ROYAL SOCIETY
OF CHEMISTRY

## COMMUNICATION

CrossMark
← click for updates

# Examining the role of Rh/Si cooperation in alkene hydrogenation by a pincer-type [P₂Si]Rh complex†

Matthew T. Whited,*[a] Alexander M. Deetz,‡[a] Theodore M. Donnell‡[a] and Daron E. Janzen[b]

A bis(phosphine)/triflatosilyl pincer-type Rh(ɪ) complex can reversibly store one equivalent of H₂ across the Si–Rh bond upon triflate migration from silicon to rhodium. The triflatosilyl complex serves as an effective precatalyst for norbornene hydrogenation, but Si–OTf bond cleavage is not implicated in the major catalytic pathway. The combined findings suggest possible strategies for M/Si cooperation in catalytic processes.
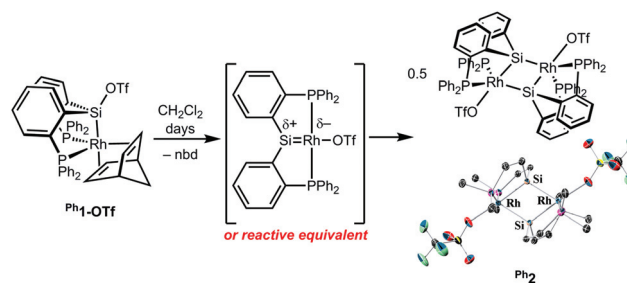
Taking inspiration from biological systems, a number of research groups have recently sought to expand the range of transformations available to transition metals through the use of non-innocent ligands. Several promising strategies have emerged, such as using redox-non-innocent ligands to support key redox steps[1] and coordinatively non-innocent ligands to stabilize reactive intermediates or control proton delivery/abstraction.[2]

As part of a research program focused on developing metal/silicon cooperative approaches to small-molecule activation,[3] we have recently investigated the coordination chemistry of bis(phosphine)/dihydrosilyl pincer-type proligands with Rh(ɪ) precursors.[4] Unlike related methylsilyl [P₂Si] pincers,[5] these ligands readily undergo double Si–H activation and H₂ loss with formation of a new silicon–chloride or –triflate bond. Such facile bond-breaking and -forming suggests the possibility of using the electropositive silyl donor together with the electron-rich Rh(ɪ) center for cooperative catalysis, potentially *via* silylene intermediates.[6]

Here we report a bis(phosphine)/silyl pincer-type rhodium system where kinetically labile Si–OTf and Si–H bonds facilitate reversible H₂ storage across the Rh–Si unit. We present

preliminary investigations into the role of such bond lability in catalytic norbornene hydrogenation, showing that these rearrangements do not occur on the major hydrogenation pathway and may hinder catalyst performance. However, the finding that pincer-supported Si–OTf and Si–H bonds are kinetically labile, including during catalysis, points toward the possibility of a new suite of cooperative processes at pincer-stabilized metal silyl and silylene complexes.

We previously reported the formation of a pincer-type triflatosilyl rhodium(ɪ) complex, [ᴾʰP₂Siᴼᵀᶠ]Rh(nbd) (ᴾʰ1-OTf in Scheme 1, nbd = norbornadiene) *via* multiple Si–H activations of a dihydrosilyl proligand.[4] ᴾʰ1-OTf is unstable in dichloromethane for extended periods, and during early attempts to crystallize ᴾʰ1-OTf we noted instead the formation of red crystals of a new compound. The decomposition product was obtained in small quantities and proved insoluble in common solvents but was identified by X-ray crystallography as the bis(μ-silylene) complex [(ᴾʰP₂Si)Rh(OTf)]₂ (ᴾʰ2, Scheme 1). ᴾʰ2 may result from dimerization of monomeric silylene triflate complexes, though related mechanisms invoking equivalently reactive species can be envisioned (*e.g.*, nucleophilic attack at silicon by a 3-coordinate triflatosilyl rhodium(ɪ) center). A mechanism invoking silylene intermediates is consistent both with the lability of silicon–triflate bonds[7] and with Ozerov's recent report of a pincer-type cationic Pt(ɪɪ) silylene complex that is isoelectronic with the proposed [ᴾʰP₂Si]Rh(OTf)

[a]*Department of Chemistry, Carleton College, Northfield, MN 55057, USA.*
*E-mail: mwhited@carleton.edu*
[b]*Department of Chemistry and Biochemistry, St. Catherine University, St. Paul, MN 55105, USA*

**Scheme 1** Decomposition of ᴾʰ1-OTf to a bis(μ-silylene) dimer ᴾʰ2 and rendering of the core of ᴾʰ2 determined by X-ray crystallography.

intermediate and exhibits substantial silylium character.[8] However, at yet we have not been able to distinguish among possible mechanisms.

We were interested in the possibility of trapping a [P₂Si]Rh(OTf) silylene intermediate or similar species with a reagent such as $H_2$, which could in principle be stored across the Rh=Si bond by a net 1,2-addition. However, **Ph1-OTf** did not react with $H_2$ (1 atm) at ambient temperature and afforded multiple products at elevated temperatures. We reasoned that $H_2$ reactivity could be enhanced by employing bulkier phosphine substituents to accelerate nbd dissociation and suppress formation of an insoluble dimeric species. Thus, we prepared the dicyclohexylphosphine analogue of **Ph1-OTf**, [**Cy**P₂Si**OTf**]Rh(nbd) (**Cy1-OTf**) (see ESI† for details, including the synthesis and crystal structure of the **Cy**P₂SiH₂ proligand).

Comparison of the crystal structures of **Ph1-OTf** and **Cy1-OTf** shows that the complexes exhibit quite similar metrical parameters (Fig. 1). The clearest difference between **Ph1-OTf** and **Cy1-OTf** is in the P–Rh–P angle, which is more obtuse for **Cy1-OTf** (122.8°) relative to **Ph1-OTf** (119.4°) due to the steric pressure exerted by the cyclohexyl groups. **Cy1-OTf** also exhibits a longer Si–OTf bond and slightly larger sum of angles about silicon excluding the triflate, $\sum \angle$Si (336.7° for **Cy1-OTf** *versus* 335.5° for **Ph1-OTf**), consistent with a modest increase in silylene character.[7b] However, in neither case do the structural parameters or the ²⁹Si NMR chemical shifts imply a substantial ground-state silylene contribution ($\delta$ 92.2 for **Cy1-OTf**, 97.8 for **Ph1-OTf** compared with $\delta$ 200–370 for free silylenes[9]).

We were delighted to find that **Cy1-OTf** reacts with $H_2$ at ambient temperature to liberate norbornane (nba) and afford the desired hydrosilyl rhodium(I) hydrido triflate complex, **Cy3-H** (Scheme 2). The ¹H NMR spectrum of **Cy3-H** exhibits a diagnostic hydride resonance ($\delta$ −22.6 (dtd, $^1J_{RhH}$ = 31.5 Hz, $^2J_{PH}$ = 13.4 Hz, $^3J_{HH(Si)}$ = 4.4 Hz)) with coupling to rhodium, the phosphine ligands, and the silicon hydride ($\delta$ 5.66, $^1J_{SiH}$ = 196 Hz,

**Scheme 2** Hydrogenation of **Cy1-OTf** and $H_2$ transfer from **Cy3-H** to nbd.

$\Delta\nu_{1/2}$ = 9 Hz). The presence of an Si–H was also confirmed by a ¹H/²⁹Si HMQC experiment (Fig. S25†).

Complex **Cy3-H** was unstable under all conditions examined, precluding microanalytical or crystallographic characterization, so we sought to confirm its identity through preparation of an analogous complex without a silicon hydride. Beginning with the known hydrido chloride complex [**Cy**P₂Si**Me**]Rh(H)(Cl),[5a] the related methylsilyl complex [**Cy**P₂Si**Me**]Rh(H)(OTf) (**Cy3-Me**) was prepared by salt metathesis with silver triflate (Scheme 3). As expected, **Cy3-H** and **Cy3-Me** possess similar spectroscopic signatures. For instance, the Rh–H ¹H NMR signal for **Cy3-Me** ($\delta$ −22.4 (dt, $^1J_{RhH}$ = 32.0 Hz, $^2J_{PH}$ = 13 Hz)) exhibits a nearly identical chemical shift and coupling constants to the Rh–H of **Cy3-H**, with the distinction that no coupling to a silicon hydride is observed upon methyl-for-hydride replacement.

By analogy with [**Cy**P₂Si**Me**]Rh(H)(Cl) and related 5-coordinate $d^6$ complexes,[10] we propose that **Cy3-H** and **Cy3-Me** exhibit Y geometries with phosphine donors approximately *trans* and an acute Si–Rh–H angle. A Y-type geometry is also supported by DFT calculations on **Me3-H**, the dimethylphosphine analogue of **Cy3-H**, which is calculated to exhibit an acute Si–Rh–H bond angle (69°) and approximately *trans*-disposed hydride and triflate ligands (156°). Consistent with our experimental observations, this geometry is also calculated to be 3.5 kcal mol⁻¹ more stable than **Me4-OTf**, the isomer of **Me3-H** with triflate bound to silicon and an $\eta^2$-dihydrogen ligand on rhodium, which is the next lowest-energy isomer identified computationally.

Exposure of **Cy3-H** to an excess of nbd results in quantitative regeneration of **Cy1-OTf** with release of norbornene (nbe) (Scheme 2), suggesting that **Cy3-H** can serve as a source of $H_2$. In contrast, **Cy3-Me** does not react with nbd. These findings emphasize the potential importance of incorporating labile
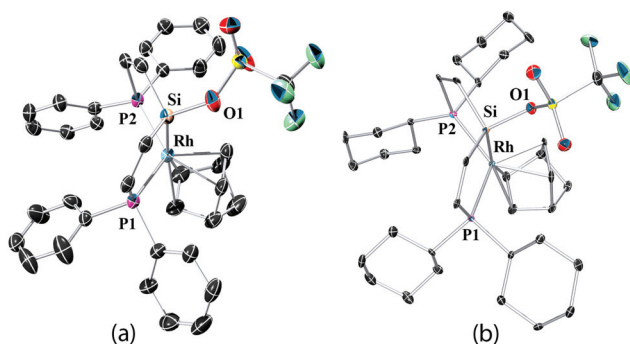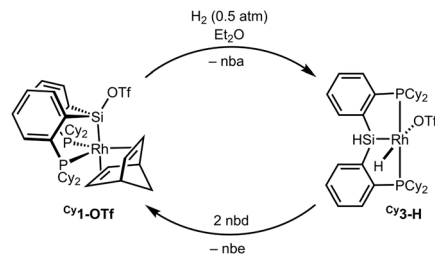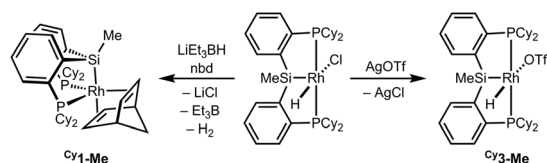
**Fig. 1** Crystal structures of (a) **Ph1-OTf** and (b) **Cy1-OTf** with thermal ellipsoids at the 50% probability level and hydrogen atoms and portions of the Si···P phenylene linkers omitted for clarity. Selected bond lengths (Å) and angles (°) for **Ph1-OTf**: Rh–Si, 2.247(1); Rh–P1, 2.336(1); Rh–P2, 2.326(1); Si–O1, 1.783(3); P1–Rh–P2, 119.38(4). For **Cy1-OTf**: Rh–Si, 2.249(1); Rh–P1, 2.351(2); Rh–P2, 2.368(2); Si–O1, 1.796(3); P1–Rh–P2, 122.81(4).

**Scheme 3** Synthesis of model complexes **Cy1-Me** and **Cy3-Me**.

silicon substituents when targeting Rh/Si cooperative reactivity, since facile rearrangement can occur with Si–OTf and Si–H bonds, whereas Si–CH₃ bonds are more often inert (see ref. 11 for exceptions).

The reactivity shown in Scheme 2 also suggests that $^{Cy}$1-OTf may serve as a precatalyst for hydrogenation of nbe, and $^{Cy}$1-OTf does hydrogenate nbe to nba at 0.5% loading (complete reaction in <30 min). However, the finding of efficient catalysis does not prove the intermediacy of $^{Cy}$3-H. In fact, several mechanistic possibilities for hydrogenation can be envisioned, as outlined in Scheme 4. Cycle A operates *via* a dihydride-type mechanism, where Si–OTf cleavage is not implicated. Cycles B and C both require Si–OTf cleavage but differ in whether the alkane release occurs upon delivery of hydrogen from a second H₂ molecule (B) or from the Si–H (C).

We have made preliminary efforts toward understanding the mechanism of nbe hydrogenation by comparing $^{Cy}$1-OTf with methylsilyl model complexes $^{Cy}$1-Me and $^{Cy}$3-Me (Scheme 3). Hydrogenation by $^{Cy}$1-Me would be expected to occur *via* cycle A, whereas $^{Cy}$3-Me would operate by cycle B, and $^{Cy}$1-OTf could access all 3 mechanisms. Under standard conditions at 0.5 mol% catalyst loading (see ESI† for further details), $^{Cy}$1-OTf and $^{Cy}$1-Me both fully hydrogenate nbe, though $^{Cy}$1-OTf is considerably slower (complete reaction in 8 min for $^{Cy}$1-Me *versus* 30 min for $^{Cy}$1-OTf). Under the same conditions, $^{Cy}$3-Me does not hydrogenate nbe (<0.5% conversion in 150 min). These combined findings suggest that nbe hydrogenation occurs primarily *via* cycle A. The fact that triflatosilyl precatalyst $^{Cy}$1-OTf is considerably less efficient than methylsilyl precatalyst $^{Cy}$1-Me may be due to the equilibrium between $^{Cy}$4-OTf and $^{Cy}$3-H (Scheme 4), which can siphon catalyst off the primary cycle. The precise role of the $^{Cy}$4-Cy/$^{Cy}$3-H equilibrium is the object of ongoing investigation.

Although these findings suggest a simple dihydride mechanism, where both hydrogen atoms are transferred from the same H₂ molecule, early experiments suggest a more complicated reality. Hydrogenation of nbe by either $^{Cy}$1-OTf or $^{Cy}$1-Me under 1 : 1 H₂/D₂ leads to a significant amount of norbornane-$d_1$ (see ESI†), suggesting that H/D scrambling can occur at $^{Cy}$4 and/or that alkane release may occur by hydrogen transfer from a second H₂ molecule rather than direct reductive elimination. In either case, an intermediate η²-silane may be implicated, consistent with recent reports of hydrogen delivery to alkenes from appended silanes at Ru and Pd[12] as well as the important role of reversible Si–H and Si–C bond formation in [PSiP]Pd-catalyzed allene hydrocarboxylation.[13] Experimental and theoretical efforts are currently directed at understanding the intimate mechanisms at play.

In conclusion, we have reported a pincer-type triflatosilyl rhodium complex where facile Si–OTf cleavage allows reversible H₂ storage across the Rh–Si bond. The complex serves as an efficient precatalyst for norbornene hydrogenation, though comparative catalytic studies with methyl-substituted analogues strongly suggest that the Si–OTf bond remains intact along the major catalytic pathway. Nevertheless, our finding that pincer-supported Si–OTf and Si–H bonds may be easily exchanged, including during catalysis, indicates that new stoichiometric and catalytic mechanisms invoking M/Si cooperation may be accessible.

## Notes and references

1 (*a*) P. J. Chirik, *Inorg. Chem.*, 2011, **50**, 9737–9740; (*b*) P. J. Chirik and K. Wieghardt, *Science*, 2010, **327**, 794–795; (*c*) M. R. Haneline and A. F. Heyduk, *J. Am. Chem. Soc.*, 2006, **128**, 8410–8411; (*d*) A. L. Smith, K. I. Hardcastle and J. D. Soper, *J. Am. Chem. Soc.*, 2010, **132**, 14358–14360.

2 (*a*) A. J. M. Miller, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2008, **130**, 11874–11875; (*b*) A. D. Wilson, R. H. Newell, M. J. McNevin, J. T. Muckerman, M. R. DuBois and D. L. DuBois, *J. Am. Chem. Soc.*, 2006, **128**, 358–366; (*c*) C. Gunanathan and D. Milstein, *Acc. Chem. Res.*, 2011, **44**, 588–602; (*d*) W. H. Harman and J. C. Peters, *J. Am. Chem. Soc.*, 2012, **134**, 5080–5082; (*e*) C. M. Moore and N. K. Szymczak, in *Pincer and Pincer-Type Complexes: Application in Organic Synthesis and Catalysis*, ed. K. J. Szabo and O. F. Wendt, Wiley-VCH, Weinheim, Germany, 2014, pp. 117–147; (*f*) J. R. Khusnutdinova and D. Milstein, *Angew. Chem., Int. Ed.*, 2015, **54**, 12236–12273.
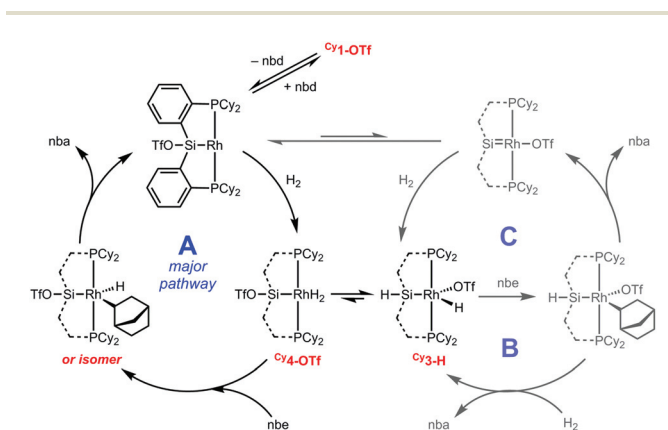


**Scheme 4** Possible catalytic cycles for nbe hydrogenation by precatalyst $^{Cy}$1-OTf.

3 (*a*) M. T. Whited, L. Qiu, A. J. Kosanovich and D. E. Janzen, *Inorg. Chem.*, 2015, **54**, 3670–3679; (*b*) M. T. Whited, A. J. Kosanovich and D. E. Janzen, *Organometallics*, 2014, **33**, 1416–1422.

4 M. T. Whited, A. M. Deetz, J. W. Boerma, D. E. DeRosha and D. E. Janzen, *Organometallics*, 2014, **33**, 5070–5073.

5 (*a*) D. F. MacLean, R. McDonald, M. J. Ferguson, A. J. Caddell and L. Turculet, *Chem. Commun.*, 2008, 5146–5148; (*b*) L. Turculet, in *Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis*, ed. K. J. Szabo and O. F. Wendt, Wiley-VCH, Weinheim, Germany, 2014, pp. 149–187.

6 M. T. Whited, *Beilstein J. Org. Chem.*, 2012, **8**, 1554–1563.

7 (*a*) S. K. Grumbine, G. P. Mitchell, D. A. Straus, T. D. Tilley and A. L. Rheingold, *Organometallics*, 1998, **17**, 5607–5619; (*b*) P. B. Glaser, P. W. Wanandi and T. D. Tilley, *Organometallics*, 2004, **23**, 693–704.

8 J. C. DeMott, W. X. Gu, B. J. McCulloch, D. E. Herbert, M. D. Goshert, J. R. Walensky, J. Zhou and O. V. Ozerov, *Organometallics*, 2015, **34**, 3930–3933.

9 R. Waterman, P. G. Hayes and T. D. Tilley, *Acc. Chem. Res.*, 2007, **40**, 712–719.

10 (*a*) W. H. Lam, S. Shimada, A. S. Batsanov, Z. Y. Lin, T. B. Marder, J. A. Cowan, J. A. K. Howard, S. A. Mason and G. J. McIntyre, *Organometallics*, 2003, **22**, 4557–4568; (*b*) J. F. Riehl, Y. Jean, O. Eisenstein and M. Pelissier, *Organometallics*, 1992, **11**, 729–737; (*c*) I. E. Rachidi, O. Eisenstein and Y. Jean, *New J. Chem.*, 1990, **14**, 671–677; (*d*) M. D. Fryzuk, P. A. Macneil and R. G. Ball, *J. Am. Chem. Soc.*, 1986, **108**, 6414–6416.

11 (*a*) S. J. Mitton, R. McDonald and L. Turculet, *Angew. Chem., Int. Ed.*, 2009, **48**, 8568–8571; (*b*) S. J. Mitton, R. McDonald and L. Turculet, *Polyhedron*, 2013, **52**, 750–754; (*c*) H. Kameo, S. Ishii and H. Nakazawa, *Dalton Trans.*, 2013, **42**, 4663–4669.

12 (*a*) T. Komuro, T. Arai, K. Kikuchi and H. Tobita, *Organometallics*, 2015, **34**, 1211–1217; (*b*) M. Kamitani, Y. Nishiguchi, R. Tada, M. Itazaki and H. Nakazawa, *Organometallics*, 2014, **33**, 1532–1535; (*c*) J. Takaya and N. Iwasawa, *Chem. – Eur. J.*, 2014, **20**, 11812–11819.

13 (*a*) H. W. Suh, L. M. Guard and N. Hazari, *Chem. Sci.*, 2014, **5**, 3859–3872; (*b*) J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2008, **130**, 15254–15255; (*c*) J. Takaya and N. Iwasawa, *Organometallics*, 2009, **28**, 6636–6638.