Dalton Transactions

This article can be cited before page numbers have been issued, to do this please use: M. Whited, A. M. Deetz, T. M. Donnell and D. E. Janzen, *Dalton Trans.*, 2016, DOI: 10.1039/C6DT00027D.

View Article Online
DOI: 10.1039/C6DT00027D

Journal Name

COMMUNICATION

# Examining the role of Rh/Si cooperation in alkene hydrogenation by a pincer-type $[P_2Si]Rh$ complex

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

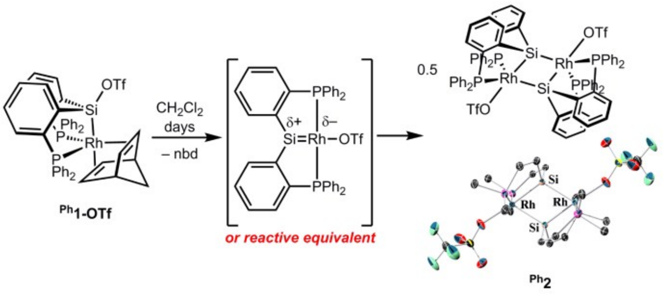
**www.rsc.org/**

**A bis(phosphine)/triflatosilyl pincer-type Rh(I) complex can reversibly store one equivalent of $H_2$ 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(I) precursors.[4] Unlike related methylsilyl $[P_2Si]$ pincers,[5] these ligands readily undergo double Si–H activation and $H_2$ 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(I) 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 $H_2$ 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.



**Scheme 1.** Decomposition of $^{Ph}$**1-OTf** to a bis($\mu$-silylene) dimer $^{Ph}$**2** and rendering of the core of $^{Ph}$**2** determined by X-ray crystallography

We previously reported the formation of a pincer-type triflatosilyl rhodium(I) complex, $[^{Ph}P_2Si^{OTf}]Rh(nbd)$ ($^{Ph}$**1-OTf** in Scheme 1, nbd = norbornadiene) via multiple Si–H activations of a dihydrosilyl proligand.[4] $^{Ph}$**1-OTf** is unstable in dichloromethane for extended periods, and during early attempts to crystallize $^{Ph}$**1-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($\mu$-silylene) complex $[(^{Ph}P_2Si)Rh(OTf)]_2$ ($^{Ph}$**2**, Scheme 1). $^{Ph}$**2** 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(I) 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(II) silylene complex

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

† Electronic Supplementary Information (ESI) available: Synthesis procedures and characterization data, including NMR spectra for all reported compounds. Crystallographic data for $^{Cy}P_2SiH_2$, $^{Ph}$**2**, $^{Ph}$**1-OTf**, and $^{Cy}$**1-OTf**. Computational and catalytic experimental details. CCDC 1444624–1444627. See DOI: 10.1039/x0xx00000x

‡ These authors contributed equally to the work described.

that is isoelectronic with the proposed $[^{Ph}P_2Si]Rh(OTf)$ intermediate and exhibits substantial silylium character.[8] However, as yet we have not been able to distinguish among possible mechanisms.

We were interested in the possibility of trapping a $[P_2Si]Rh(OTf)$ 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, **$^{Ph}$1-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 **$^{Ph}$1-OTf**, $[^{Cy}P_2Si^{OTf}]Rh(nbd)$ (**$^{Cy}$1-OTf**) (see ESI for details, including the synthesis and crystal structure of the $^{Cy}P_2SiH_2$ proligand).

Comparison of the crystal structures of **$^{Ph}$1-OTf** and **$^{Cy}$1-OTf** shows that the complexes exhibit quite similar metrical parameters (Figure 1). The clearest difference between **$^{Ph}$1-OTf** and **$^{Cy}$1-OTf** is in the P–Rh–P angle, which is more obtuse for **$^{Cy}$1-OTf** (122.8°) relative to **$^{Ph}$1-OTf** (119.4°) due to the steric pressure exerted by the cyclohexyl groups. **$^{Cy}$1-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 **$^{Cy}$1-OTf** versus 335.5° for **$^{Ph}$1-OTf**), consistent with a modest increase in silylene character.[7b] However, in neither case do the structural parameters or the $^{29}Si$ NMR chemical shifts imply a substantial ground-state silylene contribution (δ 92.2 for **$^{Cy}$1-OTf**, 97.8 for **$^{Ph}$1-OTf** compared with δ 200–370 for free silylenes[9]).

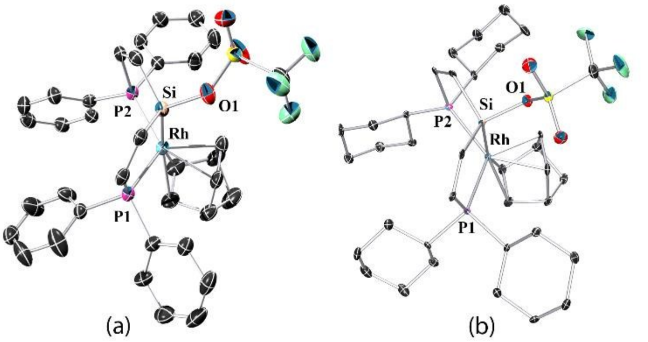
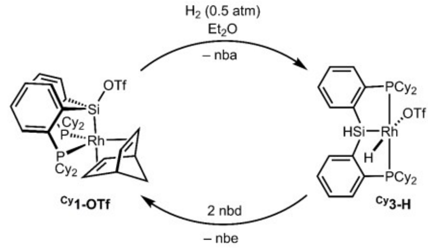


**Figure 1.** Crystal structures of (a) **$^{Ph}$1-OTf** and (b) **$^{Cy}$1-OTf** with thermal ellipsoids at the 50% probability level and hydrogen atoms and portions of the Si···P phenylene linkers omitted for clarity. Selected bond lengths (Å) and angles (°) for **$^{Ph}$1-OTf**: Rh–Si, 2.247(1); Rh–P1, 2.336(1); Rh–P2, 2.326(1); Si–O1, 1.783(3); P1–Rh–P2, 119.38(4). For **$^{Cy}$1-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)

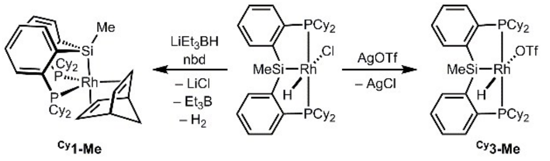
We were delighted to find that **$^{Cy}$1-OTf** reacts with $H_2$ at ambient temperature to liberate norbornane (nba) and afford the desired hydrosilyl rhodium(I) hydrido triflate complex, **$^{Cy}$3-H** (Scheme 2). The $^1H$ NMR spectrum of **$^{Cy}$3-H** exhibits a diagnostic hydride resonance (δ –22.6 (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 (δ 5.66, $^1J_{SiH}$ = 196 Hz, $\Delta\nu_{1/2}$ = 9 Hz). The presence of an Si–H was also confirmed by a $^1H/^{29}Si$ HMQC experiment (Figure S25).

Complex **$^{Cy}$3-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 $[^{Cy}P_2Si^{Me}]Rh(H)(Cl)$,[5a] the related methylsilyl complex $[^{Cy}P_2Si^{Me}]Rh(H)(OTf)$ (**$^{Cy}$3-Me**) was prepared by salt metathesis with silver triflate (Scheme 3). As expected, **$^{Cy}$3-H** and **$^{Cy}$3-Me** possess similar spectroscopic signatures. For instance, the Rh–*H* $^1H$ NMR signal for **$^{Cy}$3-Me** (δ –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 **$^{Cy}$3-H**, with the distinction that no coupling to a silicon hydride is observed upon methyl-for-hydride replacement.



**Scheme 2.** Hydrogenation of **$^{Cy}$1-OTf** and $H_2$ transfer from **$^{Cy}$3-H** to nbd

By analogy with $[^{Cy}P_2Si^{Me}]Rh(H)(Cl)$ and related 5-coordinate $d^6$ complexes,[10] we propose that **$^{Cy}$3-H** and **$^{Cy}$3-Me** exhibit Y geometries with phosphine donors approximately *trans* and an acute Si–Rh–H angle. A Y-type geometry is also supported by DFT calculations on **$^{Me}$3-H**, the dimethylphosphine analogue of **$^{Cy}$3-H**, which is calculated to exhibit an acute Si–Rh–H bond angle (69°) and approximately *trans*-disposed hydride and triflate ligands (156°). Consistent with our experimental observations, this geometry is also calculated to be 3.5 kcal/mol more stable than **$^{Me}$4-OTf**, the isomer of **$^{Cy}$3-H** with triflate bound to silicon and an $\eta^2$-dihydrogen ligand on rhodium, which is the next lowest-energy isomer identified computationally.



**Scheme 3.** Synthesis of model complexes **$^{Cy}$1-Me** and **$^{Cy}$3-Me**

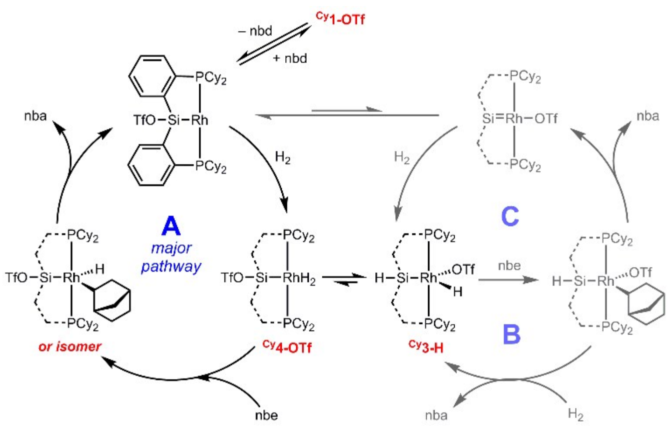
Exposure of **$^{Cy}$3-H** to an excess of nbd results in quantitative regeneration of **$^{Cy}$1-OTf** with release of norbornene (nbe) (Scheme 2), suggesting that **$^{Cy}$3-H** can serve as a source of $H_2$. In contrast, **$^{Cy}$3-Me** does not react with nbd. These findings emphasize the potential importance of incorporating labile silicon substituents when targeting Rh/Si cooperative reactivity, since facile rearrangement can occur with Si–OTf and Si–H bonds, whereas Si–$CH_3$ 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,

View Article Online
DOI: 10.1039/C6DT00027D

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 $H_2$ molecule (B) or from the Si–H (C).

We have made preliminary efforts toward understanding the mechanism of nbe hydrogenation by comparing $^{\mathrm{Cy}}$**1-OTf** with methylsilyl model complexes $^{\mathrm{Cy}}$**1-Me** and $^{\mathrm{Cy}}$**3-Me** (Scheme 3). Hydrogenation by $^{\mathrm{Cy}}$**1-Me** would be expected to occur via Cycle A, whereas $^{\mathrm{Cy}}$**3-Me** would operate by Cycle B, and $^{\mathrm{Cy}}$**1-OTf** could access all 3 mechanisms. Under standard conditions at 0.5 mol % catalyst loading (see ESI for further details), $^{\mathrm{Cy}}$**1-OTf** and $^{\mathrm{Cy}}$**1-Me** both fully hydrogenate nbe, though $^{\mathrm{Cy}}$**1-OTf** is considerably slower (complete reaction in 8 min for $^{\mathrm{Cy}}$**1-Me** versus 30 min for $^{\mathrm{Cy}}$**1-OTf**). Under the same conditions, $^{\mathrm{Cy}}$**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 $^{\mathrm{Cy}}$**1-OTf** is considerably less efficient than methylsilyl precatalyst $^{\mathrm{Cy}}$**1-Me** may be due to the equilibrium between $^{\mathrm{Cy}}$**4-OTf** and $^{\mathrm{Cy}}$**3-H** (Scheme 4), which can siphon catalyst off the primary cycle. The precise role of the $^{\mathrm{Cy}}$**4-Cy**/$^{\mathrm{Cy}}$**3-H** equilibrium is the object of ongoing investigation.



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

Although these findings suggest a simple dihydride mechanism, where both hydrogen atoms are transferred from the same $H_2$ molecule, early experiments suggest a more complicated reality. Hydrogenation of nbe by either $^{\mathrm{Cy}}$**1-OTf** or $^{\mathrm{Cy}}$**1-Me** under 1:1 $H_2/D_2$ leads to a significant amount of norbornane-$d_1$ (see ESI), suggesting that H/D scrambling can occur at $^{\mathrm{Cy}}$**4** and/or that alkane release may occur by hydrogen transfer from a second $H_2$ molecule rather than direct reductive elimination. In either case, an intermediate $\eta^2$-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 $H_2$ 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.

Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund and to Carleton College for support of this research. X-ray crystallography was supported by NSF-MRI Award No. 1125975, "MRI Consortium: Acquisition of a Single Crystal X-ray Diffractometer for a Regional PUI Molecular Structure Facility", and NMR spectroscopy was enabled by NSF-MRI Award No. 1428752, "MRI: Acquisition of a 400 MHz NMR Spectrometer to Support Research and Undergraduate Research Training at Carleton College and St. Olaf College". A. M. D. thanks the Dreyfus Foundation for a research fellowship. The authors thank D. Gross and L. Yang (Carleton College) for assistance with GC-MS experiments and B. Noll (Bruker AXS, Inc.) for crystallographic assistance with complex $^{\mathrm{Cy}}$**1-OTf**.

## 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*, eds. 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.

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*, eds. 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.

View Article Online
DOI: 10.1039/C6DT00027D

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

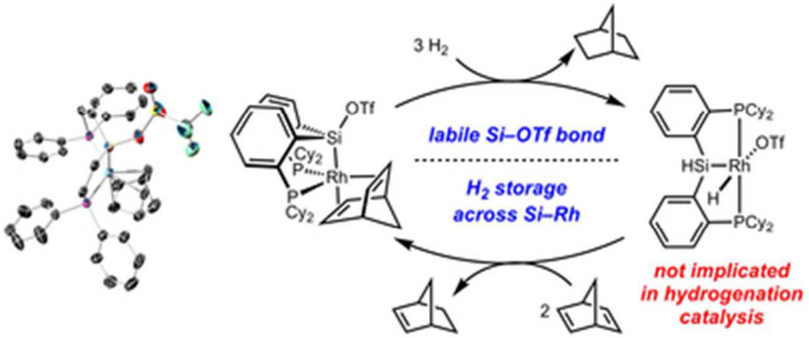
10 (a) W. H. Lam, S. Shimada, A. S. Batsanov, Z. Y. Lin, T. B. Marder, J. A. Cowan, J. A. K. Howard, S. A. Mason and G. J. McIntyre, *Organometallics*, 2003, **22**, 4557-4568; (b) J. F. Riehl, Y. Jean, O. Eisenstein and M. Pelissier, *Organometallics*, 1992, **11**, 729-737; (c) I. E. Rachidi, O. Eisenstein 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.

View Article Online
DOI: 10.1039/C6DT00027D



34x14mm (300 x 300 DPI)