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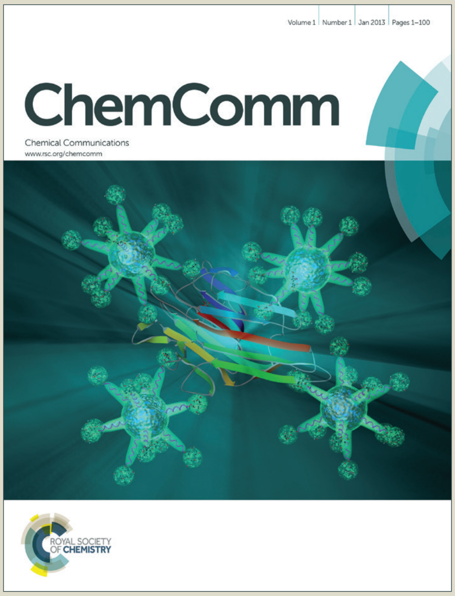

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Highly efficient regioselective hydrosilylation of allenes using a [(3IP)Pd(allyl)]OTf catalyst; first example of allene hydrosilylation with phenyl- and diphenylsilane

Hosein Tafazolian[a] and Joseph A. R. Schmidt[a*]

A [(3IP)Pd(allyl)]OTf complex was shown to function efficiently and regioselectively in allene hydrosilylation with phenyl- and diphenylsilane. The catalyst also proved to be highly active for allene hydrosilylation employing a wide range of silanes, each of which produced a single regioisomer.

The catalytic hydrosilylation of C-C unsaturated bonds has garnered great interest in recent years since the resulting products can be further utilized in a wide variety of subsequent reactions.[1] For example, allyl and vinylsilanes are indispensable organosilicon reagents due to their direct transformation into vinyl and allylalcohols and use as coupling partners in Hiyama and Sakurai reactions.[2] Catalytic hydrosilylation is one of the most economic routes to organosilicon compounds, especially when compared to traditional synthetic methods requiring stoichiometric amounts of organometallic chemicals and other reagents.[3] Although four decades of hydrosilylation studies with various catalysts have provided remarkable knowledge on Si-H bond addition to unsaturated C-C frameworks, research on the mechanism of this catalytic addition remains an area of active study.[1, 4] A recent DFT investigation has helped to confirm the mechanism of allene hydrosilylation catalyzed by NHC-supported Ni(0) and Pd(0), a hydrosilylation system displaying intriguing regiochemical outcomes.[4i] With a focus on expanding the substrate scope in the past few years, the catalytic hydrosilylation of conjugated 1,3-dienes has proven to be both interesting and challenging because of the regioselectivity issues that arise for unsymmetrical substrates,[5] ultimately leading to the formation of various allyl- and vinylsilane isomers. Although catalytic hydrosilylation of 1,3-dienes has been well studied,[5a, 5c] few examples of catalytic allene hydrosilylation have been reported, limited to only a very small set of substrates.[5e, 6]

An elegant recent example of allene hydrosilylation was reported by Montgomery et al. in which N-heterocyclic carbene complexes of Ni and Pd were shown to catalyze the hydrosilylation of allenes with a limited number of silanes to produce a variety of vinyl- and allylsilanes.[5e] In addition to the characterization of several new silane products, this previous work clearly demonstrated the effect of ligand steric bulk on the observed hydrosilylation regioselectivity with allyl- or vinylsilane products dictated by a combination of NHC steric bulk and metal center used. The vinylsilanes formed in this process were subsequently utilized as coupling reagents in Hiyama reactions with iodoarenes leading to the successful development of a one-pot Pd catalyzed regioselective hydrosilylation/cross coupling method.[2a] Also, as noted above, this allene hydrosilylation was recently investigated by DFT,[4i] further supporting the proposed mechanism operable in these reactions.

Over the past decade, our research group has isolated a variety of cationic allylpalladium complexes supported by 3-iminophosphine ligands, each of which has been fully characterized with many studied by X-ray crystallography.[7] The 3-iminophosphine (3IP) ligands supporting these catalysts are made using a versatile synthetic method, starting from known α,β-unsaturated chloroaldehydes. Treatment with a primary amine forms the chloroimine through a Schiff base condensation, while an anionic phosphide is used to directly displace the chloride producing the final 3-iminophosphine.[8] The resulting 3IP is stable to slightly acidic and basic conditions and can be kept on the benchtop for several days before undergoing slow oxidation of the phosphine. Palladium complexes of these 3IP ligands have shown excellent catalytic utility for reactions such as aryl amination and the intermolecular hydroamination of terminal alkynes, conjugated dienes, and a wide range of mono- and disubstituted allenes.[9]

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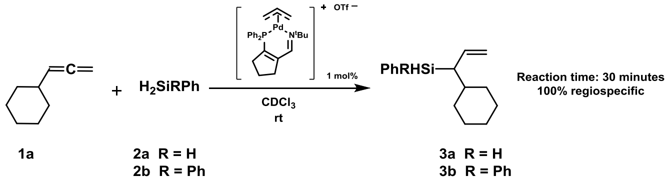
† Electronic supplementary information is available containing experimental details and spectroscopic data.

In our ongoing efforts to expand the range of their reactivity, we recently discovered that our (3-iminophosphine)palladium complexes function as active catalysts for the hydrosilylation of allenes with phenyl- and diphenylsilane. An especially notable feature of this system is the formation of new vinyl- and allylsilanes under very mild conditions with complete regioselectivity and high catalytic activity. In contrast to the work reported by Montgomery,[5e] the observed regioselectivity with (3IP)palladium complexes is dictated entirely by the nature of the silane used. Interestingly, in testing a wide range of silanes, in any case where catalytic activity was observed, only one regioisomer was detected spectroscopically and each was readily isolated. Thus, we report herein the highly efficient regioselective hydrosilylation of allenes with a wide variety of silanes, including phenyl- and diphenylsilane, employing [(3IP)Pd(allyl)]OTf precatalyst.

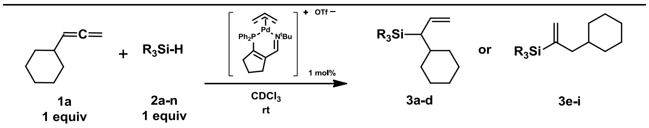
All the reactions described in this report were performed in NMR tubes prepared in a nitrogen-filled glovebox and in each case, the reaction was monitored spectroscopically until apparent completion was achieved by ^{1}H NMR. Subsequently, all products were then isolated by passage through a plug of silica to remove the catalyst and further characterized. Initial experiments showed that the reactions of cyclohexylallene with phenyl- and diphenylsilane were each complete in less than 30 minutes, yielding the allylsilane regioisomer as the only observed product of each reaction (Scheme 1). In an effort to more distinctly compare the reactivity of these two hydrosilanes, these reactions were repeated with a lower catalyst loading (0.2 mol%) and the percent conversion was determined after 1 hour by ^{1}H NMR spectroscopy. The results revealed a fairly reduced reaction rate for diphenylsilane (14.5% conversion) compared to phenylsilane (38.2% conversion). Furthermore, no hydrosilylation product was observed with triphenylsilane, even with higher catalyst loading. Thus, the results for hydrosilylation using Ph_xSiH_y appear to be directly correlated to silane steric bulk.

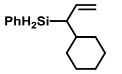
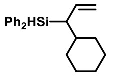
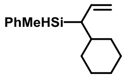
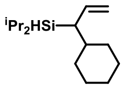
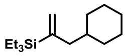
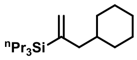
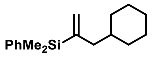
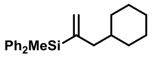
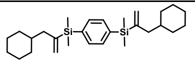


Scheme 1. Catalytic hydrosilylation of cyclohexylallene to form new allylsilanes.

Given the catalytic competence of these (3IP)palladium complexes, we screened a wide range of silanes for the hydrosilylation of cyclohexylallene (Table 1). Interestingly, in each case, ^{1}H NMR spectroscopy indicated that only one regioisomer was formed. Since the only variable in this reaction is the silane, the regioselectivity of each product seemed to be directly correlated to the steric bulk of the silane. Silanes **2a-d**, all of which are primary or secondary silanes, produced only the allylsilane product. In contrast, the vinylsilane product was formed for each of the tertiary silanes **2e-i**. The trend in reaction completion times involved a combination of weaker bond strength (with phenyl groups activating the Si-H bond) and reduced steric bulk each giving rise to faster reactions.

Table 1. Catalytic hydrosilylation of cyclohexylallene.[a]



Entry	Silane	Product	time (h)[b]	Isolated yield (%)
1	$PhSiH_3$ (2a)	 (3a)	0.5	92
2	Ph_2SiH_2 (2b)	 (3b)	0.5	87
3	$PhMeSiH_2$ (2c)	 (3c)	1	82
4	$^iPr_2SiH_2$ (2d)	 (3d)	4	75
5	Et_3SiH (2e)	 (3e)	8	82
6	$^nPr_3SiH$ (2f)	 (3f)	12	79
7	$PhMe_2SiH$ (2g)	 (3g)	0.5	91
8	Ph_2MeSiH (2h)	 (3h)	4	94
9	1,4-$(Me_2SiH)_2C_6H_4$[c] (2i)	 (3i)	1	89
10	Ph_3SiH (2j)	NR	-	-
11	$^iPr_3SiH$ (2k)	NR	-	-
12	$^tBuMe_2SiH$ (2l)	NR	-	-
13	$(EtO)_3SiH$ (2m)	NR	-	-
14	Cl_3SiH (2n)	NR	-	-

[a] Catalytic procedure: Reactions were carried out at ambient temperature in NMR tubes prepared in a glovebox using $CDCl_3$ (800 µl), catalyst (0.005 mmol), hydrosilane (0.5 mmol), and cyclohexylallene (0.5 mmol); [b] Reaction completion was monitored and recorded by ^{1}H NMR spectroscopy; [c] 2 equiv of cyclohexylallene were used, due to the presence of two Si-H sites.

In the reactions of the sterically unhindered silanes **2a-d** with cyclohexylallene, allylsilanes bearing the silane on the more substituted carbon were formed rapidly, while the more sterically bulky silanes **2e-i** generally reacted slower and gave only the vinylsilane products where the silyl group was added to the less substituted allene carbon atom.

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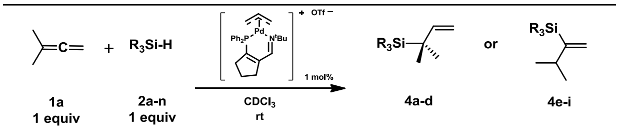
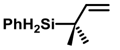
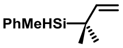
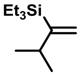
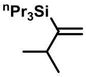
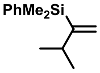
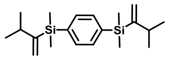
Table 2. Catalytic hydrosilylation of dimethylallene.[a]



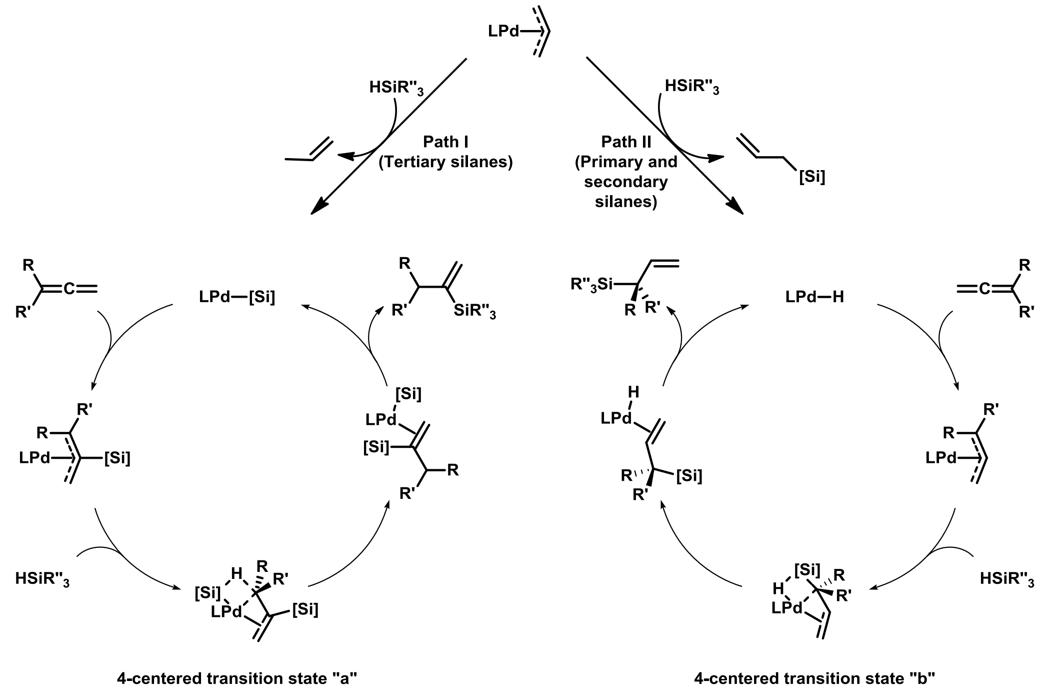
Entry	Silane	Product	time (h)[b]	Isolated yield (%)
15	$PhSiH_3$ (2a)	 (4a)	1.5	87
16	Ph_2SiH_2 (2b)	 (4b)	2	98
17	$PhMeSiH_2$ (2c)	 (4c)	14	75
18	$^iPr_2SiH_2$ (2d)	 (4d)	10	79
19	Et_3SiH (2e)	 (4e)	12	86
20	$^nPr_3SiH$ (2f)	 (4f)	24	76
21	$PhMe_2SiH$ (2g)	 (4g)	10	85
22	Ph_2MeSiH (2h)	NR	-	
23	1,4-$(Me_2SiH)_2C_6H_4$[c] (2i)	 (4i)	2	94
24	Ph_3SiH (2j)	NR	-	
25	$^iPr_3SiH$ (2k)	NR	-	
26	$^tBuMe_2SiH$ (2l)	NR	-	
27	$(EtO)_3SiH$ (2m)	NR	-	
28	Cl_3SiH (2n)	NR	-	

[a] Catalytic procedure: Reactions were carried out at ambient temperature in NMR tubes prepared in a glovebox using $CDCl_3$ (800 µl), catalyst (0.005 mmol), hydrosilane (0.5 mmol), and dimethylallene (0.5 mmol); [b] Reaction completion was monitored and recorded by ^1H NMR spectroscopy; [c] 2 equiv of dimethylallene were used, due to the presence of two Si-H sites.

In a second set of catalytic tests, dimethylallene was treated with silanes **2a-n** in order to compare the regioselectivity obtained when using a disubstituted allene (Table 2). We were somewhat surprised to find that the same regioselectivity occurs with both allenes. We expected that the additional substituent on dimethylallene would affect the regioselectivity, at least in the allylsilane cases (**4a-d**), possibly causing a change to the vinylsilane product or a mixture of regioisomeric products. It was fascinating that no change in final product regioselectivity was observed and Si-H addition occurred identically to that seen for the monosubstituted allene (cyclohexylallene). Seemingly, the only effect of two groups on the terminal carbon of the allene was to slow down the reaction, results in longer times to reach completion.This contrasts distinctly with Montgomery's work, who observed that when a disubstituted allene was utilized, an allylsilane was preferentially formed in which the silyl group added to the CH_2 allene terminus giving a regioisomer that was never observed in our work.[5e]

As proposed by Chalk and Harrod, the mechanism for the hydrosilylation of C=C bonds is assumed to be very similar to that for the hydrogenation of alkenes, in which activation of olefin by coordination of C=C to the metal center and cleavage of Si-H (instead of H-H) are necessities.[10] When these two conditions are fulfilled, the insertion of C=C into the M-H or M-Si bonds will occur, known as hydrometalation and silylmetalation, respectively.[11] Silylmetalation rates were studied in detail by Brookhart, who concluded that the insertion of C=C into Pd-Si bonds is very likely to be the rate determining step in the hydrosilylation of alkenes.[4f] Whether insertion of C=C proceeds via hydro- or silylmetalation, the catalytic intermediate subsequently undergoes sigma bond metathesis to form the product. Mechanistic preference for silylmetalation versus hydrometalation not only affects the rate of the catalysis, but can also influence the product regioselectivity, as observed in Montgomery's allene hydrosilylation,[5e] which was later supported by theoretical calculations.[4i]

Based on the regioselectivity observed in our catalytic reactions, we propose two complementary mechanistic pathways for this process dictated by the sterics of the silane used (Scheme 2). Pathway **I** is favored by the trisubstituted silanes, while less bulky mono- and disubstituted silanes prefer pathway **II**. In both cases, catalyst activation is achieved via σ-bond metathesis to form the active Pd-H or Pd-[Si] catalyst, since oxidative addition of hydrosilane to Pd(II) with formation of Pd(IV) is unfavorable. Next, insertion of the allene takes place into either the Pd-Si or Pd-H bond (depending on the pathway) to give the corresponding palladium(allyl) complex. Reaction with the substrate silane proceeds through a four-centered transition state with silane steric bulk playing a key role in the regiochemistry that is set during this step. Transition state **a** yields the vinylsilane and places Pd-Si back into the catalytic cycle, while transition state **b** leads to the allylsilane product with return of the active Pd-H catalyst into the cycle. Based on the observed regioselectivity and reaction completion times (Tables 1 and 2), we conclude that regioselectivity (pathway **I** or **II**) is dependent on the sterics of the silane whereas reaction completion time relies on both the steric bulk and bond strength of the silane. As further support for the proposed mechanism, we undertook a double-labelled crossover experiment in which Ph_2SiD_2 and $^iPr_2SiH_2$ (0.5 equiv. each) were used in the catalytic hydrosilylation of cyclohexylallene.[12] This reaction reached completion after four hours and ^1H and ^2H NMR spectroscopy revealed the production of a 1:1:1:1 mixture of $Ph_2SiDCH(Cy)CH{=}CH_2$, $Ph_2SiDCH(Cy)CD{=}CH_2$, $^iPr_2SiHCH(Cy)CH{=}CH_2$, and $^iPr_2SiHCH(Cy)CD{=}CH_2$. Thus, statistical H/D scrambling into the vinylic position was observed, while there were undetectable levels of Si-H/Si-D scrambling. These crossover results are consistent with the proposed sigma-bond metathesis mechanism, while they similarly discount the possibility of silane oxidative addition to Pd(0) intermediates.



Scheme 2. Proposed catalytic cycles for hydrosilylation of allenes by [(3IP)Pd(allyl)]OTf precatalyst (L = 3-iminophosphine; R''

In conclusion, we successfully achieved catalytic hydrosilylation of cyclohexyl- and dimethylallene with various hydrosilanes using a [(3IP)Pd(allyl)]OTf precatalyst with high efficiency (1 mol% catalyst loading) at ambient temperature. The catalyst showed excellent reactivity for the hydrosilylation of allenes with phenyl- and diphenylsilanes, the first regioselective examples using these silanes. Overall, these catalytic experiments led to the formation of many new silicon-containing molecules in moderate to high isolated yields. We were also able to understand the effect of silane substituents on the reactivity and regioselectivity. The catalytic reactions were regiospecific in every case, as tested by the usage of a mono- and a disubstituted allene. The new products can serve as potential substrates for further coupling reactions or could be used in one pot reactions directly, since only a single isomer is formed in every case.

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References

1. B. Marciniec, *Coord. Chem. Rev.*, 2005, **249**, 2374-2390.
2. a) Z. D. Miller and J. Montgomery, *Org. Lett.*, 2014, **16**, 5486-5489; b) G. R. Jones and Y. Landais, *Tetrahedron*, 1996, **52**, 7599-7662; c) Y. Hatanaka and T. Hiyama, *J. Org. Chem.*, 1988, **53**, 918-920; d) A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, 1976, 1295-1298.
3. a) S. Hayashi, K. Hirano, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2007, **129**, 12650–12651; b) M. A. Kacprzynski, T. L. May, S. A. Kazane and A. H. Hoveyda, *Angew. Chem., Int. Ed.*, 2007, **46**, 4554-4558; c) R. Moser, T. Nishikata and B. H. Lipshutz, *Org. Lett.*, 2010, **12**, 28-31; d) S. Nii, J. Terao and N. Kambe, *Tetrahedron Lett.*, 2004, **45**, 1699-1702; e) J. Terao, H. Watabe, H. Watanabe and N. Kambe, *Adv. Synth. Catal.*, 2004, **346**, 1674-1678; f) D. J. Vyas and M. Oestreich, *Angew. Chem., Int. Ed.*, 2010, **49**, 8513-8515.
4. a) T. Hayashi, S. Hirate, K. Kitayama, H. Tsuji, A. Torii and Y. Uozumi, *J. Org. Chem.*, 2001, **66**, 1441-1449; b) M. D. Greenhalgh, D. J. Frank and S. P. Thomas, *Adv. Synth. Catal.*, 2014, **356**, 584-590; c) T. Tuttle, D. Wang and W. Thiel, *Organometallics*, 2006, **25**, 4504-4513; d) T. Tuttle, D. Wang, W. Thiel, J. Koehler, M. Hofmann and J. Weis, *J. Organomet. Chem.*, 2007, **692**, 2282-2290; e) P. Gigler, M. Drees, K. Riener, B. Bechlars, W. A. Herrmann and F. E. Kuehn, *J. Catal.*, 2012, **295**, 1-14; f) A. M. LaPointe, F. C. Rix and M. Brookhart, *J. Am. Chem. Soc.*, 1997, **119**, 906-917; g) Y. Zhao, C. Guo and H. Wu, *Prog. Chem.*, 2014, **26**, 345-357; h) P. F. Fu, L. Brard, Y. W. Li and T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 7157-7168; i) H. Xie, L. Zhao, L. Yang, Q. Lei, W. Fang and C. Xiong, *J. Org. Chem.*, 2014, **79**, 4517-4527.
5. a) S. E. Parker, J. Boergel and T. Ritter, *J. Am. Chem. Soc.*, 2014, **136**, 4857-4860; b) L. Bareille, S. Becht, J. L. Cui, P. Le Gendre and C. Moise, *Organometallics*, 2005, **24**, 5802-5806; c) R. Pop, J. L. Cui, L. Adriaenssens, V. Comte and P. Le Gendre, *Synlett*, 2011, 679-683; d) J. W. Han and T. Hayashi, *Tetrahedron: Asymmetry*, 2010, **21**, 2193-2197; e) Z. D. Miller, W. Li, T. R. Belderrain and J. Montgomery, *J. Am. Chem. Soc.*, 2013, **135**, 15282-15285; f) J. Y. Wu, B. N. Stanzl and T. Ritter, *J. Am. Chem. Soc.*, 2010, **132**, 13214-13216.
6. a) T. Sudo, N. Asao, V. Gevorgyan and Y. Yamamoto, *J. Org. Chem.*, 1999, **64**, 2494-2499; b) G. B. Huang and M. Isobe, *Tetrahedron*, 2001, **57**, 10241-10246.
7. a) G. Kuchenbeiser, A. R. Shaffer, N. C. Zingales, J. F. Beck and J. A. R. Schmidt, *J. Organomet. Chem.*, 2011, **696**, 179-187; b) A. R. Shaffer and J. A. R. Schmidt, *Organometallics*, 2008, **27**, 1259-1266; c) A. R. Shaffer and J. A. R. Schmidt, *Organometallics*, 2009, **28**, 2494-2504; d) N. C. Zingales, A. R. Shaffer and J. A. R. Schmidt, *Organometallics*, 2013, **32**, 578-586.
8. A. R. Shaffer and J. A. R. Schmidt, *Chem. Eur. J.*, 2009, **15**, 2662-2673.
9. a) J. F. Beck, D. C. Samblanet and J. A. R. Schmidt, *RSC Adv.*, 2013, **3**, 20708-20718; b) J. F. Beck and J. A. R. Schmidt, *RSC Adv.*, 2012, **2**, 128-131.
10. A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 1965, **87**, 16-21.
11. Bogdan Marciniec, Hieronim Maciejewski, Cezary Pietraszuk and P. Pawlu´, *Hydrosilylation: A Comprehensive Review on Recent Advances*, Springer, Poland, 2009.
12. M. T. Haynes, II, P. Liu, R. D. Baxter, A. J. Nett, K. N. Houk, and J. Montgomery, *J. Am. Chem. Soc.*, 2014, **136**, 17495-17504.