Reactions of a hydrido(hydrogermylene)tungsten complex with some heterocumulenes: hydrogermylation and thermal rearrangement†‡

Hisako Hashimoto,* Tetsuya Fukuda and Hiromi Tobita*

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Reaction of a hydrido(hydrogermylene)tungsten complex $Cp^*(CO)_2(H)W{=}Ge(H)[C(SiMe_3)_3]$ (**1**) with isocyanate PhNCO at room temperature resulted in stoichiometric hydrogermylation at the C=O bond to give a W–Ge–O–C–N five-membered chelate complex. In contrast, the reactions of **1** with isothiocyanates RNCS (R = Ph, Me) led to hydrogermylation at the C=N bond to yield W–Ge–N–C–S five-membered chelate complexes. In both cases, the most electronegative atom in the isocyanate or isothiocyanates attacks the germanium of **1**. Gentle heating of the latter chelate complexes in hydrocarbon solvents caused rearrangement of the chelate ring to cleanly afford W–Ge–S–C–N chelate complexes. Molecular structures of these three different types of five-membered metallacycles have been determined by X-ray crystallography, and possible reaction mechanisms for the hydrogermylation and rearrangement reactions have been proposed.

Introduction

Transition metal complexes with divalent Group 14 element species as a ligand have attracted considerable attention in the fields of coordination chemistry and organometallic chemistry. These complexes are regarded to have a double bond between the transition metal (M) and Group 14 element (E), and, in the case of carbene complexes with E=C, a number of characteristic and useful reactions represented by olefin metathesis have been discovered and intensely studied.[1,2] The high and unique reactivity of the M=C double bond plays an important role to achieve these reactions. Among the other Group 14 element analogues of carbene complexes, silylene complexes have been extensively synthesised, and their chemistry investigated.[3,4] In contrast, although the heavier analogues, *viz*. germylene, stannylene and plumbylene complexes, have been known for a longer period, their reactivity has been far less investigated.[5,6] This is partly because the stabilisation effect of the π-basic and/or sterically hindered substituents on the Group 14 element is too strong to retain enough reactivity on the M=E double bond toward various reagents or organic molecules.

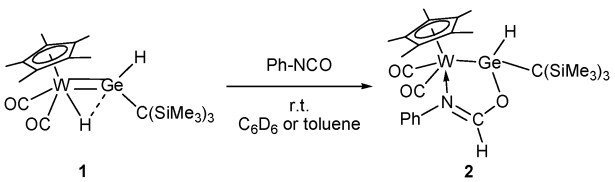
Recently, we synthesised new types of silylene tungsten[7] and ruthenium[8] complex containing a monosubstituted silylene $Si(H)[C(SiMe_3)_3]$ as a ligand, *viz*. $Cp^*(CO)_2(H)W{=}Si(H)[C(SiMe_3)_3]$[7] and $Cp^*(CO)(H)Ru{=}Si(H)[C(SiMe_3)_3]$,[8] and found that these complexes showed unprecedentedly high reactivity toward a variety of organic substrates.[7,8] More recently, we prepared a new type of germylene complex using the same concept, $Cp^*(CO)_2(H)W{=}Ge(H)[C(SiMe_3)_3]$ (**1**), and revealed that it reacted with nitriles and ketones cleanly under mild conditions to give hydrogermylation products.[9] We soon found that **1** was also highly reactive toward various organic substrates, but the reaction patterns were rather different from those of its silicon analogue. We now report the unprecedented reactions of **1** with two types of heterocumulenes, *viz*. isocyanate and isothiocyanate, and a unique thermal rearrangement of the products with isothiocyanate.

Results and discussion

Reaction of 1 with phenylisocyanate

Reaction at room temperature. In an NMR-scale reaction, germylene complex **1** was allowed to react with 2.4 equiv. of phenylisocyanate at room temperature in C_6D_6. After 24 h, **1** was observed to be consumed completely by the 1 : 1 reaction with phenylisocyanate to give $Cp^*(CO)_2W[Ge(H)(OCH{=}NPh)\{C(SiMe_3)_3\}]$ (**2**) in 85% NMR yield. On the basis of this observation, we next performed a synthetic-scale reaction of **1** with phenylisocyanate in 1 : 1 ratio. As a result, **2** was obtained in 61% yield as reddish-orange crystals (Scheme 1).

In the ^1H NMR spectrum of **2**, the signal assigned to N=CH is observed at δ 7.58 as a singlet, with satellites by a coupling to ^{183}W together with the strong signals of $SiMe_3$ and Cp^*. The signal of GeH overlaps with those of phenyl protons and cannot be distinguished from them. The ^{13}C NMR spectrum shows the signal of imidate carbon N=CH–O at δ 170.7. The IR spectrum exhibits two CO stretching bands for carbonyl ligands at 1918 (sym) and 1832 (asym) cm^{-1}. The intensity ratio is I_{sym}/I_{asym} = 1.27, which indicates that the



Scheme 1 Reaction of **1** with phenylisocyanate.

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan. E-mail: hhashimoto@m.tains.tohoku.ac.jp, tobita@m.tains.tohoku.ac.jp; Fax: +81 22 795 6543; Tel: +81 22 795 6539

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angle made by the two carbonyl ligands and tungsten center 2θ is 82° based on the relationship $I_{sym}/I_{asym} = \text{cotan}^2\theta$.[10] This values roughly agrees with the experimental value 73.5(2)° determined by X-ray crystallography (*vide infra*), and demonstrates that the two carbonyl ligands are located in a *cis* configuration.

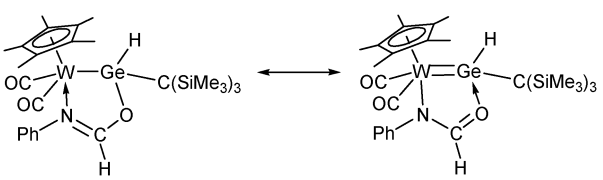
X-ray structure of 2. The ORTEP drawing of complex **2** is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. The tungsten center takes a four-legged piano-stool geometry, and has a W–Ge–O–C–N five-membered chelate ring. The W–Ge bond length is 2.6080(5) Å, which is in the range of normal W–Ge single bonds (2.50–2.75 Å).[11] The O–C and C–N bond lengths in the chelate ring are 1.267(7) and 1.306(6) Å, respectively, which are intermediate values between the corresponding single and double bonds: C=O 1.19–1.32 Å,[12] C–O 1.26–1.39 Å;[13] C=N 1.15–1.36 Å,[14,15] C–N 1.27–1.37 Å.[16] This structural feature can be rationalised by the significant contribution of two canonical forms for **2** depicted in Scheme 2.

A possible reaction mechanism. A possible mechanism for formation of the five-membered chelate ring of **2** is illustrated in Scheme 3. Because the W=Ge bond of **1** is considered to be polarized as $W^{\delta-}=Ge^{\delta+}$, if the steric effect of the substituent can be neglected, the most electronegative atom in a phenylisocyanate molecule is expected to attack the germanium atom of **2** in the initial step. Since the Pauling electronegativity of oxygen (3.44) is larger than that of nitrogen (3.04), oxygen is coordinated to the germylene ligand of **2** to form intermediate **A**. This coordination makes the isocyanate carbon more electrophilic, and induces the migration of a hydrido ligand on the tungsten center to the isocyanate carbon to produce intermediate **B**. Finally, the lone pair on the nitrogen atom attacks the tungsten center to give **2**. This reaction mechanism is closely akin to those of the reactions of **1** with nitriles[9] and ketones[9] up to the stage of the formation of intermediate **B**, but the final step is different from them.

This clean reaction is in sharp contrast to the reaction of the silicon analogue of **1** with phenylisocyanate that gave a complicated reaction mixture.[17]

Reactions of 1 with phenyl- and methylisothiocyanate

Reactions at room temperature. Sulfur is less electronegative not only than oxygen but also than nitrogen (Pauling electronegativity of sulfur: 2.58). Moreover, as a nucleophilic site of heterocumulenes, sulfur is softer than oxygen and nitrogen. Therefore, we became interested in whether or not these differences could render the reaction mode of **1** with isothiocyanate different from that of **1** with isocyanate.



Scheme 2 Principal canonical forms for **2**.

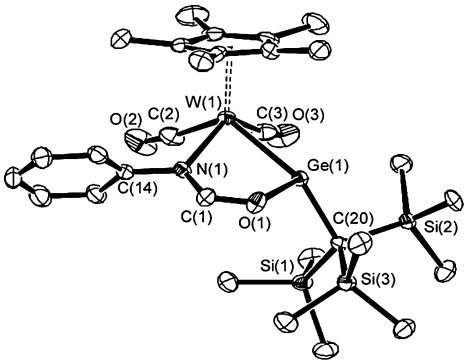
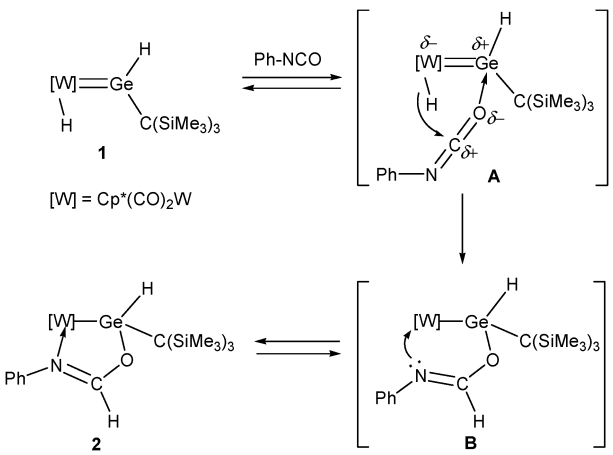


Fig. 1 ORTEP drawing of **2** with 50% thermal ellipsoids. H atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for **2**

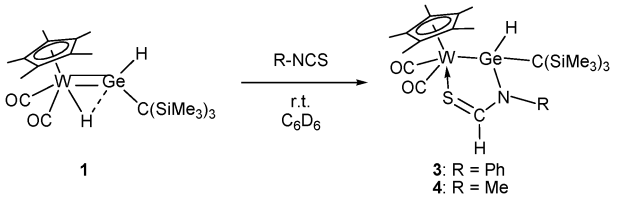
W(1)–Ge(1)	2.6080(5)	N(1)–W(1)–Ge(1)	74.77(11)
Ge(1)–O(1)	1.945(4)	W(1)–Ge(1)–O(1)	95.54(11)
O(1)–C(1)	1.267(7)	Ge(1)–O(1)–C(1)	115.2(3)
C(1)–N(1)	1.306(6)	O(1)–C(1)–N(1)	126.0(5)
W(1)–N(1)	2.250(4)	C(1)–N(1)–W(1)	123.3(3)
W(1)–C(2)	1.944(6)	C(1)–N(1)–C(14)	113.7(4)
W(1)–C(3)	1.968(6)	C(14)–N(1)–W(1)	122.7(3)
N(1)–C(14)	1.436(6)	C(20)–Ge(1)–O(1)	99.44(17)
Ge(1)–C(20)	2.017(5)	C(2)–W(1)–C(3)	73.5(2)



Scheme 3 A possible mechanism for the reaction of **1** with phenylisocyanate.

The reaction of **1** with phenylisothiocyanate (2.1 equiv.) was first carried out in C_6D_6 in an NMR tube and was monitored by ^{1}H NMR spectroscopy. After 67 h at room temperature, it was observed that the 1 : 1 reaction gave $Cp^*(CO)_2W[Ge(H)(NPhCH{=}S)\{C(SiMe_3)_3\}]$ (**3**) in 87% NMR yield (Scheme 4). In a similar manner, the reaction of **1** with methylisothiocyanate (1.9 equiv.) provided $Cp^*(CO)_2W[Ge(H)(NMeCH{=}S)\{C(SiMe_3)_3\}]$ (**4**) in 89% NMR yield after 27 h at room temperature (Scheme 4). Both **3** and **4** were isolated as orange-red crystals in 71 and 63% yields, respectively, in the synthetic-scale reactions and were fully characterized.

The structure of **3** was unambiguously determined by X-ray crystal structure analysis (*vide infra*). Importantly, the germanium atom in **3** is bound to nitrogen instead of sulfur.



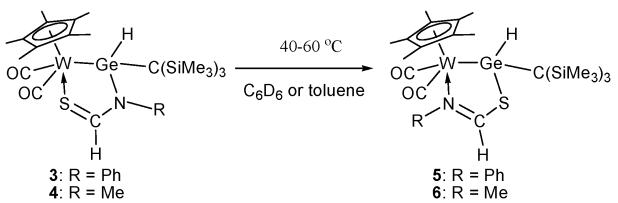
Scheme 4 Reactions of **1** with isothiocyanates.

In the ^{1}H NMR spectrum of **3**, the signals assigned to GeH and NCH are observed as doublets at δ 7.20 and 8.46, respectively, which are coupled to each other through four bonds with ^4J = 1.8 Hz. The observation of this long-range coupling is attributable to the geometry of the H–Ge–N–C–H linkage fixed in the shape of letter W. The ^{13}C NMR spectrum of **3** shows the carbon of NCH=S at δ 190.6, which is about 20 ppm downfield-shifted from the corresponding N=CH–O signal (δ 170.7) of **2**. The IR spectrum of **3** exhibits two C=O stretching bands for carbonyl ligands at 1922 (sym) and 1845 (asym) cm^{-1}, and the intensity ratio (I_{sym}/I_{asym} = 1.21) shows that the two carbonyl ligands are mutually *cis* in configuration.

The spectroscopic features of **4** closely resemble those of **3** except those originating from the existence of a methyl group on the nitrogen instead of a phenyl group. The methyl group appears at δ 2.97 in the ^{1}H NMR and at δ 45.6 in the ^{13}C NMR. In addition, the mass spectrum of **4** clearly shows the molecular ion peak at m/z 755.

Thermal rearrangement under gentle heating. Interestingly, heating of a C_6D_6 or toluene solution of **3** at 40 °C for several days induced clean conversion to an isomer, Cp*(CO)$_2$W[Ge(H)(SCH=NPh){C(SiMe$_3$)$_3$}] (**5**), which was isolated in 54% yield as orange-red crystals (Scheme 5). Similarly, heating of a C_6D_6 solution of **4** at 60 °C for several days resulted in clean rearrangement to Cp*(CO)$_2$W[Ge(H)-(SCH=NMe){C(SiMe$_3$)$_3$}] (**6**), which was isolated in 49% yield as orange-red crystals (Scheme 5).

The molecular structure of **5** was determined by X-ray crystal structure analysis (*vide infra*), which revealed that the structure was identical with that of **2** except that the sulfur atom was present instead of the oxygen atom. In the ^{1}H NMR spectrum of **5**, the signals assigned to GeH and NCH are observed as doublets at δ 6.42 and 8.18, respectively, which are coupled to each other through four bonds with ^4J = 1.8 Hz. This spectroscopic feature is analogous to that of complex **3**, but the chemical shifts are somewhat upfield-shifted compared to **3**. The ^{13}C NMR spectrum of **5** shows the carbon of N=CHS at δ 188.7, which is close to the chemical shift of the NCH=S of **3** (δ 190.6) and significantly downfield-shifted



Scheme 5 Thermal rearrangement of **3** and **4**.

from the corresponding N=CH–O signal (δ 170.7) of **2**. The IR spectrum of **5** exhibits two C=O stretching bands for carbonyl ligands at 1920 (sym) and 1835 (asym) cm^{-1}, and the intensity ratio (I_{sym}/I_{asym} = 1.61) shows that the two carbonyl ligands are mutually *cis* in configuration.

The spectroscopic features of **6** also closely resemble those of **5** and also **4**, and the methyl group on the nitrogen appears at δ 3.17 in the ^{1}H NMR and at δ 58.9 in the ^{13}C NMR. In the mass spectrum of **6**, the molecular ion peak is observed at m/z 755, more strongly than that of the isomer **4**.

X-ray structures of 3 and 5. The ORTEP drawings of complexes **3** and **5** are shown in Fig. 2 and 3, and selected bond lengths and angles are given in Tables 2 and 3, respectively.

Complex **3** has a W–Ge–N–C–S five-membered chelate ring, while the rearrangement product **5** has a W–Ge–S–C–N five-membered chelate ring. The W–Ge, C–S and C–N bond lengths of **3** are 2.6326(3), 1.688(3) and 1.303(4) Å, respectively, and those of **5** are 2.6364(8), 1.715(8) and 1.303(11) Å, respectively. The W–Ge lengths correspond to the normal single-bond lengths, while the C–S and C–N lengths lie between the lengths of typical double bonds (C=S 1.60–1.70 Å)[18] and single bonds (C–S 1.65–1.80 Å).[15,19] These structural features of **3** and **5** are attributable to the resonance between two canonical forms illustrated in Scheme 6. The C–S bond of **5** is slightly longer than in **3**, probably because the affinity of germanium toward sulfur is stronger than that toward nitrogen, and this makes the contribution of the canonical form on the left-hand side in Scheme 6(b) more important.

Comparison of the structure of **5** with that of the oxygen analogue **2** is also important. The W–Ge bond of **5** (2.6364(8) Å) is significantly longer than that of **2** (2.6080(5) Å). This elongation is attributable to the higher contribution of the canonical form on the left-hand side in Scheme 6(b) for **5** compared to that on the left-hand side in Scheme 2 for **2**, which is caused by the stronger affinity of germanium toward sulfur compared to that toward oxygen. The Ge–S (2.343(2) Å) and C–S (1.715(8) Å) bonds in **5** are much longer than the corresponding Ge–O (1.945(4) Å) and C–O (1.267(7) Å) bonds

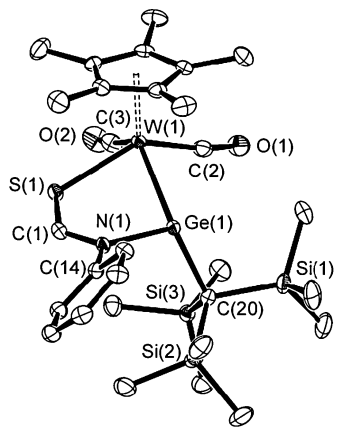


Fig. 2 ORTEP drawing of **3** with 50% thermal ellipsoids. H atoms are omitted for clarity.

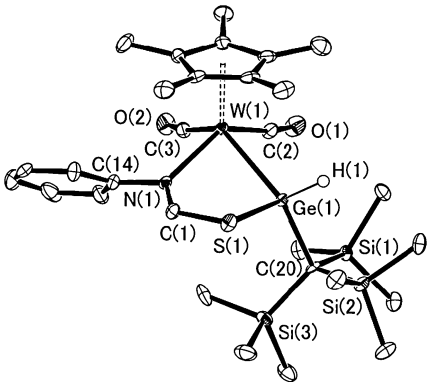


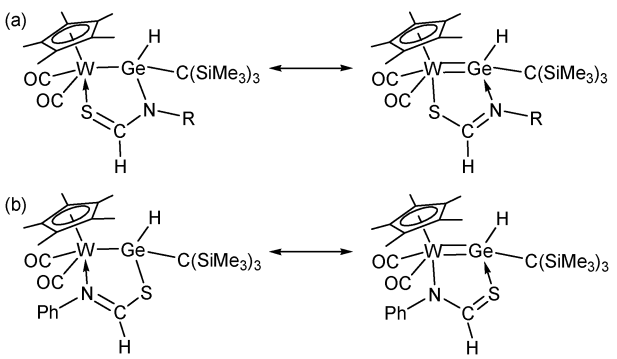
Fig. 3 ORTEP drawing of **5** with 50% thermal ellipsoids. H atoms except H(1) are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for **3**

W(1)–Ge(1)	2.6326(3)	S(1)–W(1)–Ge(1)	78.453(19)
Ge(1)–N(1)	2.068(2)	W(1)–Ge(1)–N(1)	97.35(7)
S(1)–C(1)	1.688(3)	Ge(1)–N(1)–C(1)	115.3 (2)
C(1)–N(1)	1.303(4)	S(1)–C(1)–N(1)	126.0(2)
S(1)–W(1)	2.4657(7)	C(1)–S(1)–W(1)	109.29(11)
W(1)–C(2)	1.957(3)	C(1)–N(1)–C(14)	115.7(3)
W(1)–C(3)	1.953(4)	C(14)–N(1)–Ge(1)	129.1(2)
N(1)–C(14)	1.447(4)	W(1)–Ge(1)–C(20)	133.58(9)
Ge(1)–C(20)	2.055(3)	C(20)–Ge(1)–N(1)	109.13(11)
		C(2)–W(1)–C(3)	74.68(14)

Table 3 Selected bond lengths (Å) and angles (°) for **5**

W(1)–Ge(1)	2.6364(8)	N(1)–W(1)–Ge(1)	78.91(17)
Ge(1)–S(1)	2.343(2)	W(1)–Ge(1)–S(1)	95.42(6)
S(1)–C(1)	1.715(8)	Ge(1)–S(1)–C(1)	96.4(3)
C(1)–N(1)	1.303(11)	S(1)–C(1)–N(1)	127.8(7)
N(1)–W(1)	2.243(7)	C(1)–N(1)–W(1)	125.1(6)
W(1)–C(2)	1.949(9)	C(1)–N(1)–C(14)	113.2(7)
W(1)–C(3)	1.966(9)	C(14)–N(1)–W(1)	120.9(5)
N(1)–C(14)	1.447(11)	W(1)–Ge(1)–C(20)	140.8(2)
Ge(1)–C20)	2.031(7)	C(20)–Ge(1)–S(1)	103.0(2)
Ge(1)–H(1)	1.47(9)	C(2)–W(1)–C(3)	71.6(4)



Scheme 6 Principal canonical forms for (a) **3** and (b) **5**.

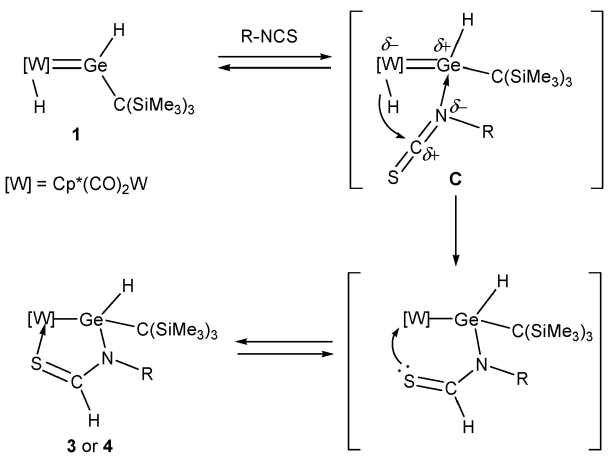
in **2**. These differences almost exactly correspond to the increase of the atomic radii from oxygen (0.66 Å) to sulfur (1.04 Å).

A possible reaction and rearrangement mechanism. The primary formation of **3** and **4** followed by slow conversion to **5** and **6** on warming clearly shows that **3** and **4** are kinetically-controlled products, while **5** and **6** are thermodynamically-controlled products. Thus, because nitrogen is more electronegative than sulfur, the attack of the nitrogen atom in isothiocyanates to germanium of **1** dominates the attack of the sulfur atom in the same molecule. This leads to intermediate **C** with a N→Ge dative bond, and then hydride migration from tungsten to the carbon of isothiocyanates followed by coordination of sulfur to the tungsten center gives **3** and **4** as kinetically-controlled products (Scheme 7).

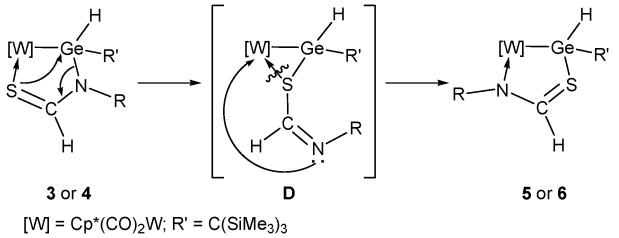
Complexes **5** and **6** are thermodynamically more stable than **3** and **4** not only because the Ge–S bond is stronger than the Ge–N bond but also because the steric repulsion between the substituent on nitrogen and the $C(SiMe_3)_3$ group on germanium in **3** or **4** is relieved by rearrangement to **5** or **6**. The steric repulsion between Ph and $C(SiMe_3)_3$ groups in **3** seems to be larger than that between Me and $C(SiMe_3)_3$ groups in **4**, and this perhaps requires a higher reaction temperature for **4** compared to **3**. For the rearrangement from **3** and **4** to **5** and **6**, there are at least two possible mechanisms. One mechanism involves the elimination of free isothiocyanate from **3** or **4** *via* the reverse reaction of Scheme 7, followed by the attack of the sulfur atom of the isothiocyanate to the germanium of **1** to give **5** or **6**. Another mechanism involves chelate-ring contraction and expansion *via* three-membered-ring intermediate **D** with a bridging sulfur ligand (Scheme 8). At present, we have no experimental results to rule out either of these.

Conclusions

A hydrido(hydrogermylene)tungsten complex **1** was highly reactive toward some heterocumulenes. Thus, PhNCO attacks the germylene ligand of **1** with the oxygen atom at room temperature, and subsequent hydride migration from tungsten to the isocyanate carbon followed by coordination of the nitrogen atom afforded a five-membered chelate complex **2**. In contrast, RNCS attacks the germylene ligand of **1** with the nitrogen atom, and subsequent hydride migration followed by sulfur coordination gave five-membered chelate complexes **3** and **4**. Complexes **3** and **4** were found to be kinetically-controlled



Scheme 7 A possible mechanism for the reaction of **1** with isothiocyanates.



Scheme 8 A possible mechanism for thermal rearrangement of **3** or **4** to **5** or **6**.

products, and rearranged to thermodynamically-controlled products **5** and **6**, respectively, on gentle heating in solution. The unprecedented unique structures of **2**, **3** and **5** were determined by X-ray crystallography. In this work, we have demonstrated that the reactions of germylene complexes with heterocumulenes can provide a convenient synthetic route to novel metallacycles with unprecedented combinations of elements or linkages.

Experimental

General procedures and materials

All manipulations of air- and moisture-sensitive compounds were carried out under a dry nitrogen or argon atmosphere in a glovebox. Toluene, benzene, hexane and pentane were distilled from sodium–benzophenone ketyl and then from calcium hydride, and stored in a glovebox prior to use. Benzene-d_6 was distilled from calcium hydride and stored in a glovebox before use. Reagent-grade phenylisocyanate, phenylisothiocyanate and methylisothiocyanate were distilled and stored in a glove box before use. $Cp^*(CO)_2(H)W{=}Ge(H)[C(SiMe_3)_3]$ (**1**) was prepared according to the literature method.[9] NMR spectra were recorded on a Bruker AVANCE300 spectrometer. The residual proton (C_6D_5H: 7.15 ppm) and the carbon (C_6D_6: 128.0 ppm) resonances of deuterated solvents were used as internal references for ^1H and ^{13}C NMR spectroscopy, respectively. IR spectra were measured on a Horiba FT-200 spectrometer. Mass spectral data were obtained using a Shimadzu GCMS-QP5050 spectrometer.

Reaction of 1 with phenylisocyanate

NMR-scale reaction. An NMR sample tube equipped with a ground joint was charged with **1** (10 mg, 0.014 mmol), phenylisocyanate (3.8 μL, 0.035 mmol) and a small amount of hexamethylbenzene as an internal standard, and then C_6D_6 (0.6 mL) was added. This sample tube was connected to a vacuum line and degassed with freeze–pump–thaw cycles, and was flame-sealed. The reaction in this solution at room temperature was monitored by ^1H NMR spectroscopy, which showed that, after 24 h, all of **1** was consumed to give $Cp^*(CO)_2W[Ge(H)(OCH{=}NPh)\{C(SiMe_3)_3\}]$ (**2**) in 85% NMR yield.

Synthetic-scale reaction. A 15 mL Schlenk tube equipped with a magnetic stirrer was charged with **1** (100 mg, 0.14 mmol), phenylisocyanate (16 μL, 0.147 mmol) and benzene (3 mL). The solution was stirred at room temperature for 26 h, then the volatiles were removed under reduced pressure and the residue was recrystallised from hexane to give **2** (69 mg, 61%) as reddish-orange crystals. (Found: C, 43.79; H, 6.25; N, 1.87. Calc. for $C_{29}H_{49}GeNO_3Si_3W$: C, 43.52; H, 6.17; N, 1.75%); ν_{max}/cm^{-1} 1918 and 1832 (CO); δ_H (300 MHz; C_6D_6) 0.48 (27H, s, $C(SiMe_3)_3$), 1.52 (15H, s, Cp*), 6.88 (1H, t, ^3J 7.0, Ph), 6.98 (3H, m, Ph + GeH), 7.04 (2H, t, ^3J 7.0, Ph), 7.58 (1H, s, ^3J(WH satellite) 11.4, N=CH); δ_C (75.5 MHz; C_6D_6) 4.7 ($SiMe_3$), 10.5 ($C_5\mathit{Me}_5$), 13.6 ($\mathit{C}(SiMe_3)_3$), 101.9 (C_5Me_5), 126.0, 126.2, 128.6, 152.2 (Ph), 170.7 (N=CH), 245.3 (CO), 245.6 (CO); δ_{Si} (59.6 MHz; C_6D_6; DEPT; 298 K) −1.4; *m*/*z* (EI) 801 (M^+, 10.0%), 773 (M^+ − CO, 13.2), 680 (M^+ − PhNHCHO, 100), 514 (M^+ − $C(SiMe_3)_3$ − 2CO, 10.4), 439 ($Cp^*W(PhNCHO)^+$, 18.9), 332 ($W(CO)(PhNCHO)^+$, 8.5), 73 ($SiMe_3^+$, 83).

Reaction of 1 with phenylisothiocyanate

NMR-scale reaction. In a manner similar to that for the reaction of **1** with phenylisocyanate, reaction of **1** (10 mg, 0.014 mmol) with phenylisothiocyanate (4.0 mg, 0.030 mmol) in a C_6D_6 solution (0.6 mL) was monitored at room temperature by ^1H NMR spectroscopy. After 67 h, all of **1** was consumed and $Cp^*(CO)_2W[Ge(H)(NPhCH{=}S)\{C(SiMe_3)_3\}]$ (**3**) was formed in 87% NMR yield. Then, the solution was heated at 40 °C while being monitored periodically by ^1H NMR spectroscopy. After 4 days, the signals of **3** disappeared and new signals for $Cp^*(CO)_2W[Ge(H)(SCH{=}NPh)\{C(SiMe_3)_3\}]$ (**5**) were observed in 83% NMR yield based on **1**.

Synthetic-scale reaction. A 20 mL Schlenk tube equipped with a magnetic stirrer was charged with **1** (50 mg, 0.070 mmol), phenylisothiocyanate (9 μL, 0.07 mmol) and toluene (3 mL). The solution was stirred at room temperature for 6 days, then the volatiles were removed under reduced pressure and the residual solid was washed with pentane to give **3** (40 mg, 71%) as orange-red crystals. (Found: C, 42.91; H, 6.15; N, 1.92. Calc. for $C_{29}H_{49}GeNO_2SSi_3W$: C, 42.66; H, 6.05; N, 1.72%); ν_{max}/cm^{-1} 1922 and 1845 (CO); δ_H (300 MHz; C_6D_6) 0.31 (27H, s, $C(SiMe_3)_3$), 1.64 (15H, s, Cp*), 6.86 (1H, t, ^3J 7.0, Ph), 6.96 (2H, t, ^3J 7.0, Ph), 7.04 (2H, t, ^3J 7.0, Ph), 7.20 (1H, d, ^4J 1.8, GeH), 8.46 (1H, d, ^4J 1.8, N=CH); δ_C (75.5 MHz; C_6D_6) 6.1 ($SiMe_3$), 10.3 ($C_5\mathit{Me}_5$), 18.3 ($\mathit{C}(SiMe_3)_3$), 101.6 (C_5Me_5), 124.2, 126.7, 129.2, 148.2 (Ph), 190.6 (S=CHN), 239.8 (CO), 240.8 (CO); δ_{Si} (59.6 MHz; C_6D_6; DEPT; 298 K) −2.3; *m*/*z* (EI) 817 (M^+, 0.1%), 761 (M^+ − 2CO, 1.3), 683 (12.9), 680 (M^+ − PhNHCHS, 9.1), 511 (M^+ − $GeHC(SiMe_3)_3$, 17.7), 455 ($Cp^*WH(PhNCHS)^+$, 30.0), 421 ($Cp^*W(CO)Ge^+$, 9.1), 348 ($W(CO)(PhNCHS)^+$, 8.0), 73 ($SiMe_3^+$, 100).

The solid of **3** was dissolved in 3 mL of toluene and stirred for 7 days at 40 °C. After removal of volatiles, the residue was washed with pentane to afford **5** (30 mg, 54%) as orange-red crystals. (Found: C, 42.42; H, 5.79; N, 1.70. Calc. for $C_{29}H_{49}GeNO_2SSi_3W$: C, 42.66; H, 6.05; N, 1.72%); ν_{max}/cm^{-1} 1920 and 1835 (CO); δ_H (300 MHz; C_6D_6) 0.50 (27H, s, $C(SiMe_3)_3$), 1.53 (15H, s, Cp*), 6.42 (1H, d, ^4J 1.8,

GeH), 6.83 (2H, dd, ^3J 7.5, ^4J 1.1, Ph), 6.88 (1H, tt, ^3J 7.5, ^4J 1.1, Ph), 7.04 (2H, t, ^3J 7.0, Ph), 8.18 (1H, d, ^4J 1.8, N=CH); δ_C (75.5 MHz; C_6D_6) 5.2 ($SiMe_3$), 10.3 (C_5Me_5), 12.9 ($C(SiMe_3)_3$), 102.3 (C_5Me_5), 123.8, 126.7, 128.9, 159.0 (Ph), 188.7 (N=CHS), 243.5 (CO), 246.2 (CO); δ_{Si} (59.6 MHz; C_6D_6; DEPT; 298 K) −1.2; *m*/*z* (EI) 817 (M^+, 2.1%), 759 (M^+ − 2CO− 2H, 4.3), 682 (M^+ − PhNCS, 13.5), 511 (M^+ − $GeHC(SiMe_3)_3$, 15.8), 455 (Cp*WH(PhNCS), 27.0), 421 (Cp*W(CO)Ge^+, 8.8), 348 (W(CO)(PhNCS)H, 7.1), 73 ($SiMe_3^+$, 100).

Reaction of 1 with methylisothiocyanate

NMR-scale reaction. In a manner similar to that for the reaction of **1** with phenylisocyanate, reaction of **1** (10 mg, 0.014 mmol) with methylisothiocyanate (2.0 mg, 0.027 mmol) in a C_6D_6 solution (0.6 mL) was monitored at room temperature by ^{1}H NMR spectroscopy. After 27 h, all of **1** was consumed and $Cp^*(CO)_2W[Ge(H)(NMeCH{=}S)\{C(SiMe_3)_3\}]$ (**4**) was formed in 89% NMR yield. A solution of **4** newly prepared was heated at 60 °C while the solution was monitored by ^{1}H NMR spectroscopy. After 124 h, the signals of **4** disappeared and new signals for $Cp^*(CO)_2W[Ge(H)(SCH{=}NMe)\{C(SiMe_3)_3\}]$ (**6**) were observed in 93% NMR yield.

Synthetic-scale reaction. An NMR sample tube equipped with a Teflon needle valve was charged with **1** (30 mg, 0.044 mmol), methylisothiocyanate (5.2 mg, 0.071 mmol) and C_6D_6 (0.6 mL). The solution was stirred at room temperature for 96 h, then the volatiles were removed under reduced pressure and the residual solid was washed with hexane to give **4** (21 mg, 63%) as orange-red crystals. (Found: C, 38.34; H, 6.29; N, 1.87. Calc. for $C_{24}H_{47}GeNO_2SSi_3W$: C, 38.21; H, 6.28; N, 1.86%); ν_{max}/cm^{-1} 1927 and 1841 (CO), 1513 (CN); δ_H (300 MHz; C_6D_6) 0.42 (27H, s, $C(SiMe_3)_3$), 1.59 (15H, s, Cp*), 2.97 (3H, d, ^4J 0.7, NMe), 6.30 (1H, d, ^4J 1.6, ^3J(WH satellite) 9.0, GeH), 7.61 (1H, dd, ^4J 1.6, ^4J 0.7, N=CH); δ_C (75.5 MHz; C_6D_6) 6.3 ($SiMe_3$), 10.3 (C_5Me_5), 14.6 ($C(SiMe_3)_3$), 45.6 (NMe), 101.4 (C_5Me_5), 189.4 (S=CHN), 241.3 (CO), 241.5 (CO); δ_{Si} (59.6 MHz; C_6D_6; DEPT; 298 K) −1.9; *m*/*z* (EI) 755 (M^+, 7.9), 710 (M^+ − HCS, 3.0), 699 (M^+ − 2CO, 8.6), 680 (M^+ − MeNHCHS, 17.2), 652 (M^+ − MeNHCHS − CO, 10.8), 449 ($Cp^*W(CO)_2Ge^+$, 40.9), 421 (Cp*W(CO)Ge^+, 15.2), 393 (Cp*W(MeNCHS)$^+$, 31.8), 73 ($SiMe_3^+$, 100).

In a similar manner, **1** (35.5 mg, 0.052 mmol) and methylisothiocyanate (13.0 mg, 0.177 mmol) were dissolved in C_6D_6 (0.6 mL) and the solution was stirred for 21 h at room temperature to prepare a solution of **4**. The solution was then heated at 60 °C for 187 h. Removal of volatiles from the solution and recrystallisation of the residue from hexane afforded **6** (19.2 mg, 49%) as orange-red crystals. ν_{max}/cm^{-1} 1919 and 1834 (CO), 1525 (CN); δ_H (300 MHz; C_6D_6) 0.47 (27H, s, $C(SiMe_3)_3$), 1.54 (15H, s, Cp*), 3.17 (3H, s, NMe), 6.30 (1H, d, ^4J 1.5, ^3J(WH satellite) 12.6, GeH), 7.81 (1 H, bs, N=CH); δ_C (75.5 MHz; C_6D_6) 5.0 ($SiMe_3$), 10.0 (C_5Me_5), 11.4 ($C(SiMe_3)_3$), 58.9 (NMe), 102.1 (C_5Me_5), 186.2 (N=CHS), 244.6 (CO), 247.3 (CO); δ_{Si} (59.6 MHz; C_6D_6; DEPT; 298 K) −1.1; *m*/*z* (ESI) 778.1266 (M^+, $C_{24}H_{47}GeNO_2SSi_3W$ + Na requires 778.1249); *m*/*z* (EI) 755 (M^+, 32.1), 710 (M^+ − HCS, 13.6), 699 (M^+ − 2CO, 20.2), 680 (M^+ − MeNHCHS, 25.7), 652 (M^+ − MeNHCHS − CO, 9.9), 522 (M^+ − $C(SiMe_3)_3$ − 2H, 18.8), 494 (M^+ − $C(SiMe_3)_3$ − 2H − CO, 11.9), 466 (M^+ − $C(SiMe_3)_3$ − 2H − 2CO, 27.9), 449 ($Cp^*W(CO)_2Ge^+$, 100), 421 (Cp*W(CO)Ge^+, 13.2), 393 (Cp*W(MeNCHS)$^+$, 74.8), 73 ($SiMe_3^+$, 67.2).

X-Ray crystal structure determinations of 2, 3 and 5

XRD-quality single crystals of **2**, **3** and **5** were obtained by recrystallisation from a mixture of toluene–hexane (1:6). Diffraction measurements were made on a RIGAKU RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo-Kα radiation. Single crystals of **2**, **3** and **5** were coated with liquid paraffin and were mounted on a nylon loop, and transferred into the cold gas stream of the diffractometer. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with 2 different goniometer settings. Empirical absorption collections were made using the program NUMABS.[20] The structures were solved by Patterson and Fourier transform methods (SHELXS-97)[21] and refined by the full-matrix least-squares method on F^2 with SHELXL-97[22] using Yadokari-XG.[23]

For **2**, one molecule of C_6D_6 was found in the asymmetric unit cell. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. The position of the hydrogen atom of Ge–H was not found from the Fourier-difference electron-density. All other hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. For **3**, all non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. The position of the hydrogen atom of Ge–H was not found from the Fourier-difference electron-density. All other hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. For **5**, all non-hydrogen atoms except C(7) were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. The atom C(7) was refined with isotropic thermal parameters because it gave a negative value when it was treated with anisotropic displacement parameters. The position of the hydrogen atom of Ge–H was found from the Fourier-difference electron-density and refined with isotropic thermal parameters. All other hydrogen atoms of **5** were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. ORTEP drawings of **2**, **3** and **5** are depicted in Fig. 1, 2 and 3, respectively. Selected bond lengths and angles for **2**, **3** and **5** are listed in Tables 1, Table 2, Table 3, respectively. Crystallographic data of **2**, **3** and **5** are summarized in Table 4.

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Table 4 Crystallographic data for complexes **2**·C_6D_6, **3**, and **5**

	2·C_6D_6	**3**	**5**
Formula	$C_{29}H_{49}GeNO_3Si_3W \cdot C_6D_6$	$C_{29}H_{49}GeNO_2SSi_3W$	$C_{29}H_{49}GeNO_2SSi_3W$
FQ	884.53	816.46	816.46
T, K	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/n$
a, Å	8.8560(3)	12.8240(6)	8.9678(4)
b, Å	13.7380(5)	16.7658(5)	25.2891(6)
c, Å	15.9500(7)	17.5750(6)	15.0542(6)
β, °	99.9596(18)	108.9913(9)	94.9373(10)
Z	2	4	4
V, Å^3	1911.29(13)	3573.0(2)	3401.4(2)
ρ, Mg m^{-3}	1.527	1.518	1.594
μ, mm^{-1}	3.920	4.242	4.456
Crystal size, mm^3	0.23 × 0.21 × 0.14	0.31 × 0.30 × 0.23	0.12 × 0.11 × 0.08
2θ range, °	1.30–27.46	1.73–27.48	1.58–27.48
No. of unique data	8545 [R(int) = 0.0458]	8159 [R(int) = 0.0355]	7689 [R(int) = 0.0802]
No. of data with $I > 2\sigma(I)$	8291	7542	6505
No. of params	411	357	356
GOF on F^2	1.145	1.267	1.326
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0274, 0.0748	0.0240, 0.0746	0.0646, 0.1257
$R1$, $wR2$ (all data)	0.0301, 0.0824	0.0285, 0.0801	0.0830, 0.1358
Flack parameter	−0.016(7)	—	—

References

1 For recent reviews of carbene complexes and olefin metathesis: T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18–29; R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2006, **45**, 3760–3765; M. T. Whited and R. H. Grubbs, *Acc. Chem. Res.*, 2009, **42**, 1607–1616 and references cited therein; R. R. Schrock, *Chem. Rev.*, 2002, **102**, 145–179; R. R. Schrock, *Angew. Chem., Int. Ed.*, 2006, **45**, 3748–3759; R. R. Schrock, *Chem. Rev.*, 2009, **109**, 3211–3226 and references cited therein; *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, vol. 1–3, 2003.

2 For recent reviews of N-heterocyclic carbene complexes: F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172; S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676.

3 For recent reviews of silylene complexes: H. Ogino, *Chem. Rec.*, 2002, **2**, 291–306; M. Okazaki, H. Tobita and H. Ogino, *Dalton Trans.*, 2003, 493–506; T. D. Tilley, *Acc. Chem. Res.*, 2007, **40**, 712–719.

4 S. R. Klei, T. D. Tilley and R. G. Bergman, *Organometallics*, 2002, **21**, 4648–4661; P. B. Glaser and T. D. Tilley, *J. Am. Chem. Soc.*, 2003, **125**, 13640–13641; E. Calimano and T. D. Tilley, *J. Am. Chem. Soc.*, 2008, **130**, 9226–9227; E. Calimano and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 11161–11173; M. Hirotsu, T. Nunokawa and K. Ueno, *Organometallics*, 2006, **25**, 1554–1556.

5 For reviews of germylene, stannylene and plumbylene complexes: W. Petz, *Chem. Rev.*, 1986, **86**, 1019–1047; M. S. Holt, W. L. Wilson and J. H. Nelson, *Chem. Rev.*, 1989, **89**, 11–49; M. F. Lappert and R. S. Rowe, *Coord. Chem. Rev.*, 1990, **100**, 267–292; A. V. Zabula and E. Hahn, *Eur. J. Inorg. Chem.*, 2008, 5165–5179.

6 T. J. Marks, *J. Am. Chem. Soc.*, 1971, **93**, 7090–7091; P. Jutzi and W. Steiner, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 684–685; M. F. Lappert, S. J. Miles, P. P. Power, A. J. Carty and N. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1977, 458–459; P. Jutzi, W. Steiner and E. König, *Chem. Ber.*, 1978, **111**, 606–614; P. Jutzi, W. Steiner and K. Stroppel, *Chem. Ber.*, 1980, **113**, 3357–3365; P. Jutzi and B. Hampel, *J. Organomet. Chem.*, 1986, **301**, 283–288; K. E. Lee, A. M. Arif and J. A. Gladysz, *Organometallics*, 1991, **10**, 751–760; N. Tokitoh, K. Manmaru and R. Okazaki, *Organometallics*, 1994, **13**, 167–171; F. Schager, K. Seevogel, K.-R. Pörschke, M. Kessler and C. Krüger, *J. Am. Chem. Soc.*, 1996, **118**, 13075–13076; K. Ueno, K. Yamaguchi and H. Ogino, *Organometallics*, 1999, **18**, 4468–4470; Z. T. Cygan, J. E. Bender IV, K. E. Litz, J. W. Kampf and M. M. B. Holl, *Organometallics*, 2002, **21**, 5373–5381; Z. T. Cygan, J. W. Kampf and M. M. B. Holl, *Inorg. Chem.*, 2003, **42**, 7219–7226; P. G. Hayes, R. Waterman, P. B. Glaser and T. D. Tilley, *Organometallics*, 2009, **28**, 5082–5089.

7 T. Watanabe, H. Hashimoto and H. Tobita, *Angew. Chem., Int. Ed.*, 2004, **43**, 218–221; T. Watanabe, H. Hashimoto and H. Tobita, *J. Am. Chem. Soc.*, 2006, **128**, 2176–2177; T. Watanabe, H. Hashimoto and H. Tobita, *J. Am. Chem. Soc.*, 2007, **129**, 11338–11339; H. Hashimoto, M. Ochiai and H. Tobita, *J. Organomet. Chem.*, 2007, **692**, 36–43.

8 M. Ochiai, H. Hashimoto and H. Tobita, *Angew. Chem., Int. Ed.*, 2007, **46**, 8192–8194; M. Ochiai, H. Hashimoto and H. Tobita, *Dalton Trans.*, 2009, 1812–1814.

9 H. Hashimoto, T. Tsubota, T. Fukuda and H. Tobita, *Chem. Lett.*, 2009, **38**, 1196–1197.

10 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn, 1988, ch. 22, pp. 1035–1037.

11 A. C. Filippou, R. Steck and G. Kociok-Kohn, *J. Chem. Soc., Dalton Trans.*, 1999, 2267–2268; A. Yu. Khalimon, K. Yu. Dorogov, A. V. Churakov, L. G. Kuzmina, D. A. Lemenovskii, J. A. K. Howard and G. I. Nikonov, *Dalton Trans.*, 2007, 2440–2449; H. Wagner, J. Baumgartner and C. Marschner, *Organometallics*, 2005, **24**, 4649–4653.

12 Z.-K. Chan, T.-R. Chen, Y.-F. Tsai, J.-D. Chen and J.-C. Wang, *Polyhedron.*, 2007, **26**, 3715–3723; L. Grøndahl, A. Hammershøi, R. M. Hartshorn and A. M. Sargeson, *Acta Chem. Scand.*, 1995, **49**, 781–791.

13 I. B. Baranovskii, M. D. Surazhskaya and M. A. Golubnichnaya, *Zh. Neorg. Chim. (Russ.)*, 2007, **52**, 1983–1991; I. Kalikhman, O. Girshberg, L. Lameyer, D. Stalke and D. Kost, *J. Am. Chem. Soc.*, 2001, **123**, 4709–4716; M. Baumann, I. R. Baxendale, S. V. Ley, C. D. Smith and G. K. Tranmer, *Org. Lett.*, 2006, **8**, 5231–5234.

14 M. Kato, M. Kawano, H. Taniguchi, M. Funaki, H. Moriyama, T. Sato and K. Matsumoto, *Inorg. Chem.*, 1992, **31**, 26–35; L. D. Field, W. J. Shaw and P. Turner, *Chem. Commun.*, 2002, 46–47.

15 L. D. Field, W. J. Shaw and P. Turner, *Organometallics*, 2001, **20**, 3491–3499.

16 T. Olszewska, A. Pyszno, M. J. Milewska, M. Gdaniec and T. Połoński, *Tetrahedron: Asymmetry*, 2005, **16**, 3711–3717; H. Borrmann, I. Persson, M. Sandström and C. M. V. Stålhandske, *J. Chem. Soc., Perkin Trans. 2*, 2000, 393–402.

17 An unpublished result.

18 E. Allenstein, F.-J. Hofmann and H. Riffel, *Z. Anorg. Allg. Chem.*, 1986, **534**, 7–12; K. S. Murray, P. J. Newman, B. M. Gatehouse and D. Taylor, *Aust. J. Chem.*, 1978, **31**, 983–992; H. G. Raubenheimer, R. Otte, L. Linford, W. E. V. Zyl, A. Lombard and G. J. Kruger, *Polyhedron*, 1992, **11**, 893–900.

19 S. Krompiec, N. Kuźnik, M. Krompiec, R. Penczek, J. Mrzigod and A. Tórz, *J. Mol. Catal. A: Chem.*, 2006, **253**, 132–146.
20 T. Higashi, *NUMBUS*, Rigaku Corporation, Tokyo, Japan.
21 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, 1997.
22 G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, 1997.
23 K. Wakita, Yadokari-XG, Software for Crystal Structure Analyses, 2001Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**(3), 218–224.

