez, M. D.; Escribano, J. *Organometallics* **1991,** *10*, 3380.



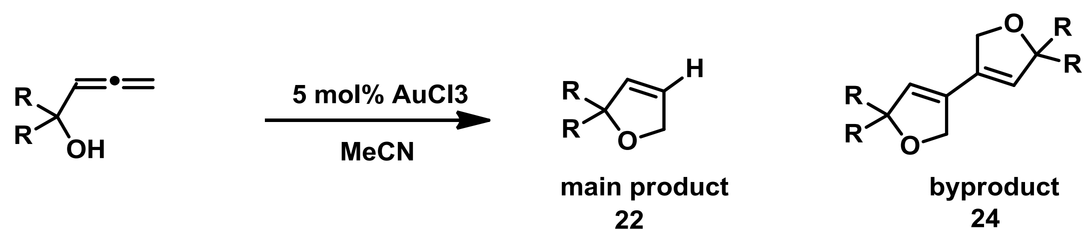


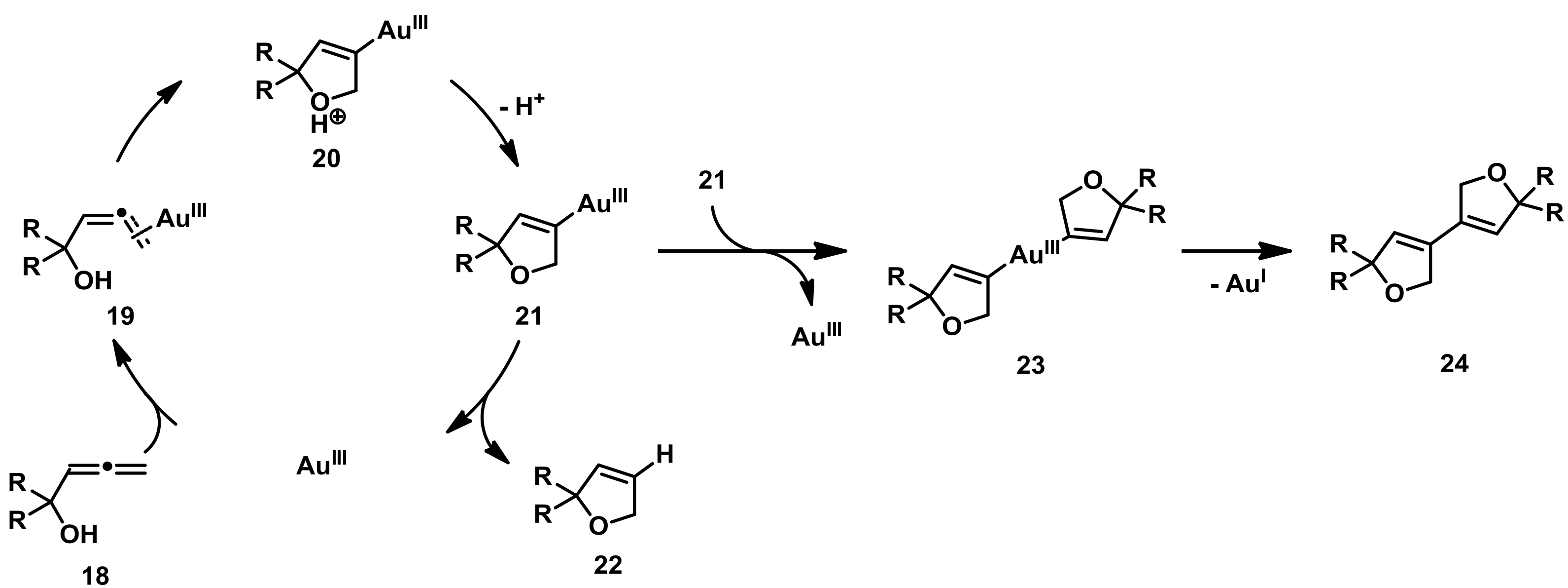
Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Science* **2012**, *337*, 1644. Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *J. Am. Chem. Soc.* **2014**, *136*, 254.

C(sp²)-C(sp²) facile reductive elimination



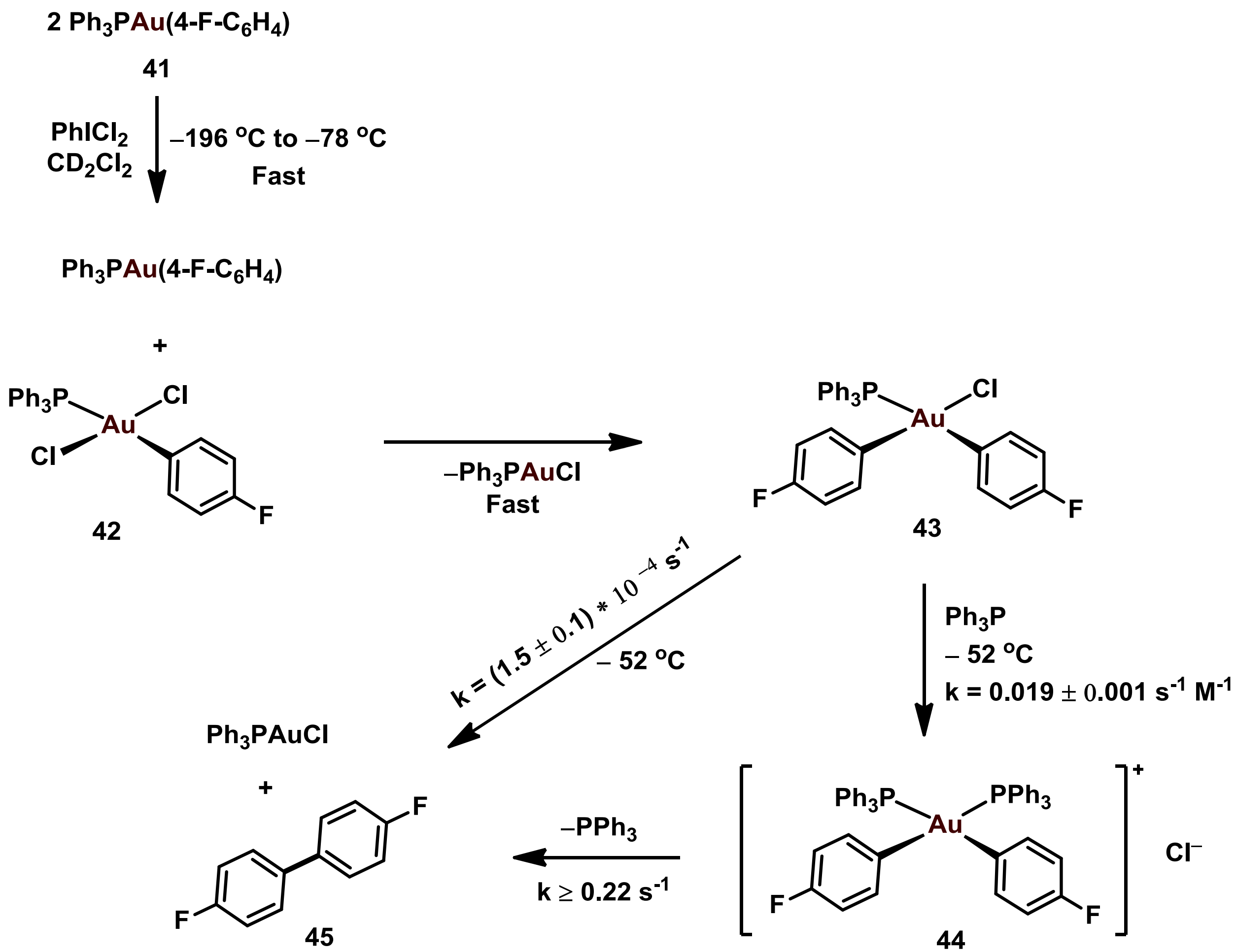
C(sp²)-C(sp²) facile reductive elimination





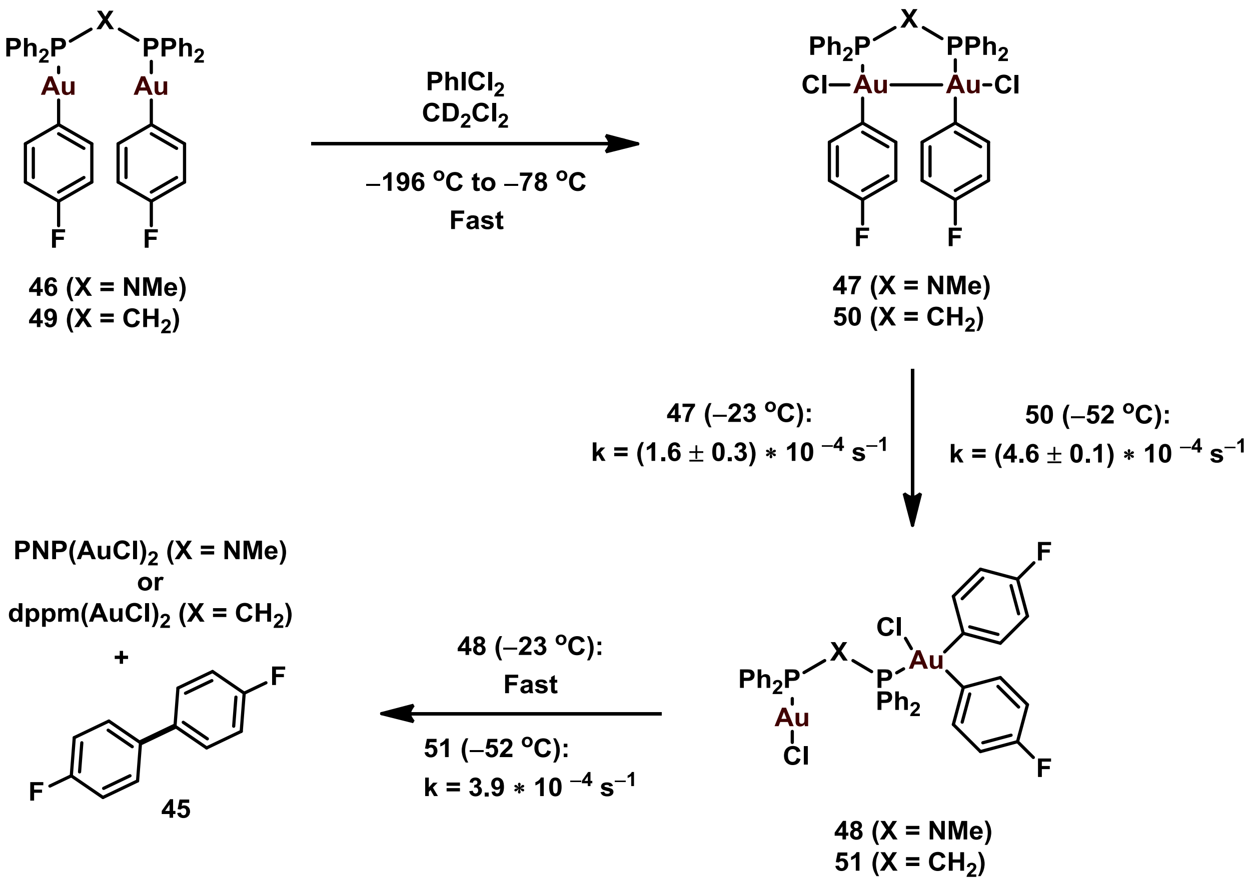
Hashmi, A. S. K.; Blanco, M. C.; Fischer, D.; Bats, J. W. *Eur. J. Org. Chem*. **2006**, 1387.

C(sp²)-C(sp²) facile reductive elimination



Wolf, W. J.; Winston, M. S.; Toste, F. D. *Nat. Chem.* **2014**, *6*, 159.

C(sp²)-C(sp²) facile reductive elimination

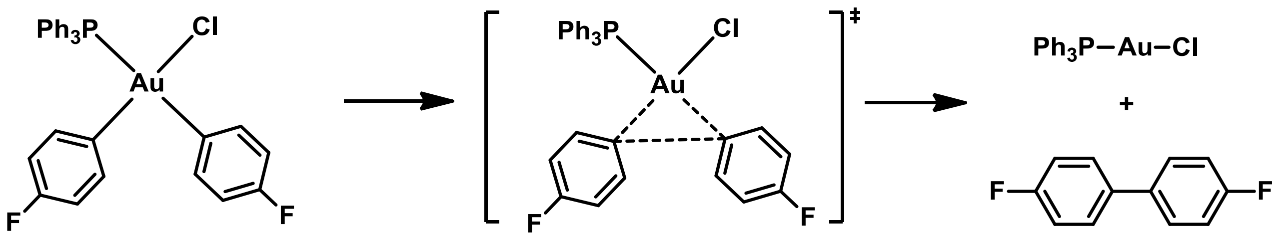


Wolf, W. J.; Winston, M. S.; Toste, F. D. *Nat. Chem.* **2014**, *6*, 159.

C(sp^2)-C(sp^2) facile reductive elimination

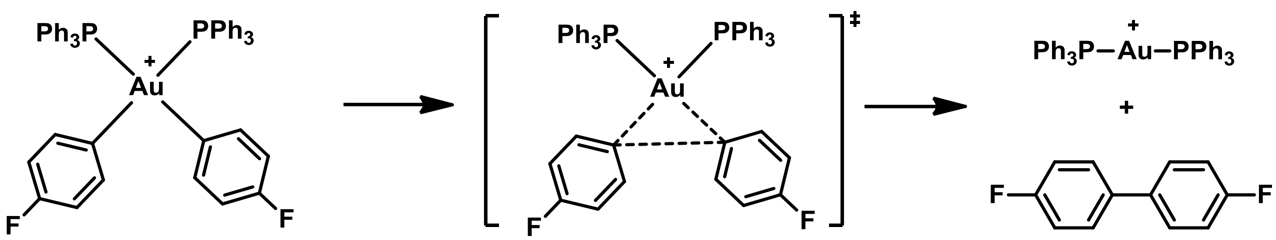
To understand such fast reductive elimination

calculation results



$\Delta H^{\neq}$ = 17.1 kcal mol^{-1}

ΔH = -49.8 kcal mol^{-1}

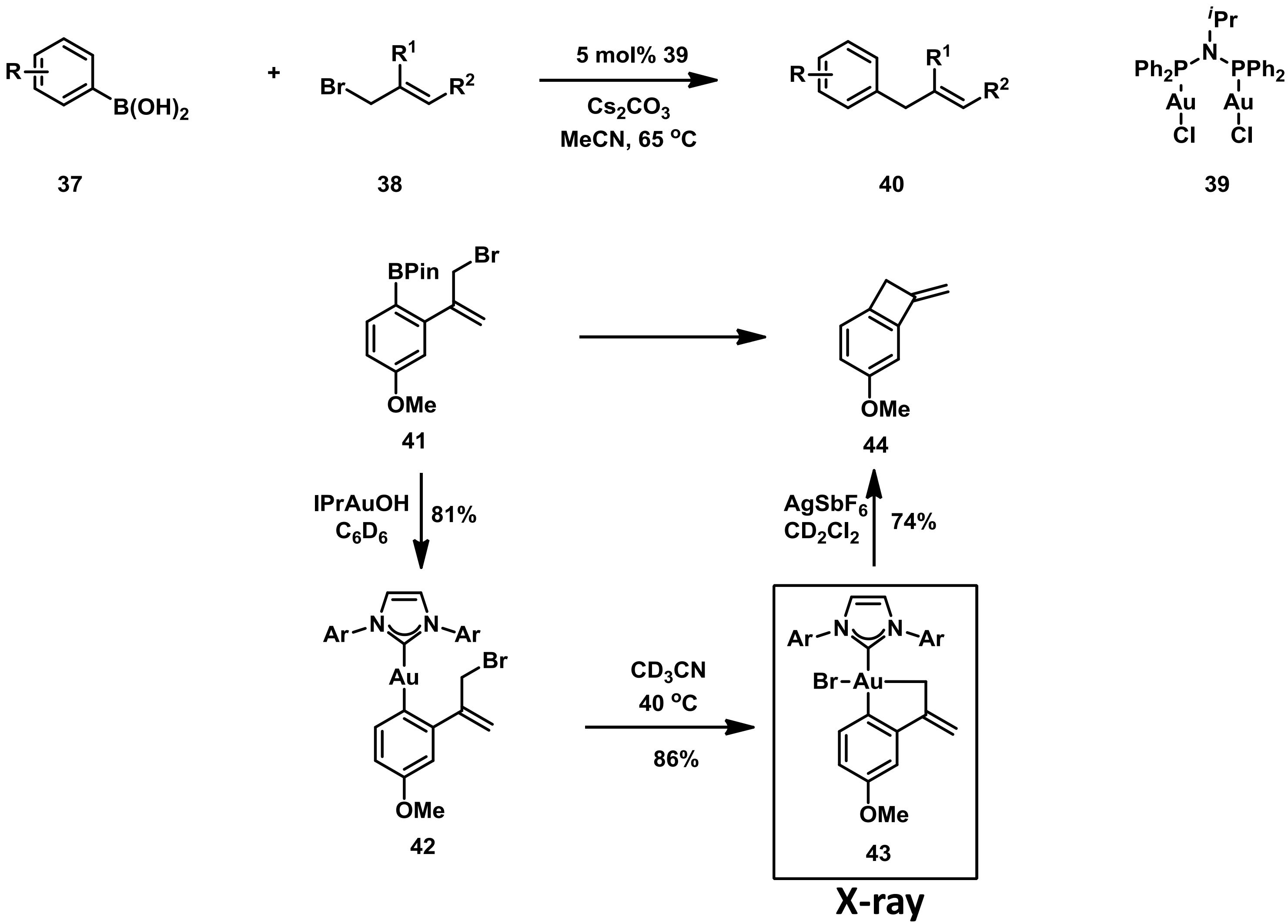


$\Delta H^{\neq}$ = 11.1 kcal mol^{-1}

ΔH = close to -49.8 kcal mol^{-1}

Nijamudheen, A.; Karmakar, S.; Datta, A. *Chem. Eur. J.* **2014**, *20*, 14650.

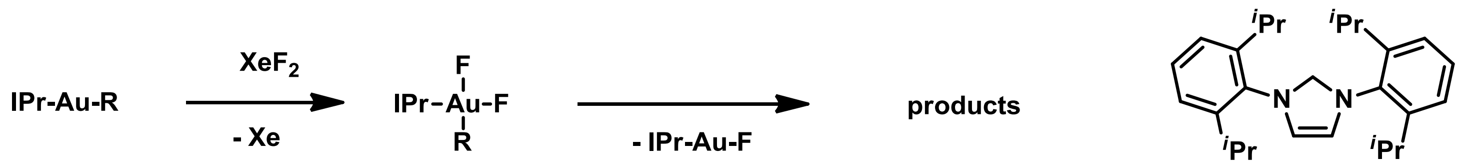
C(sp²)- C(sp³) facile reductive elimination



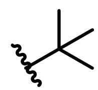
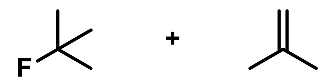
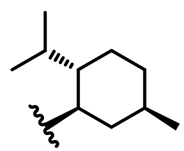
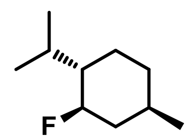
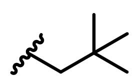
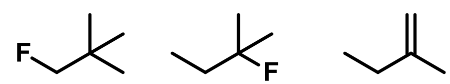
Levin, M. D.; Toste, F. D *Angew. Chem., Int. Ed.* **2014**, *53*, 6211

C(sp^3)-F facile reductive elimination

C(sp^3)-F reductive elimination

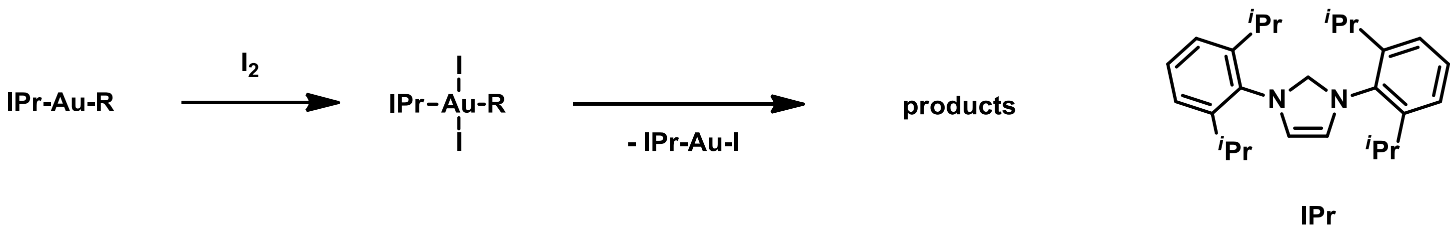


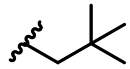
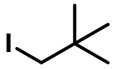
25 26 IPr

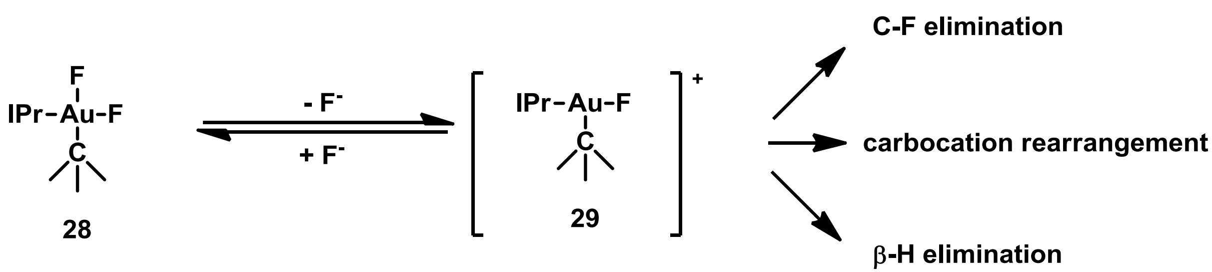
entry	R	product mixture
1	CH_3	None
2		 17% + 66%
3		 95%
4		 12% 63% 16%

Mankad, N. P.; Toste, F. D. *Chem. Sci*. **2012**, *3*, 72

C(sp^3)-F facile reductive elimination



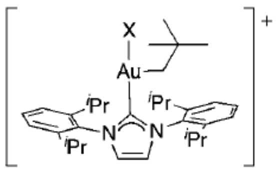
entry	R	product mixture
1	CH_3	I—CH_3 quant.
2		 I 84%



Mankad, N. P.; Toste, F. D. *Chem. Sci*. **2012**, *3*, 72

C(sp³)-F facile reductive elimination

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



X	q(Au)[b]	q(X)[b]	$q(CH_2)$[b]	$\Delta q(Au\text{–}CH_2)$[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.

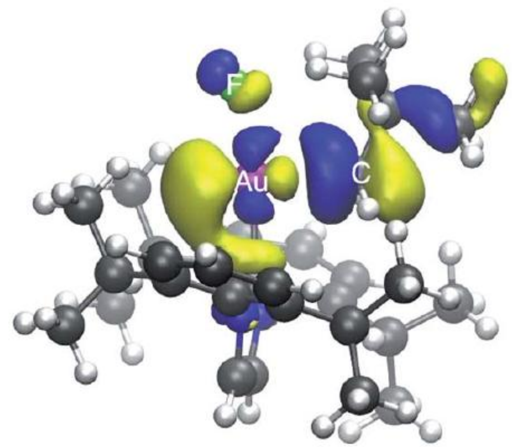
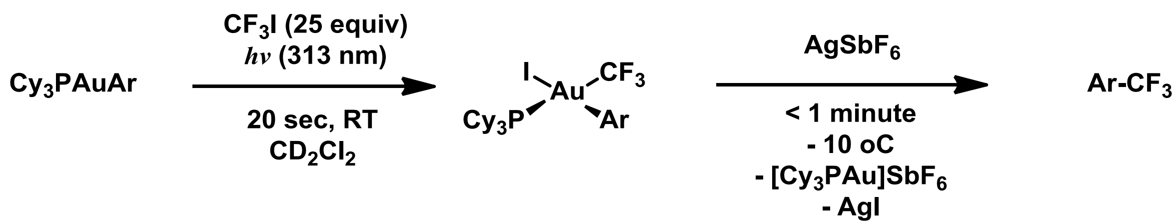


Fig. 3 Calculated LUMO (BPV86/LANL2DZ/6-311G++**, implicit CH_2Cl_2 solvation, 0.04 isocontour) of $[(IPr)Au(CH_2tBu)(F)]^+$ (**10-F⁺**).

- The predominantly C_{alkyl}-centric nature of the LUMO in complexes in this complex 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 is to accentuate carbocation-like character by having a highly ionic interaction with Au^{III} relative to other.

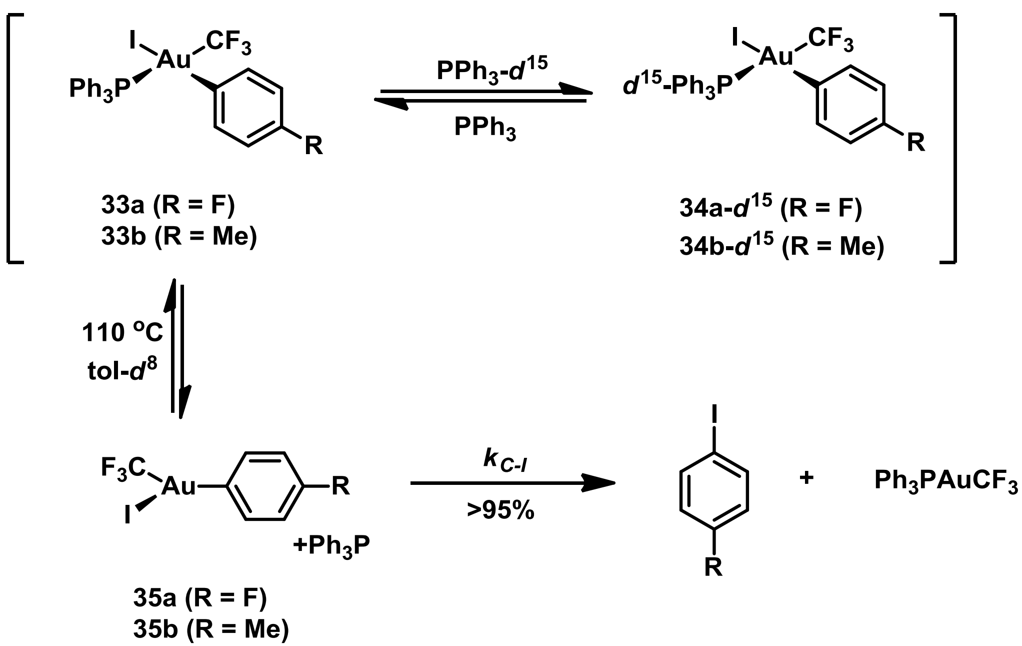
Mankad, N. P.; Toste, F. D. *Chem. Sci*. **2012**, *3*, 72

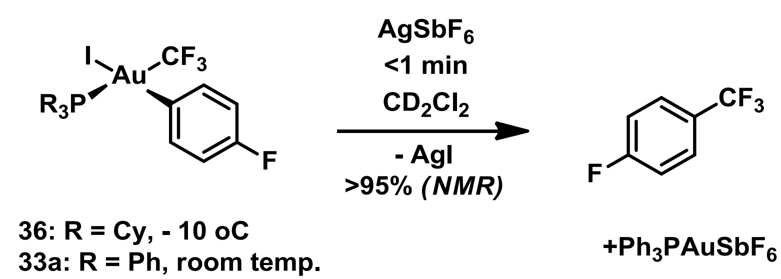
C(sp^2)-CF_3 facile reductive elimination



30 31 32

Reductive Elimination from Au(III) Complexes





Winston, M. S.; Wolf, W. J.; Toste, F. D . *J. Am. Chem. Soc.* **2014**, *136*, 7777.

Summary and Outlook

Summary

Exceptionally fast reductive elimination can be achieved from a gold(III) intermediate even at low temperature.

Outlook

1. According to the facile reductive elimination , catalysis may be achieved at temperatures low enough to avoid unwanted side reactions between oxidant and substrate.
2. According to the facile reductive elimination under low temperature, some unique reaction maybe be accomplished.

謝 謝！