Synthesis of silyl cobalt hydrides and their catalytic activity on hydrosilylation of alkenes

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Two silyl [P,Si]-chelate cobalt hydrides, $[(o\text{-Si(Ph)}_2\text{-(P}^i\text{Pr}_2)\text{C}_6\text{H}_4)\text{Co(H)(PMe}_3)_2]$ (**1**) and $[(o\text{-Si(Ph)}_2\text{-(PPh}_2)\text{C}_6\text{H}_4)\text{Co(H)(PMe}_3)_2]$ (**2**), were prepared through the chelate-assisted Si–H activation of bidentate preligand, $o\text{-HSi(Ph)}_2\text{-(P}^i\text{Pr}_2)\text{C}_6\text{H}_4$ (**L1**) and $o\text{-HSi(Ph)}_2\text{-(PPh}_2)\text{C}_6\text{H}_4$ (**L2**) by $[\text{Co(PMe}_3)_4]$ or $[\text{Co(Me)(PMe}_3)_4]$, respectively. Both cobalt(II) hydrides **1** and **2** can efficiently catalyze hydrosilylation of olefins, and the catalytic effect of complex **1** is better than that of complex **2**. The Markovnikov products were formed from aryl alkenes, whereas the *anti*-Markovnikov products were produced from aliphatic alkenes. In the mechanism study, a silyl cobalt(II) intermediate, $[(o\text{-Si(Ph)}_2\text{-(P}^i\text{Pr}_2)\text{C}_6\text{H}_4)\text{Co(SiHPh}_2)(\text{PMe}_3)_2]$, as the real catalyst is proposed and supported by in situ infrared (IR) study. The molecular structure of complex **1** was determined by single crystal X-ray diffraction analysis.

KEYWORDS
alkene hydrosilylation, cobalt hydride, Si–H bond activation, silyl cobalt complex

1 | INTRODUCTION

Hydrosilylation of olefins provides important organic silicon raw materials for organic synthesis in industry. So far, the catalysts used are noble metal Pt catalysts. Therefore, how to use base metals instead of noble metal catalysts for olefin hydrosilylation has become the focus of the research in recent years.[1] It has been found that cobalt(II) chlorides have good catalytic activity for hydrosilylation of olefins.[2–6] In the study of the mechanism of olefin hydrosilylation, it is found that metal hydrides do play a catalytic role in the catalytic process although the pre-catalyst is metal halides or metal nitrogen complex.[4,5,7] However, due to the difficult synthesis and instability of metal hydrides, there are relatively few reports on the direct use of cobalt hydrides as catalysts for olefin hydrosilylation.[8]

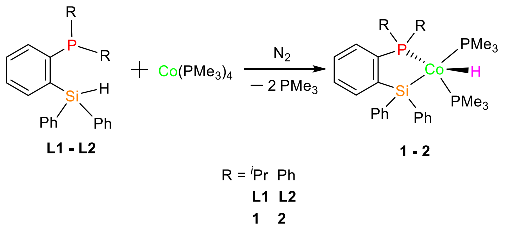
In this paper, two silyl [P, Si]-chelate cobalt hydrides, $[(o\text{-Si(Ph)}_2\text{-(P}^i\text{Pr}_2)\text{C}_6\text{H}_4)\text{Co(H)(PMe}_3)_2]$ (**1**) and $[(o\text{-Si(Ph)}_2\text{-(PPh}_2)\text{C}_6\text{H}_4)\text{Co(H)(PMe}_3)_2]$ (**2**), were prepared through the chelate-assisted Si–H activation of bidentate preligand $o\text{-HSi(Ph)}_2\text{-(P}^i\text{Pr}_2)\text{C}_6\text{H}_4$ (**L1**) and $o\text{-HSi(Ph)}_2\text{-(PPh}_2)\text{C}_6\text{H}_4$ (**L2**) with $[\text{Co(PMe}_3)_4]$ or $[\text{Co(Me)(PMe}_3)_4]$, respectively. The experiments indicate that both cobalt(II) complexes **1** and **2** can efficiently catalyze hydrosilylation of olefins and the catalytic effect of complex **1** is better than that of complex **2**. The Markovnikov products were formed from aryl alkenes, whereas the *anti*-Markovnikov products were produced from aliphatic alkenes. In the mechanism study, the silyl cobalt intermediate is believed as a real catalyst. The related catalytic mechanism is proposed on the basis of the experimental information and literature reports.

2 | RESULTS AND DISCUSSION

2.1 | Syntheses of silyl cobalt hydrides 1 and 2

Preligand **L1** was added to a solution of [Co(PMe_3)$_4$] in THF at 0°C. The reaction mixture was stirred for 24 h at r.t. (Scheme 1). The volatiles were removed, and the residue was extracted with n-pentane and diethyl ether. After work-up, complex **1** was obtained as reddish brown cuboid crystals from n-pentane in the yield of 65%. The preparation method of complex **2** is the same as that of complex **1**.

In the infrared (IR) spectra of complexes **1** and **2**, the stretching vibration of Co–H bond in complex **1** appeared at 1755 cm^{-1}, whereas the stretching vibration of Co–H bond in complex **2** was recorded at 1776 cm^{-1}. The Si–H vibrational signals in ligand **L1** (2137 cm^{-1}) and ligand **L2** (2162 cm^{-1}) had disappeared. In these two complexes, the rocking vibrations of trimethylphosphine appeared at 932 (**1**) and 936 (**2**) cm^{-1}, respectively.



SCHEME 1 The syntheses of complexes **1** and **2**

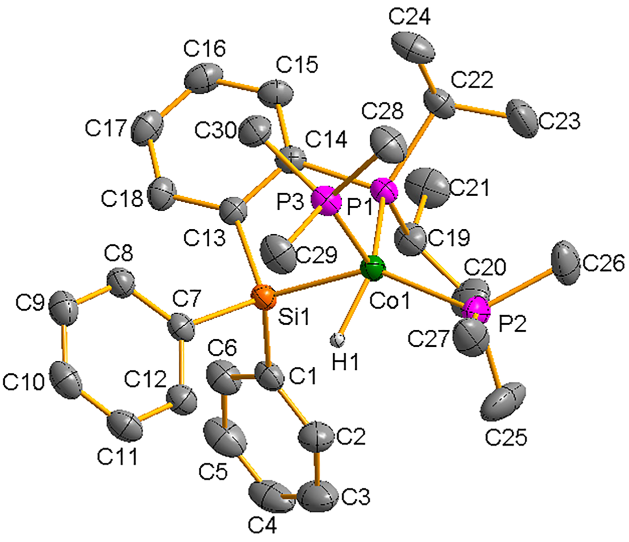
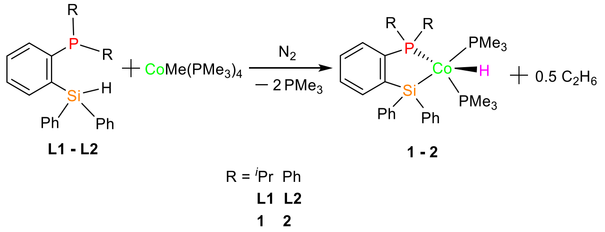


FIGURE 1 Oak Ridge Thermal Ellipsoid Plot (ORTEP) of complex **1** at the 50% probability level (most of hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1–P1 2.1891(4), Co1–P2 2.2167(4), Co1–P3 2.2203(4), Co1–Si1 2.2339(4), Co1–H1 1.49(2), P1–Co1–P2 117.51(2), P1–Co1–P3 105.41(2), P1–Co1–Si1 84.63(2), P2–Co1–P3 101.54(2), P2–Co1–Si1 145.97(2), P3–Co1–Si1 96.23(2), H1–Co1–P1 141.4(9), H1–Co1–P2 87.2(9), H1–Co1–P3 97.1(9), H1–Co1–Si1 61.8(9)

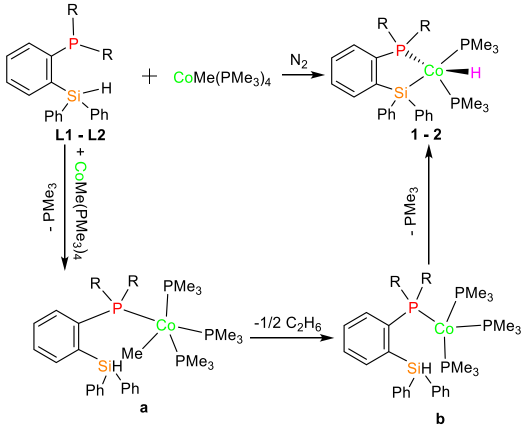
Complexes **1** and **2** are paramagnetic substances with d^7 configuration. The molecular structure of complex **1** was confirmed by single crystal X-ray diffraction analysis (Figure 1). Complex **1** has a severely distorted trigonal bipyramidal coordination geometry with cobalt atom in the center (τ_5 0.68).[9] P2–Co1–Si1 (145.97(2)°) is the axial direction while the trigonal plane is determined by P1, P3, and H1 atom. The sum of coordination bond angles (P1–Co1–P3 105.41(2)°, P1–Co1–H1 141.4(9)°, P3–Co1–H1 97.1(9)°) in the trigonal plane is 343.91°, significantly deviated from 360°. Co1–H1 bond length is 1.49(2) Å.

Complex **1** or **2** could also be synthesized via the reaction of preligand **L1** or **L2** with CoMe(PMe_3)$_4$ (Scheme 2).

We propose the following mechanism (Scheme 3). Ligand replacement of PMe_3 by preligand **L1** or **L2** to form intermediate **a** is the first step. Intermediate **a** transforms into cobalt(0) intermediate **b** via single-electron reductive elimination with the release of ethane.[10] Intramolecular oxidative addition of Si–H bond at



SCHEME 2 The alternative to prepare complexes **1** and **2**



SCHEME 3 The mechanism of formation of complexes **1** and **2**

Co(0) center affords the final product **1** or **2**, the cobalt(II) hydride, with the dissociation of a PMe_3 ligand.

2.2 | Catalytic application of silyl cobalt hydrides 1 and 2 in alkene hydrosilylation

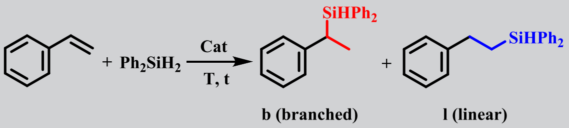
We found that when the reaction with complex **1** as catalyst was carried out at 70°C for 4 h, the conversion could reach 98%, and good selectivity could be obtained (Entries 1–3, Table 1). Our optimized condition experiments show that under the same experimental conditions, the catalytic effect of complex **1** is better than that of complex **2** (Entries 2 and 4, Table 1). Compared with several solvents, the absence of solvent is more beneficial to the catalytic reaction (Entries 3 and 5–8, Table 1). The conversion and selectivity of the catalytic system at 70°C are better than those at 50°C and 30°C (Entries 3, 9, and 10, Table 1). When the amount of catalyst was reduced to 0.5 mol%, the conversion decreased to 61%, but the selectivity changed little (b/l 95:5) (Entry 11, Table 1). Therefore, the optimized catalytic reaction conditions are as the same as those for Entry 3 in Table 1.

The substrate scope with complex **1** as catalyst was expanded (Table 2). For most of the tested aromatic substrates, good yields were reached with Markovnikov selectivity (**3a–3i**, **3k**, and **3l–3o**, Table 2). The substrates with the substitute group at *ortho*-position have poor yield even the reaction time was extended to 10 h (**3j**, Table 2). Complex **1** has no catalytic activity to *para*-vinylbenzenenitrile (**3p**, Table 2). For aliphatic substrates, the hydrosilylation with complex **1** as catalyst has *anti*-Markovnikov selectivity (**3q–3t**, Table 2). Triethoxyethene has poor yield with good selectivity (**3t**, Table 2). The hydrosilylation of benzylvinylether could not be catalyzed by complex **1** (**3u**, Table 2).

2.3 | Mechanistic investigation

In order to explore the catalytic mechanism of alkene hydrosilylation, we tried to study the stoichiometric reaction of catalyst **1** with Ph_2SiH_2 or styrene, respectively. When the reaction time of catalyst **1** with Ph_2SiH_2 was 5 min, the (Co–H) signal at 1755 cm^{-1} disappeared in the IR spectrum (Figure S3, SI). We speculate that silyl cobalt(II) intermediate **A** was formed (Scheme 4). However, intermediate **A** is not stable and could not be separated from the reaction mixture. The stoichiometric reaction of catalyst **1** and styrene did not proceed under the catalytic conditions, and the (Co–H) signal at 1755 cm^{-1} did not disappear (Figure S4, SI).

TABLE 1 Optimization of reaction conditions

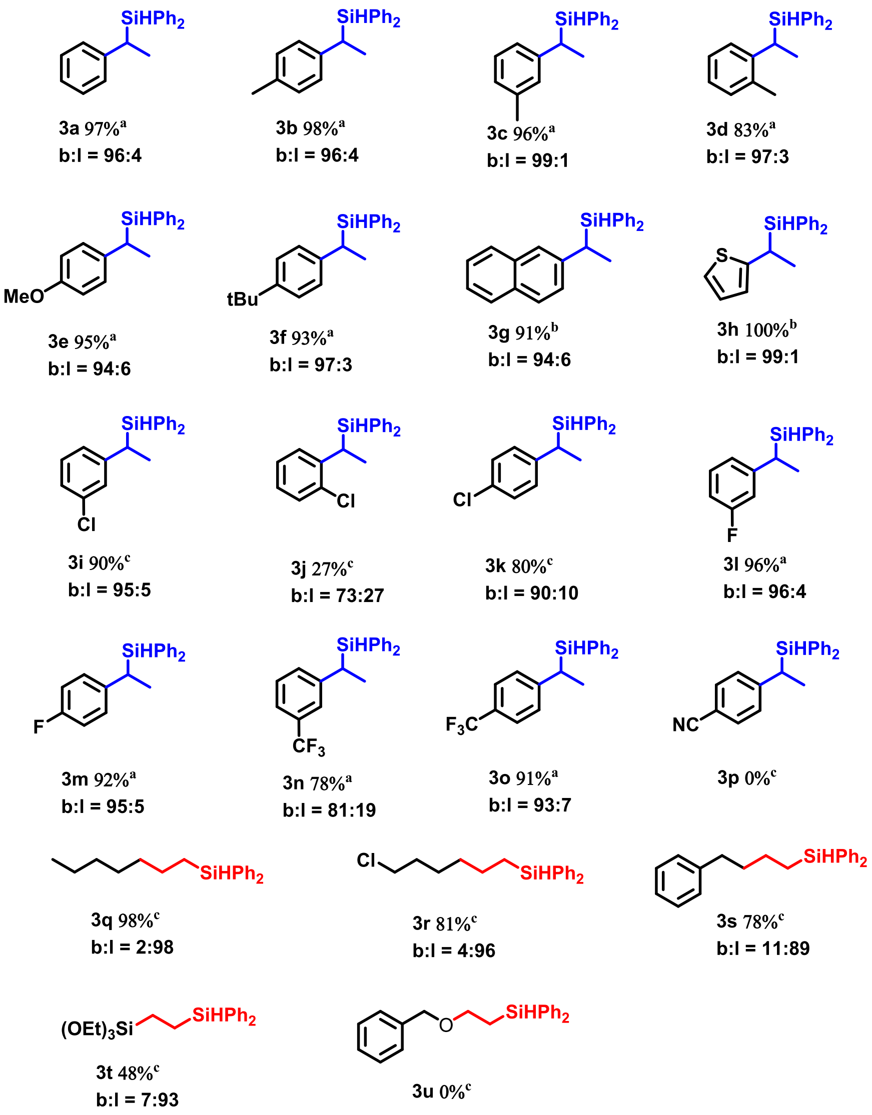


Entry	Catalyst	Loading (mol %)	Solvent	Temp (°C)	Time (h)	Conv[a] (%)	Select[b] (b/l)[b]
1	**1**	1	Neat	70	6.5	98	98:2
2	**1**	1	Neat	70	5	98	98:2
3	**1**	1	Neat	70	4	98	96:4
4	**2**	1	Neat	70	5	88	94:6
5	**1**	1	THF	70	4	95	96:4
6	**1**	1	PhMe	70	4	97	97:3
7	**1**	1	DME	70	4	81	93:7
8	**1**	1	DMF	70	4	72	93:7
9	**1**	1	Neat	50	4	87	92:8
10	**1**	1	Neat	30	4	26	80:20
11	**1**	0.5	Neat	70	4	61	95:5

[a] b/l: branched/linear.

[b] Catalytic reaction conditions: styrene (1.0 mmol), Ph_2SiH_2 (1.2 mmol), conversions, and product ratios were determined by GC with *n*-dodecane as an internal standard.

TABLE 2 Scope of alkenes for complex **1**-catalyzed hydrosilylation



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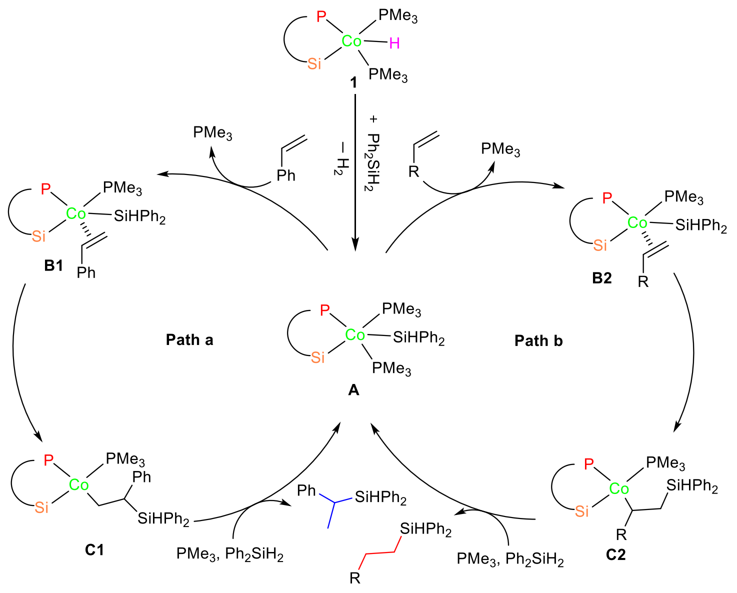
[a] Catalytic reaction conditions: alkene (1.0 mmol), Ph_2SiH_2 (1.2 mmol), complex **1** (1 mol %), neat at 70°C for 4 h; GC yield.
[b] Catalytic reaction conditions: alkene (1.0 mmol), Ph_2SiH_2 (1.2 mmol), complex **1** (1 mol %), neat at 70°C for 5 h; GC yield.
[c] Catalytic reaction conditions: alkene (1.0 mmol), Ph_2SiH_2 (1.2 mmol), complex **1** (1 mol %), neat at 70°C for 10 h; GC yield.

Based on these experimental results and literature reports,[8,11] a possible catalytic reaction mechanism is proposed (Scheme 4). Complex **1** as precatalyst is converted to real catalyst **A** through the reaction with Ph_2SiH_2 with the release of H_2. The silyl intermediate **A** transforms into alkene π-coordinate cobalt intermediate **B1** or **B2** via ligand replacement. The insertion of coordinated alkene into the Co–Si bond of **B1** or **B2** affords alkyl intermediate **C1** or **C2**. The reaction of **C1** or **C2** with Ph_2SiH_2 in the presence of PMe_3 delivers the final product, a novel silane, with the recovery of **A**. Aromatic alkene provides Markovnikov product via **Path a**, whereas aliphatic alkene gives rise to *anti*-Markovnikov product via **Path b**. Although the reaction of *anti*-Markovnikov rule is favorable in thermodynamics, the π,π-interaction between the benzene ring in the substrate and the benzene ring in the catalyst complex makes the hydrosilylation of aromatic olefins proceed according to **Path a.**[12] However, in both mechanisms, we cannot rule out the effect of steric hindrance of substituents on olefin C C bonds on product selectivity.

SCHEME 4 Proposed catalytic mechanism



3 | CONCLUSION

Two silyl [P, Si]-chelate cobalt hydrides, [(*o*-Si(Ph)$_2$-(P^{i}Pr$_2$)C_6H_4)Co(H)(PMe$_3$)$_2$] (**1**) and [(*o*-Si(Ph)$_2$-(PPh$_2$)C_6H_4Co(H)(PMe$_3$)$_2$] (**2**), were prepared through the chelate-assisted Si–H activation of bidentate preligand *o*-HSi(Ph)$_2$-(P^{i}Pr$_2$)C_6H_4 (**L1**) and *o*-HSi(Ph)$_2$-(PPh$_2$)C_6H_4 (**L2**) with [Co(PMe$_3$)$_4$] or [Co(Me)(PMe$_3$)$_4$], respectively. Both cobalt(II) hydrides **1** and **2** can efficiently catalyze hydrosilylation of olefins, and the catalytic effect of complex **1** is better than that of complex **2**. The Markovnikov products were formed from aryl alkenes, whereas the *anti*-Markovnikov products were produced from aliphatic alkenes. In the mechanism study, a silyl cobalt(II) intermediate, [(*o*-Si(Ph)$_2$-(P^{i}Pr$_2$)C_6H_4)Co(SiHPh$_2$)(PMe$_3$)$_2$], as the real catalyst is proposed and supported by in situ-IR study. The molecular structure of complex **1** was determined by single crystal X-ray diffraction analysis.

4 | EXPERIMENTAL SECTION

4.1 | General procedures and materials

Standard vacuum techniques were used in the manipulations of volatiles and air-sensitive substances. Solvents were dried by sodium and distilled under nitrogen before use, and all other chemicals were purchased and used without further purification. The ligands **L1** and **L2** were prepared according to the literature.[13] The MeCo(PMe$_3$)$_4$[14] and Co(PMe$_3$)$_4$[15] were prepared according to reported procedures. IR spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR instrument. Gas chromatography (GC) was performed by using a Shimadzu GC 2014 instrument with *n*-dodecane as an internal standard. The samples were sealed in capillaries for melting point measurement with a WRR instrument.

4.2 | Synthesis of complex 1

Method a:**L1** (0.69 g, 1.83 mmol) in 30 mL THF was added into the solution of Co(PMe$_3$)$_4$ (0.68 g, 1.85 mmol) in 40 mL toluene. The reaction solution was stirred for 24 h at r.t. and the color of the solution gradually changed from brown to red. The volatiles of the solution were removed under vaccum. The residue was extracted with 50 mL *n*-pentane and 50 mL diethyl ether. Complex **1** was obtained as orange-red crystals at −20°C in the yield of 65% (0.70 g). **Method b**:**L1** (0.71 g, 1.89 mmol) in 30 mL THF was added into the solution of CoMe(PMe$_3$)$_4$ (0.74 g, 1.95 mmol) in 30 mL toluene. The reaction solution was stirred for 24 h at r.t., and the color of the solution gradually changed from brown to red. The volatiles of the solution were removed under vaccum. The residue was extracted with 50 mL *n*-pentane and 50 mL diethyl ether. Complex **1** was obtained as orange-red crystals in the yield of 68% (0.73 g). Dec : > 149°C. IR (Nujol mull, KBr, cm^{-1}): 1755 ν(Co–H), 932 ρ(PCH$_3$).

4.3 | Synthesis of complex 2

The synthetic methods of complex **2** are the same as those of complex **1**.

Method a: yield (60%). **Method b**: yield (65%). M.p.: 116–118°C. IR (Nujol mull, KBr, cm^{-1}): 1776 ν(Co–H), 936 $\rho(PCH_3)$.

4.4 | General procedure for cobalt-catalyzed hydrosilylation

Under an N_2 atmosphere, complex **1** (1% mmol) was added to a 20 mL Schlenk tube containing a magnetic stirrer. Styrene (0.11 g, 1.0 mmol), diphenylsilane (0.22 g, 1.2 mmol), and *n*-dodecane (0.17 g, 1.0 mmol) were added in order. The mixture was stirred at 70°C for 4 h. The resulting solution was quenched with ethyl acetate. The combined organic fractions were concentrated in vacuum. The yield was determined by GC.

4.5 | Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction data of complex **1** were collected on a STOE STADIVARI Cu diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 using the SHELXL program[16] through the OLEX interface.[17] All non-hydrogen atoms were refined anisotropically. CCDC-1913000 contains supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223–336-033; e-mail: deposit@ccdc.cam.ac.uk).

ACKNOWLEDGMENT

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CONFLICT OF INTEREST

There are no conflicts to declare.

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