

# In Search of Cationic Germanium(II)–Transition Metal Complexes $L^2Ge^+W(CO)_5$ and $L^2Ge^+W(CO)_4Ge^+L^2$

Isabelle Saur,<sup>†</sup> Sonia Garcia Alonso,<sup>†</sup> Heinz Gornitzka,<sup>†</sup> Virginie Lemierre,<sup>‡</sup>  
Anna Chrostowska,<sup>‡</sup> and Jacques Barrau<sup>\*,†</sup>

Laboratoire Hétérochimie Fondamentale et Appliquée, UMR 5069, Université Paul Sabatier, 118, Route de Narbonne, F-31062 Toulouse Cedex 04, France, and Laboratoire de Chimie Théorique et Physico-Chimie Moléculaire, UMR 5624, FR 2606, Université de Pau et des Pays de l'Adour, Avenue de l'Université, BP 1159, F-64013 Pau Cedex, France

Received March 21, 2005

New germanium(II)–tungsten complexes  $[L^2(X)Ge]_nW(CO)_{6-n}$  ( $L^2 = NPhC(Me)CHC(Me)-NPh$ ,  $n = 1$ ,  $X = OTf$  (**2**);  $n = 2$ ,  $X = Cl$  (**13**)) have been synthesized and characterized by X-ray crystallography. In compound **2** the triflate was found to be very weakly coordinating to the germanium in the solid state, and this result is confirmed by DFT calculations. All the spectroscopic data are consistent with the  $L^2(X)Ge$  ligands being good  $\sigma$ -donors and poor  $\pi$ -acceptors in these complexes, similar to the phosphine ligands in homologous  $R_3P$  complexes. Starting from the chlorogermanium(II)–tungsten complexes  $(L^2(Cl)Ge)_nW(CO)_{6-n}$  ( $n = 1$  (**1**),  $n = 2$  (**13**)), metathesis reactions with halide or weakly coordinating anions  $A^-$  ( $A^- = TfO^-$ ,  $BPh_4^-$ ,  $PF_6^-$ ) have been investigated as a general approach to obtain the cationic germanium species  $[L^2Ge^+]_nW(CO)_{6-n}$ . In the case of  $A^- = TfO^-$ , spontaneous dissociation of the anion leading to an equilibrium between a neutral and a cationic tetracoordinated germanium species is observed in coordinating solvents. Treatment of  $L^2(X)Ge$  with  $MX_3$  ( $M = Ga$ ,  $X = Cl$ ;  $M = In$ ,  $X = I$ ) afforded the neutral complexes  $L^2MX_2$  ( $M = Ga$  (**7**) and  $In$  (**8**)) by ligand transfer reactions. The crystal structure of **8** was determined by X-ray structure analysis.

## Introduction

During the past few years, the chemistry of stable homoleptic and heteroleptic divalent compounds of germanium<sup>1</sup> and of their transition metal complexes<sup>2</sup> has been the focus of considerable attention. A variety of such compounds have been reported, but very little has been published on cationic germanium(II) derivatives<sup>3</sup>  $RGe^+$ . Similarly, except the pioneering work of Filippou<sup>4</sup> concerning the cationic germylydine complex  $trans-[(MeCN)(dppp)_2W\equiv Ge(\eta^1-Cp^*)]^+[B(C_6F_5)_4]^-$ , to our knowledge no other studies have dealt with cationic germanium(II)–transition metal complexes  $RGe^+M'L_n$ , probably because of the absence of suitable precursors.

Like cationic transition metal phosphonium complexes, the analogous  $M_{14}(II)$ –transition metal complexes are of potential interest for many applications (e.g., as catalysts for cationic or ring-opening polymerizations) because of the possibility that the increased electrophilicity that results from the positive charge may enhance substrate coordination and activation. Ligands with nitrogen donors, particularly  $\beta$ -diketiminato ligands  $L^2$ , are well-suited for stabilizing neutral germanium(II) species such as  $L^2(X)Ge$  ( $X = Cl$ ,  $I$ )<sup>5</sup> and the related complexes  $L^2(Cl)GeY$  ( $Y = S$ ,  $Se$ )<sup>6</sup> and  $L^2(X)GeM'L_n$  ( $M'L_n = W(CO)_5$ ,  $X = Cl$ ,  $I$ ;  $M'L_n = Fe(CO)_4$ ,  $X = Cl$ )<sup>2h,j</sup> as well as cationic germanium(II) derivatives  $L^2Ge^+$ .<sup>3i</sup> In a previous paper, we showed that the three-coordinate germanium compounds  $L^2(X)Ge$  are best described by a model structure corresponding to a divalent germanium species weakly coordinated with the halide group  $L^2Ge^+\cdots X^-$ .<sup>5c</sup> Following our work on the corresponding  $\beta$ -diketiminato halogermanium(II)–

\* To whom correspondence should be addressed. E-mail: barrau@chimie.ups-tlse.fr. Fax: +33561558204. Phone: +33561556172.

<sup>†</sup> Université Paul Sabatier.

<sup>‡</sup> Université de Pau et des Pays de l'Adour.

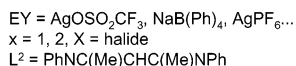
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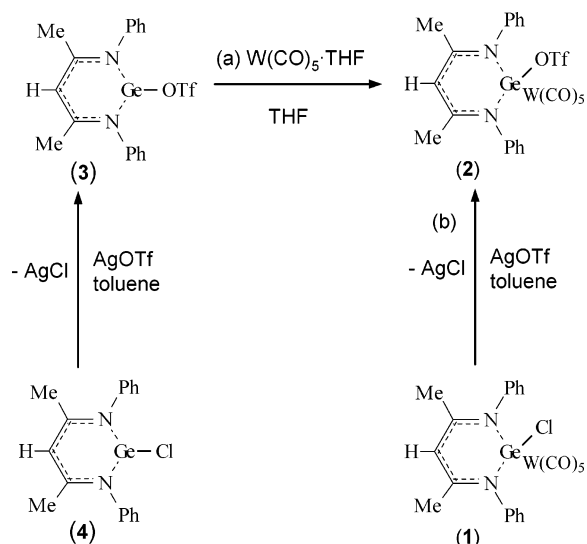
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## Scheme 1



## Scheme 2



transition metal complexes  $L^2(X)GeW(CO)_5$  ( $X = Cl, I$ ,  $L^2 = PhNC(Me)CH(Me)NPh$ ),<sup>2i</sup> we have sought to develop synthetic routes to the mono[cationic-germanium(II)]– and bis[cationic-germanium(II)]–transition metal complexes  $L^2Ge^+W(CO)_5$  and  $(L^2Ge^+)_2W(CO)_4$ , respectively.

In this paper, we describe the results of our first approach to the synthesis of these compounds, which involves replacement of the halide ligand in halogermanium(II)–transition metal complexes  $[L^2(X)Ge]_x M^L_{n-x}$  through anion metathesis with the salts of weakly coordinating anions ( $F_3CS(O)_2O^-$ ,  $BPh_4^-$ ,  $PF_6^-$ ) (Scheme 1).

## Results and Discussion

**1. Attempted Synthesis of  $L^2Ge^+W(CO)_5$ . 1.1.  $L^2(OTf)GeW(CO)_5$ .** Our first attempts were directed at triflate-substituted germanium(II) complexes in search of evidence for dissociation of the triflate group ( $TfO^-$ ), and so we examined the preparation of the triflate germanium(II)–tungsten complex  $L^2(TfO)GeW(CO)_5$  (**2**). Two alternative synthetic methods were investigated (Scheme 2): (i) treatment of photochemically produced  $W(CO)_5 \cdot THF$  with the germanium(II) triflate  $L^2Ge(OTf)$

(**3**) in THF (method a) and (ii) direct treatment of the germanium complex  $L^2(Cl)GeW(CO)_5$  (**1**) with  $AgOTf$  in toluene (method b).

(a)  $L^2(OTf)Ge$  (**3**). Compound **3** was obtained in high yield from a metathesis reaction between  $L^2(Cl)Ge$  (**4**) and  $AgOTf$  in toluene at room temperature, as a light yellow air- and moisture-sensitive solid, soluble in polar and aromatic solvents. The EI (70 eV) mass spectrum shows a base peak corresponding to  $[L^2Ge]^+$ ; the presence of the molecular ion  $M^{+•}$  with a relative intensity of 45% suggests that the triflate group is relatively strongly bound to germanium, indicating some degree of ion pairing in the gas phase. The chemical shifts of the methine and methyl groups in the <sup>1</sup>H NMR spectrum ( $CDCl_3$ ,  $\delta_{Me} = 2.07$  ppm,  $\delta_{CH} = 5.66$  ppm) lie slightly downfield from the corresponding resonances in the halides **4** and **5** ( $L^2(X)Ge$ ,  $X = Cl$  and  $I$ , respectively) ( $CDCl_3$ ,  $\delta_{Me} = 1.96$  (**4**), 2.05 (**5**);  $\delta_{CH} = 5.39$  (**4**), 5.64 (**5**)).<sup>5a</sup>

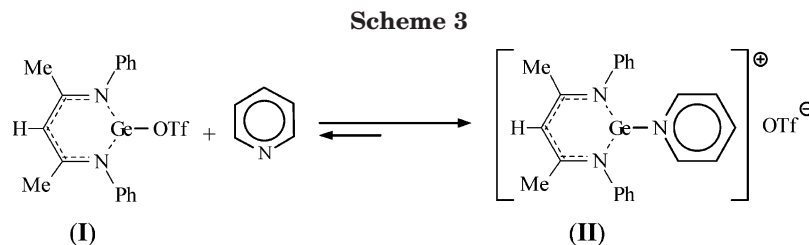
This may be an indication of an increased positive charge on the germanium. The infrared spectrum ( $C_6D_6$ ) exhibits several  $\nu(CF_3SO_3)$  absorptions between 1368 and 1000  $cm^{-1}$ ; the highest frequency band is the strongest and is characteristic of a monodentate-covalently bound triflate ( $\nu = 1365–1395$   $cm^{-1}$  for covalently bound triflate;  $\nu = 1270–1280$   $cm^{-1}$  for ionic bound triflate).<sup>7</sup> Interestingly, two  $\nu(SO_3)$  bands are observed at 1367.4  $cm^{-1}$  (weak) and 1271.7  $cm^{-1}$  (very strong) for **3** in pyridine solvent, suggesting an equilibrium between covalent and ionic forms.

(b)  $L^2(TfO)GeW(CO)_5$ . The tungsten complex  $L^2(TfO)GeW(CO)_5$  (**2**) was obtained in good yields by both methods (a) and (b) (Scheme 2). Complex **2** is a yellow air- and moisture-sensitive solid, soluble in polar and aromatic solvents and insoluble in pentane. It has been fully characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR, IR, and mass spectroscopies. The complex shows low thermal stability, as indicated by decomposition at its melting point of 119–123 °C and by the EI (70 eV) mass spectrum, which displays a just-detectable molecular ion peak  $[M]^+$  (intensity <0.1% of the  $[L^2Ge]^+$  base peak) in addition to fragmentations characteristic of such structures, such as facile successive losses of the carbonyl groups and loss of the weakly coordinating triflate group, giving rise to a strong peak due to the  $[L^2GeW(CO)_5]^+$  ion. The <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra of **2** feature signals with chemical shifts downfield from those of the germanium(II) compound **3**, suggesting diminution of the electronic density on the  $L^2(TfO)Ge$  ligand due to bonding with the  $W(CO)_5$  fragment. Compared to the halide complexes  $L^2(X)GeW(CO)_5$  ( $X = Cl$ , **1**;  $X = I$ , **6**)<sup>2j</sup> ( $CDCl_3$ :  $\delta_{Me} = 2.02$  (**1**), 2.01 (**6**), 2.11 (**2**);  $\delta_{CH} = 5.56$  (**1**), 5.82 (**6**), 5.85 (**2**) ppm), all the corresponding <sup>1</sup>H NMR resonances due to the protons in **2** appear at downfield positions. This observation reflects the lower coordinating ability of the anion  $TfO^-$  compared to  $Cl^-$  and  $I^-$ , suggesting that the triflate group is weakly bound to the germanium. The two <sup>13</sup>C NMR chemical resonances for the CO groups and three bands in the carbonyl region of the IR spectrum are characteristic of  $C_{4v}$  local symmetry around the tungsten in **2**. The IR spectrum of the complex **2** determined in

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**Table 1. Crystallographic Data for 2 and 13**

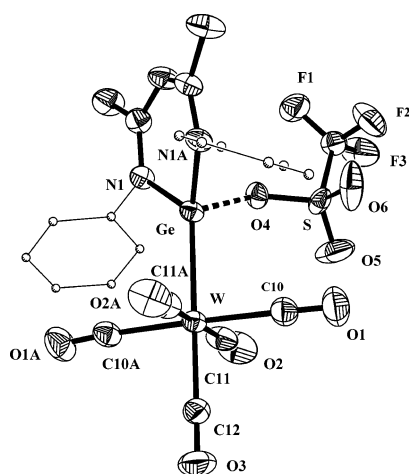
	<b>2</b>	<b>13</b>
empirical formula	C <sub>23</sub> H <sub>17</sub> F <sub>3</sub> GeN <sub>2</sub> O <sub>8</sub> SW	C <sub>38</sub> H <sub>34</sub> Cl <sub>2</sub> Ge <sub>2</sub> N <sub>4</sub> O <sub>4</sub> W
fw	794.95	1010.62
cryst syst	orthorhombic	monoclinic
space group	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>
unit cell dimens		
<i>a</i> (Å)	16.970(2)	10.480(1)
<i>b</i> (Å)	19.859(2)	9.542(1)
<i>c</i> (Å)	9.587(10)	19.334(3)
β (deg)		2
<i>V</i> (Å <sup>3</sup> )	3230.7(6)	1881.5(4)
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.824	1.784
no. of reflns collected	17 367	12 712
no. of indep reflns	3405	3835
no. of params	356	234
R1 [ <i>I</i> > 2σ( <i>I</i> )]	0.0216	0.0275
wR2 [all data]	0.0539	0.0567
largest diff peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	0.713 and -0.746	1.225 and -0.531

C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub> solution contains a strong band at ~1366 cm<sup>-1</sup> (C<sub>6</sub>D<sub>6</sub>: 1365.4 cm<sup>-1</sup>; CDCl<sub>3</sub>: 1366.5 cm<sup>-1</sup>), which is in the typical range for a covalent triflate.<sup>7</sup> As in the case of the starting material **3**, in pyridine solvent two bands were detected at 1379.1 cm<sup>-1</sup> (weak) and 1274.0 cm<sup>-1</sup> (very strong) in the ν(CF<sub>3</sub>SO<sub>3</sub>) region; this is probably the result of an equilibrium between the pyridine-free neutral germanium(II)–tungsten complex and the corresponding pyridine-coordinated ionic complex, pushed toward the ionic side by the electron-

releasing solvent. The equilibrium is not completely shifted to the ionic form; this is evident also from the <sup>1</sup>H NMR spectrum in pyridine-*d*<sub>5</sub>, which features two signals each (30/70%) for the methine and methyl protons (C<sub>5</sub>D<sub>5</sub>N: <sup>1</sup>H δ<sub>Me</sub>: 1.77, 2.11 ppm; δ<sub>CH</sub>: 5.12, 5.32 ppm).

Suitable crystals of **2** for crystallographic analysis were obtained from toluene at -35 °C. The molecular structure is depicted in Figure 1, while the pertinent crystallographic data are given in Table 1.

The single-crystal X-ray analysis of **2** reveals that in the solid state the molecular structure of **2** is very similar to that of **1**, with the germanium taking a distorted tetrahedral configuration (the sum of the N(1)–Ge–N(1A), N(1)–Ge–O(4), O(4)–Ge–W, W–Ge–N(1A) bond angles is 432.05°) and bound covalently to the triflate ligand. The geometry around the tungsten is nearly octahedral, and the β-diketiminato ligand is symmetrically bound to the germanium atom. The Ge–W bond in **2** is shorter (2.55 Å) than typical Ge–W single bonds (2.59–2.67 Å)<sup>8</sup> and is also slightly shorter than those in the halogenated complexes **1** and **6** (**1**, 2.57 Å; **6**, 2.57 Å),<sup>2j</sup> which are among the shortest reported for compounds of the R<sub>2</sub>GeW(CO)<sub>5</sub> type.<sup>8,9</sup> In comparison with the Ge–O distances (2.020–2.48 Å) reported for R(TfO)Ge(II) or R<sub>2</sub>(TfO)(Σ)Ge(IV) compounds with very weakly binding triflate,<sup>4b,7b,10</sup> the Ge–O bond distance in **2** (2.04 Å) is slightly shorter and in the same range



**Figure 1.** Solid-state structure of L<sup>2</sup>(OTf)GeW(CO)<sub>5</sub> (**2**) (ellipsoids are drawn at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge–O(4) 2.044(7), Ge–N(1) 1.891(2), Ge–N(1A) 1.891(2), Ge–W 2.5473(5), W–C(12) 1.995(5), W–C(10) 2.044(3), W–C(11) 2.036(4), O(4)–S 1.475(9), S–O(5) 1.421(7), S–O(6) 1.421(9), C(12)–O(3) 1.142(6), C(10)–O(1) 1.135(4), C(11)–O(2) 1.135(4), N(1)–Ge–N(1A) 94.93(16), N(1)–Ge–O(4) 98.7(3), N(1A)–Ge–O(4) 86.8(3), N(1)–Ge–W 127.82(8), N(1A)–Ge–W 127.82(8), O(4)–Ge–W 110.6(3), Ge–W–C(12) 179.71(13), Ge–W–C(11) 88.51(10), Ge–W–C(10) 92.80(9).

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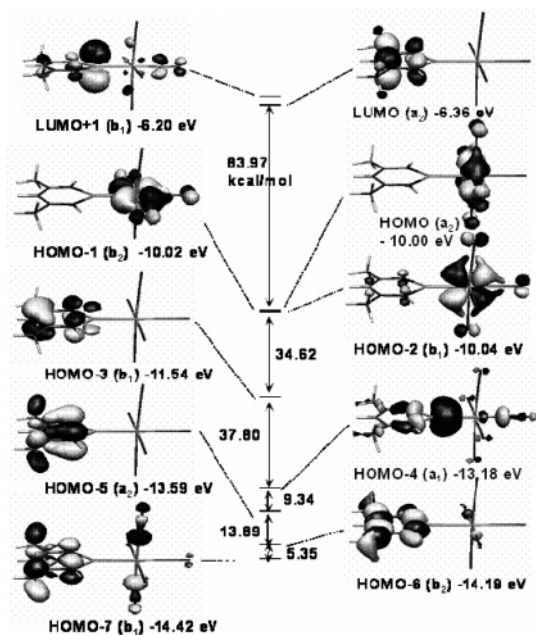
of that in [(8-MeO)Np]<sub>2</sub>(H)Ge(IV)OTf], where the germanium is weakly linked to the triflate anion (1.99 Å).<sup>11</sup> This distance is significantly longer than a covalent Ge–O bond (1.75–1.85 Å)<sup>12</sup> and appreciably shorter than the sum of the van der Waals radii (3.66 Å).<sup>13</sup> The short Ge–W and the long Ge–O distances may be rationalized as resulting from the tetracoordination of the germanium, combined with d<sub>π</sub>–σ\* (GeO) π-donation from the tungsten to the L<sup>2</sup>(TfO)Ge germanium ligand (Ge–W multiple-bond character), which is favored by the high electronegativity of the triflate group. Accordingly, the L<sup>2</sup>(TfO)Ge moiety is seen by W(CO)<sub>5</sub> as a strong σ-donor with weak π-acceptor capacity, but nevertheless superior to that postulated for the L<sup>2</sup>(X)-Ge ligands in other known base-stabilized germylene-pentacarbonyl complexes L<sup>2</sup>(X)GeW(CO)<sub>5</sub>.<sup>2j</sup>

To confirm the overall bonding situation of the triflate ligand in compound **2** as derived from the X-ray results, we have performed DFT (B3LYP) theoretical calculations of geometrical parameters for the neutral and cationic model compounds **1'**, **2'**, and **2''**, respectively (see Supporting Information).

The calculated geometrical parameters for **1'** are in good qualitative agreement with the available experimental data for the dihalogermanium(II)–tungsten complex **1**.<sup>2j</sup> As expected, they show that the Ge–N and Ge–W bond lengths shorten and the N<sub>1</sub>GeN<sub>2</sub>, N<sub>1</sub>GeW, and N<sub>2</sub>GeW bond angles widen on going from the neutral molecule **1'** to the cationic species **2'** and the neutral **2''**, but less strongly for the latter one. For **2'** (optimized with C<sub>2v</sub> symmetry), the germanium atom is sp<sup>2</sup> hybridized and the Ge–W bond length is predicted to be only 0.1 Å shorter than that calculated for **1'** and **2''**. It is noteworthy that the calculated structure of **2'** matches the experimental X-ray data for **2** very closely; for example, the experimental Ge–N<sub>1</sub> and Ge–W distances in **2** are 1.891 and 2.547 Å, respectively, while those calculated for **2'** are 1.901 and 2.538 Å, respectively. The experimental and calculated values of the various bond angles also agree well, the experimental values for **2** being closer to those calculated for the cation **2'** than for the neutral molecules **1'** or **2''**.

Considering the total natural charges provided by the NBO calculations (see Supporting Information), the negative charges on tungsten, the two nitrogen atoms, and the C<sub>8</sub> carbon atom are modified as a result of the increase of the positive charge on germanium in **2'** compared with **1'**. This positive charge is stronger in **2''** mainly due to the more pronounced withdrawing effect of the OTf substituent. In the cationic molecule **2'**, the negative charge on the C<sub>8</sub> atom is smaller than in the neutral compounds **1'** and **2''**, which is in agreement with the deshielding observed in the <sup>13</sup>C and <sup>1</sup>H NMR spectra of **2** compared with those of **1**. As postulated from the X-ray results, the theoretical trends are indicative of a triflate anion that is very weakly bound to the germanium atom and weak π-back-donation of tungsten to germanium.

It is also of interest to look at the electronic structure of the cationic tungsten complex **2'** in comparison with



**Figure 2.** Calculated energies of the frontier molecular orbitals in **2'** and their Molekel visualization.

the previously studied germanium cation [Ge(NHCH)<sub>2</sub>CH]<sup>+</sup><sup>3i</sup> and examine the effect of tungsten complexation on the nature and ordering of the molecular energy levels. The energies of the frontier orbitals in **2'** and their Molekel visualization are shown in Figure 2.

The LUMO is associated with the C–N π\*–orbital and lies only 3.69 kcal/mol lower than LUMO+1, which is localized mainly on the Ge 4p-orbital. Thus, complexation of [Ge(NHCH)<sub>2</sub>CH]<sup>+</sup> to tungsten restores the unoccupied molecular orbital ordering observed for low-valent Al and Ga analogues.<sup>3i</sup> However, these results have to be taken with caution because of the considerable influence of the choice of basis set on the energies and nature of unoccupied MOs. The three highest occupied molecular orbitals (HOMO, HOMO–1, and HOMO–2) correspond to the a<sub>2</sub>, b<sub>2</sub>, and b<sub>1</sub> molecular orbitals of the carbonyl groups, while the lower energy orbitals HOMO–3 to HOMO–7 correspond to HOMO–HOMO–4 in [Ge(NHCH)<sub>2</sub>CH]<sup>+</sup>.<sup>3i</sup> In **2'** HOMO–3 corresponds to the antibonding interaction between the bonding combination of the π nitrogen lone pairs delocalized in the Ge 4p-orbital and the C–C π-bond, while the strongly stabilized HOMO–4 (antibonding with respect to the Ge–N bond, Δ(HOMO–3 – HOMO–4) = 37.8 kcal) is associated mainly with the germanium lone pair coordinated to tungsten. It is noteworthy that the energy gap between the two corresponding orbitals in [Ge(NHCH)<sub>2</sub>CH]<sup>+</sup> (HOMO and HOMO–1 calculated with B3LYP/SDD) is only 22.75 kcal/mol. These results provide strong evidence for Lewis base behavior of the germanium lone pair in these complexes.

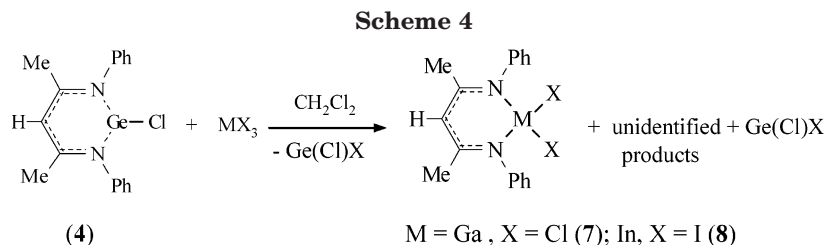
**1.2. Reactions of L<sup>2</sup>(Cl)GeW(CO)<sub>5</sub> with GaCl<sub>3</sub>, NaBPh<sub>4</sub>, and AgPF<sub>6</sub>.** Given the indication from the preceding results of some degree of ion pairing in the triflate complex **2**, we decided to attempt to abstract the chloride ions in **1** and **4** with MX<sub>3</sub> (M = Ga, X = Cl; M = In, X = I), NaBPh<sub>4</sub>, or AgPF<sub>6</sub>. Disappointingly, however, all these attempts were unsuccessful.

The reactions of **4** with MX<sub>3</sub> in dichloromethane afforded mainly the neutral gallium and indium com-

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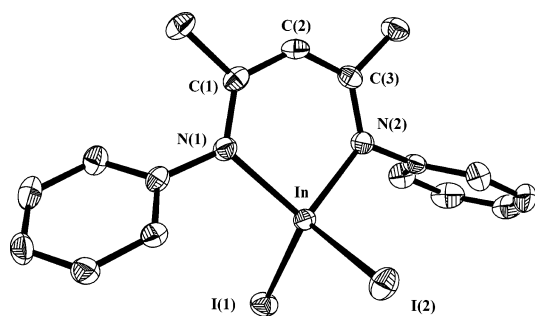
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pounds  $L^2MX_2$  (**7** and **8**) resulting from ligand transfer reactions<sup>14</sup> (Scheme 4).

Compound **7** has been fully characterized by MS and  $^1H$ ,  $^{13}C$ , and  $^{71}Ga$  NMR spectroscopies. The  $^{71}Ga$  NMR spectrum of **7** ( $CDCl_3$ ,  $[Ga(H_2O)_6]^{3+}$ :  $\delta = 246$  ppm) is in good agreement with the chemical shift observed for the analogous tetracoordinate vinamidin gallium complex.<sup>15</sup> Hence the reactions of the germanium–tungsten complex **1** with  $MX_3$  have not been studied for fear of obtaining similar ligand–halogen exchange reactions. Compound **8** was isolated as a yellow powder by evaporation of a  $CH_2Cl_2$  solution of **8** under reduced pressure. Crystals of **8** were obtained by crystallization from toluene at room temperature, and the structure of **8** was determined crystallographically. The molecular structure of **8** is shown in Figure 3; selected bond lengths and angles are given in Table 2.

The structure consists of discrete monomeric molecular units with a distorted tetrahedral geometry at In. The  $L^2$  ligand is coordinated in an approximately symmetrical fashion. The  $InNCCN$  fragment is almost planar, the indium and carbon C(2) distances from the N(1)C(1)C(3)N(2) plane being 0.286 and 0.137 Å, respectively; the sum of the angles at each nitrogen atom is close to 360°. The In–N distances (2.11, 2.12 Å) are in the range normally observed for In–N bonds in tetracoordinate indium complexes incorporating  $N,N'$ -bidentate monoanionic ligands<sup>16</sup> and, as expected, are slightly shorter than those in pentacoordinated indium complexes containing two  $N,N'$ -bidentate ligands<sup>17</sup> and considerably shorter than the In–N distances (average 2.49 Å) in Lewis acid–base adducts.<sup>18</sup> The In–I distances (2.67, 2.69 Å) are in the normal range for tricoordinate or tetracoordinate indium compounds.<sup>16b,19</sup> The structural features are quite similar to those recently reported for the sterically encumbered iodide



**Figure 3.** Solid-state structure of  $L^2(I)_2In$  (**8**) (ellipsoids are drawn at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): In–I(1) 2.6723(3), In–I(2) 2.6861(3), In–N(1) 2.119(2), In–N(2) 2.113(2), N(2)–C(3) 1.340(4), C(2)–C(3) 1.396(4), C(2)–C(1) 1.403(4), N(1)–C(1) 1.343(4), N(1)–In–N(2) 93.34(9), N(1)–In–I(1) 113.84(7), N(1)–In–I(2) 114.45(7), N(2)–In–I(1) 111.31(7), N(2)–In–I(2) 108.95(7).

**Table 2. Crystallographic Data for 8**

empirical formula	$C_{17}H_{17}I_2InN_2$
fw	617.95
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	
$a$ (Å)	13.924(1)
$b$ (Å)	9.798(1)
$c$ (Å)	14.103(1)
$\beta$ (deg)	2
$V$ (Å <sup>3</sup> )	1919.7(2)
$Z$	4
$D_{calc}$ (Mg m <sup>-3</sup> )	2.138
no. of reflns collected	10 920
no. of indep reflns	3883
no. of params	201
R1 [ $I > 2\sigma(I)$ ]	0.0217
wR2 [all data]	0.0557
largest diff peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	0.934 and -0.798

indium derivatives  $Dipp_2nacnacInI_2$ ,<sup>16b</sup> the most noticeable differences are in the N(1)–In–N(2) and I(1)–In–I(2) angles, which are wider in **8**, and in the C(3)N(2) ring, which is closer to planar in **8**. The  $^1H$  and  $^{13}C$  NMR spectra are very similar to those of **7**, indicating that the methyl and phenyl groups are equivalent, probably as a result of a fluxional process in solution.

The reaction of **1** with  $NaBPh_4$  in dichloromethane resulted in a mixture of the novel germanium(II) tungsten complexes  $L^2(Ph)GeW(CO)_5$  (**9**) and  $L^2(Ph_2BO)GeW(CO)_5$  (**10**). These results are rationalized in Scheme 5.

The cationic species  $[L^2Ge^+W(CO)_5]$  is likely formed first and then reacts by competing phenyl group transfer from  $BPh_4^-$  to the germanium center (leading to **9**; (a)) and hydrolysis to form complex **10** (b). This rationale is supported by the fact that, in boron chemistry, phenyl group transfers from  $BPh_4^-$  to metal<sup>20,21</sup> and even germanium<sup>3h</sup> centers are extremely common, as are protodeboronation reactions (cleavage of a B–C bond by a protic reagent).<sup>21</sup> However, the exact mechanism for the formation of **10** is uncertain since we cannot exclude the possibility of initial hydrolysis of the boron compound  $NaBPh_4$  to afford  $Ph_2B(OH)$ , which may then react directly with  $L^2(Cl)GeW(CO)_5$ .

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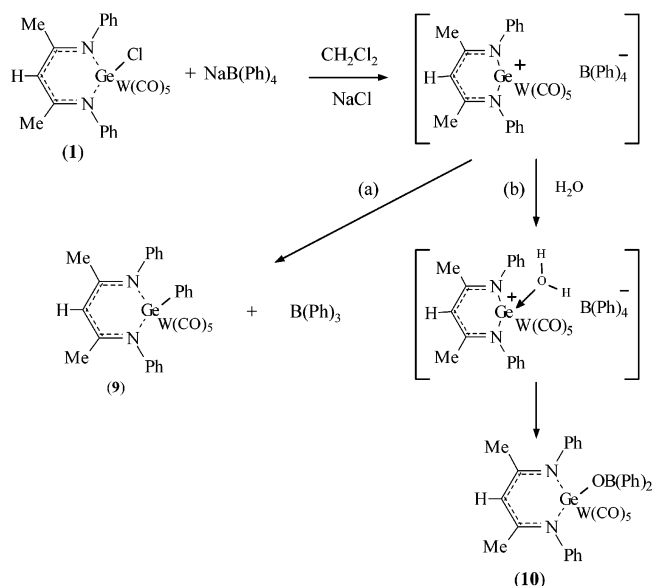
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Scheme 5



The reactivity of  $\text{AgPF}_6$  with **1** was also examined in a final attempted metathesis reaction. This resulted in a complicated mixture of products, of which the hydrolysis products  $\text{L}^2\text{H}^+\text{PF}_6^-$  (**11**) and  $\text{L}^2\text{GeOP(O)F}_2$  (**12**) were the only compounds that we were able to identify.

## 2. Attempted Synthesis of $\text{L}^2\text{Ge}^+[\text{W(CO)}_4]\text{Ge}^+\text{L}^2$ .

**2.1.  $[\text{L}^2(\text{Cl})\text{Ge}]_2\text{W(CO)}_4$ .** As for the monocation  $\text{L}^2\text{Ge}^+\text{W(CO)}_5$ , we sought to obtain the dication species  $[\text{L}^2\text{Ge}^+]_2\text{W(CO)}_4$  by a similar synthetic approach, namely, abstraction of the halide  $\text{X}^-$  ligand from the trinuclear bis(germanium(II))–tungsten complex  $\text{L}^2(\text{X})\text{GeW(CO)}_4\text{Ge(X)L}^2$ . To investigate these reactions, we first synthesized the chloride disubstituted tungsten complex  $[\text{L}^2(\text{Cl})\text{Ge}]_2\text{W(CO)}_4$  (**13**) by irradiation of a mixture of 2 equiv of  $\text{L}^2(\text{Cl})\text{Ge}$  and 1 equiv of  $\text{W(CO)}_6$  in THF (Scheme 6, method a). Compound **13** was also obtained in 35% yield by direct irradiation of  $\text{L}^2(\text{Cl})\text{GeW(CO)}_5$  in THF (Scheme 6, method b).

Complex **13** is a yellow solid insoluble in pentane and slightly soluble (less than **1**) in polar solvents. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra showed that the two  $\text{L}^2(\text{Cl})\text{Ge}$  fragments are equivalent and are thus consistent with a *trans* structure (Table 1). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of complex **13** showed different chemical shifts for the signals of the  $\beta$ -diiminate ligand relative to those of the monosubstituted germanium(II)–tungsten com-

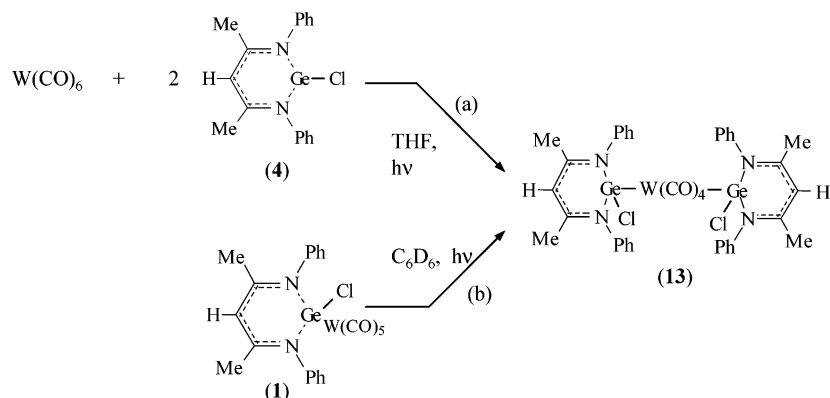
pound (**1**).<sup>2j</sup> The chemical shifts of the signals corresponding to the methine and methyl protons appear at higher field compared to the corresponding resonances in **1** ( $\text{CDCl}_3$ ,  $\delta_{\text{CH}} = 5.38$  (**13**), 5.56 (**1**);  $\delta_{\text{CH}_3} = 1.88$  (**13**), 2.02 (**1**) ppm).<sup>2j</sup> The  $^{13}\text{C}$  spectrum shows the characteristic chemical shifts of the carbon atom of the  $\beta$ -diketiminate ligand, shifted slightly upfield from those in the spectrum of **1** ( $\text{CDCl}_3$ ,  $\delta_{\text{CH}} = 101.11$  (**13**), 101.58 (**1**);  $\delta_{\text{CH}_3} = 24.81$  (**13**), 24.60 (**1**) ppm). Only one carbonyl resonance is observed ( $\text{CDCl}_3$   $\delta_{\text{CO}} = 200.96$  ppm), indicative of  $D_{4h}$  symmetry at the tungsten atom (*trans* geometry). In the carbonyl region of the IR spectrum, only one strong band, characteristic of  $D_{4h}$  symmetry at the tungsten, is observed; this band appears at significantly lower frequencies ( $\nu_{\text{CO}} = 1898$   $\text{cm}^{-1}$ ) than the corresponding bands for  $\text{L}^2(\text{Cl})\text{GeW(CO)}_5$  ( $\nu_{\text{CO}} = 2072, 1984, 1943$   $\text{cm}^{-1}$ ).<sup>2j</sup>

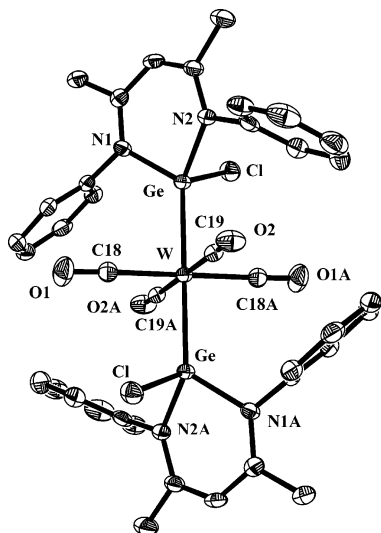
It is interesting to note that formation of *cis*- $[\text{L}^2(\text{Cl})\text{Ge}]_2\text{W(CO)}_4$  was not observed, contrary to what has been reported in the cases of  $[(\text{salen})\text{Sn}]_2\text{W(CO)}_4$  (*salen* = 2,2'-*N,N'*-bis(salicylidene)ethylenediamine)<sup>2h</sup> and  $(\text{carbene})_2\text{W(CO)}_4$  complexes.<sup>22</sup>

The structure of **13** was unambiguously established by single-crystal X-ray diffraction. Compound **13** is the first digermanium(II)–tungsten complex to be structurally characterized. Suitable crystals of **13** were obtained in chloroform at room temperature. The molecular structure of **13** is depicted in Figure 4, while the crystallographic data are reported in Table 1.

The molecular structure confirms the monomeric nature of **13** and the *trans* orientation of the two  $\text{L}^2(\text{Cl})\text{Ge}$  fragments. Compound **13** is achiral, with the inversion center located at the tungsten atom. In each  $\text{L}^2(\text{Cl})\text{Ge}$  moiety of the trinuclear complex **13** the germanium adopts a distorted tetrahedral geometry; the geometry around the tungsten is nearly octahedral. The  $\text{N}(1)\text{--Ge--N}(2)$  angles observed in the two  $\text{L}^2(\text{Cl})\text{Ge}$  fragments ( $93.11^\circ$ ) are slightly smaller than those observed in  $\text{L}^2(\text{Cl})\text{GeW(CO)}_5$  ( $93.90^\circ$ ).<sup>2j</sup> The Ge–W bond distances (2.51 Å) are shorter than those observed in the corresponding monosubstituted  $\text{L}^2(\text{X})\text{GeW(CO)}_5$  complexes (X = Cl, I: 2.57 Å; X = OTf: 2.55 Å), indicating that the strength of the interaction between the tungsten and the germanium atom is slightly influenced by the number of ligands on the transition metal. The Ge–N (1.93, 1.94 Å) and Ge–Cl (2.29 Å) bond lengths are in the same range as those in the  $\text{L}^2(\text{Cl})\text{GeW(CO)}_5$  complex (Ge–N: 1.92, 1.93 Å; Ge–Cl: 2.26 Å). The W–C<sub>cis</sub> (2.02–2.03 Å) and the C–O<sub>cis</sub> (1.15, 1.15 Å) bond

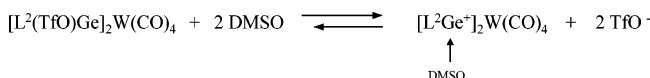
Scheme 6





**Figure 4.** Solid-state structure of  $[L^2(Cl)Ge]_2W(CO)_4$  (**13**) (ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) and bond angles (deg): Ge–Cl = 2.8880(10), Ge–N(1) 1.937(3), Ge–N(2) 1.930(3), Ge–W 2.5125(4), W–C(18) 2.016(4), W–C(18A) 2.016(4), W–C(19) 2.026(4), W–C(19A) 2.026(4), C(18)–O(1) 1.153(5), C(19)–O(2) 1.153(4), N(1)–Ge–N(2) 93.11(13), N(1)–Ge–Cl 95.41(9), N(2)–Ge–Cl 93.41(9), N(1)–Ge–W 126.14(9), N(2)–Ge–W 125.57(9), Cl–Ge–W 115.15(3), Ge–W–C(18) 94.44(11), Ge–W–C(18A) 85.56(11), Ge–W–C(19) 93.64(10), Ge–W–C(19A) 86.36(10).

#### Scheme 7



lengths are also nearly identical to those in the dinuclear  $L^2(X)GeW(CO)_5$  complexes ( $X = Cl, I, OTf$ ). As postulated for the monosubstituted complexes  $L^2(X)GeW(CO)_5$ ,<sup>21</sup> these data are consistent with an unsaturated character (hyperconjugative  $d_w-\sigma^*(GeCl, GeN)$ ,  $d_w-\pi^*(CN)$ ) of the Ge–W units and underline the strong  $\sigma$ -donor and the weak  $\pi$ -acceptor (poorer than CO) nature of the  $L^2(Cl)Ge$  ligand toward tungsten.

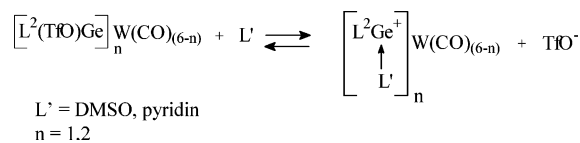
#### 2.2. Reactions of $[L^2(Cl)Ge]_2W(CO)_4$ with $AgOTf$ .

Complex **13** reacts with  $AgOTf$  in toluene at room temperature to yield a yellow, air-sensitive solid (**14**) that is insoluble in  $CHCl_3$ ,  $CH_2Cl_2$ , pentane, and toluene, but is soluble in DMSO. The  $^1H$  NMR spectrum of **14** in  $DMSO-d_6$  is similar to that of **2** in pyridine, showing two signals for the methine and methyl groups of the  $\beta$ -diketiminate ligand ( $\delta_{CH} = 5.57, 5.92$ ;  $\delta_{CH_3} = 2.03, 2.30$  ppm). In addition, evidence for the presence of ionic triflate is given by the IR spectrum in  $DMSO-d_6$  solution, which reveals a strong  $\nu(SO_3)$  vibration mode at  $1271.4 \text{ cm}^{-1}$  characteristic of ionic triflate and a weak vibration at  $1370.5 \text{ cm}^{-1}$  corresponding to covalently bound triflate (Scheme 7).

#### Conclusion

As a general approach to the synthesis of highly reactive cationic germanium species, we have carried out a study of halide abstraction reactions from the

#### Scheme 8



mono- and bis(substituted)germanium(II)–tungsten complexes  $[L^2(X)Ge]_nW(CO)_{6-n}$ . The metathesis reactions investigated demonstrate that the classical “weakly coordinating” anions  $TfO^-$ ,  $BPh_4^-$ , and  $PF_6^-$  are not useful for the synthesis of such germanium cations. In effect, while  $BPh_4^-$  and  $PF_6^-$  are not stable toward germanium, the triflate was found to be weakly coordinating to germanium in the solid state and in neutral or polar solvents; interestingly, however, the weakness of the interaction results in spontaneous dissociation of the  $TfO^-$  ligand in coordinating solvents, giving an equilibrium mixture of neutral and ionic tetracoordinated complexes (Scheme 8).

Further studies focusing on anions that are larger and even more weakly coordinating than those investigated in this work are currently in progress, keeping in mind that as the anion becomes more weakly coordinating and less nucleophilic, the halide complexes  $[L^2(X)Ge]_nW(CO)_{6-n}$  will not be useful precursors to  $[L^2Ge^+]_nW(CO)_{6-n}$  cations. Consequently, the alkoxygermanium(II)–tungsten complexes  $[L^2(OR)Ge]_nW(CO)_{6-n}$  are being investigated as precursors of these cations via their reactions with boron compounds. In the course of this work, several new stable mono- and *trans*-disubstituted germanium(II)–tungsten carbonyl complexes have been prepared and structurally characterized. The Ge–W bond lengths observed in these complexes are among the shortest that have been observed; this indicates that the heteroleptic divalent species  $L^2(X)Ge$  ( $X = \text{halide, TfO}^-$ ) in these complexes behave as  $\sigma$ -donors with weak hyperconjugative  $\pi$ -acceptor character.

It is interesting to note a few analogies between the P–W bonds in some phosphorus–tungsten complexes and the Ge–W bonds studied in the present work. Complexes of the type  $R_3P \cdot W(CO)_5$  are tetracoordinate phosphorus compounds, but physical and chemical evidence suggests that in these compounds the P–W bond is not a pure donor bond, but rather possesses some double-bond character depending on the R group. The molecular structures and carbonyl stretching frequencies of the  $\beta$ -diketiminate germanium(II)– and the related phosphine–tungsten complexes of general formula  $L'_nW(CO)_{6-n}$  are compared in Table 3.

Each of the five  $L'_nW(CO)_5$  and both  $L^2W(CO)_4$  complexes are isostructural around tungsten. For each of these complexes, the  $W-C_{trans}$  distance is shorter than the  $W-C_{cis}$  distance. These observations are in accord with the notion that  $W-C$   $\pi$ -bonding is more pronounced for the  $W-CO$  bond *trans* to  $L'$  when the latter is a weaker  $\pi$ -acceptor than CO. Both the  $W-C_{cis}$  and the  $W-C_{trans}$  distances vary little with the nature of  $L'$  in these complexes. Consequently, the  $\pi$ -acceptor character of the  $L^2(X)Ge$  ligand in the complexes **1**, **2**, **6**, and **13** seems comparable or slightly weaker than that of the phosphine ligand in complexes **15**–**17**. In addition the CO stretching frequencies are closely similar in the Ge(II)– and related P–W complexes. This suggests an almost identical back-donation from the tungsten atom

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**Table 3. Average Bond Distances (in Å) and IR ( $\nu_{\text{CO}}$  in  $\text{cm}^{-1}$ ) for  $\text{L}'_n\text{W}(\text{CO})_{6-n}$  Complexes**

$\text{L}'_n\text{W}(\text{CO})_{6-n}$		W–E <sup>a</sup>	W–C <sub>trans</sub>	W–C <sub>cis</sub>	IR
$\text{Ph}_3\text{PW}(\text{CO})_5$	<b>15</b> <sup>23a,b</sup>	2.545(1)	2.006(5)	2.033(5)	2072, 1980, 1942 <sup>b</sup>
$\text{Cl}_3\text{PW}(\text{CO})_5$	<b>16</b> <sup>23b,c</sup>	2.378(4)	2.020(20)	2.033(12)	2094, 1994, 1980 <sup>c</sup>
$\text{L}^2(\text{Cl})\text{GeW}(\text{CO})_5$	<b>1</b>	2.567(1)	1.995(5)	2.038(1)	2072, 1984, 1943 <sup>d</sup>
$\text{L}^2(\text{I})\text{GeW}(\text{CO})_5$	<b>6</b>	2.571(1)	1.978(8)	2.036(1)	2071, 1984, 1945 <sup>e</sup>
$\text{L}^2(\text{TfO})\text{GeW}(\text{CO})_5$	<b>2</b>	2.547(1)	1.995(5)	2.040(4)	2062, 1974, 1932 <sup>d</sup>
$[\text{L}^2(\text{Cl})\text{Ge}]_2\text{W}(\text{CO})_4$	<b>13</b>	2.513(1)		2.021(4)	1898 <sup>d</sup>
$(\text{Ph}_3\text{P})_2\text{W}(\text{CO})_4$	<b>17</b> <sup>24</sup>	2.479(1)		2.041(1)	1886 <sup>f</sup>

<sup>a</sup> E = P or Ge. <sup>b</sup> Cyclohexane. <sup>c</sup> Cyclopentane. <sup>d</sup> Chloroform. <sup>e</sup> Tetrahydrofuran. <sup>f</sup> Dichloromethane.

to the carbonyl ligands in these complexes, consistent with the view that the  $\text{L}^2(\text{X})\text{Ge}$  and  $\text{R}_3\text{P}$  phosphine ligands possess weak and nearly identical  $\pi$ -acceptor capacities.

## Experimental Section

**General Procedures and Materials.** All manipulations were carried out under an argon atmosphere with the use of standard Schlenk and high-vacuum-line techniques. Solvents were distilled from conventional drying agents and degassed twice prior to use.<sup>25</sup>  $\text{L}^2(\text{Cl})\text{Ge}$  (**4**) and  $\text{L}^2(\text{Cl})\text{GeW}(\text{CO})_5$  (**1**) were prepared according to the previously reported methods.<sup>2i,5a</sup>  $^1\text{H}$  NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80.13 MHz (chemical shifts are given in ppm ( $\delta$ ) relative to  $\text{Me}_4\text{Si}$ ) and  $^{13}\text{C}$  spectra on a AC-250 spectrometer operating at 62.9 MHz.  $^{19}\text{F}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 188.3 and 81.02 MHz, respectively.  $^{71}\text{Ga}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AC 300 WB spectrometer operating at 91.531 MHz; chemical shifts are given in ppm ( $\delta$ ) relative to  $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ . Mass spectra were recorded on a Nermag R10-10H or a Hewlett-Packard 5989 instrument operating in the electron impact mode at 70 eV, and samples were contained in glass capillaries under argon. IR spectra were obtained on a Perkin-Elmer 1600 FT-IR spectrometer. Irradiations were carried out at 25 °C using a low-pressure mercury immersion lamp in a quartz tube. Melting points were measured on a hot-plate microscope apparatus from Leitz Biomed. Elemental analyses (C, H, N) were performed by the Microanalysis Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse.

Theoretical calculations were performed with the Gaussian 98 program.<sup>26</sup> The density functional theory was used with the hybrid exchange functional B3LYP.<sup>27</sup> Calculations were realized with the SDD basis set, which adopts the Dunning/

Huzinaga valence double- $\zeta$  basis set for the first-row atoms<sup>28</sup> and the Stuttgart/Dresden<sup>29</sup> effective core potential basis set for the others. Geometry optimizations were followed by frequency calculations in order to verify that the stationary points obtained are true minima. For NBO calculations and Molekel visualizations, see refs 30 and 31, respectively.

**Synthesis of  $\text{L}^2(\text{OTf})\text{GeW}(\text{CO})_5$  (**2**).** (a) A tetrahydrofuran solution (60 mL) of  $\text{W}(\text{CO})_6$  (510 mg, 1.45 mmol) was irradiated for 2 h. CO was eliminated by bubbling of argon in the reaction mixture for 15 min, and then a tetrahydrofuran solution (30 mL) of  $\text{L}^2(\text{OTf})\text{Ge}$  (684 mg, 1.45 mmol) was slowly added at room temperature. The mixture was stirred for 2 h. The volatile materials were removed under reduced pressure to obtain **2** as a yellow solid (75% yield, 863 mg). (b) A toluene solution (15 mL) of  $\text{L}^2(\text{Cl})\text{GeW}(\text{CO})_5$  (80 mg, 0.12 mmol) was added to a suspension of  $\text{AgOTf}$  (30 mg, 0.12 mmol) in toluene (10 mL). The reaction mixture was then stirred at room temperature in the absence of light for 1 h and filtered. The volatile materials were removed under reduced pressure to yield **2** as a yellow solid (80% yield, 76 mg). Crystallization from toluene at –30 °C gave yellow crystals of **2**. Mp: 119–123 °C (dec). IR: ( $\text{CHCl}_3$ )  $\nu$  2062.4, 1973.9, 1932.3 (CO), 1366.5 (OTf); ( $\text{C}_6\text{D}_6$ )  $\nu$  2079.3, 1986.2, 1943.1 (CO), 1365.4 (OTf); ( $\text{C}_5\text{H}_5\text{N}$ )  $\nu$  2063.8, 1934.4, 1920.5 (CO), 1379.1, 1274.0 (OTf)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.58 (s, 6H,  $\text{CH}_3$ ), 5.24 (s, 1H, CH), 6.93–7.29 (m, 10H,  $\text{C}_6\text{H}_5$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.11 (s, 6H,  $\text{CH}_3$ ), 5.85 (s, 1H, CH), 7.19–7.51 (m, 10H,  $\text{C}_6\text{H}_5$ ).  $^1\text{H}$  NMR ( $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$  1.77 (s, 6H,  $\text{CH}_3$ ), 2.11 (s, 6H, 2 $\text{CH}_3$ ), 5.12 (s, 1H, CH), 5.32 (s, 1H, CH), 7.20–7.55 (m, 20H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  24.02 (s,  $\text{CH}_3$ ), 103.83 (s, CH), 121.4 (s,  $\text{CF}_3$ ), 127.57 (s, *m*-aryl-C), 128.13 (s, *p*-aryl-C), 129.09 (s, *o*-aryl-C), 141.54 (s,  $\text{C}_{\text{ipso}}$ ), 169.53 (s, C–N), 194.64 (s, CO), 197.41 (s, CO).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  –1.65 (s,  $\text{CF}_3$ ). MS:  $m/z$  794 [ $\text{M}]^+$ , 766 [ $\text{M} - \text{CO}]^+$ , 645 [ $\text{M} - \text{OTf}]^+$ . Anal. Calcd for  $\text{C}_{23}\text{F}_3\text{GeH}_{17}\text{N}_2\text{O}_8\text{SW}$  (794.95): C, 34.75; H, 2.16; N, 3.52. Found: C, 34.68; H, 2.08; N, 3.47.

**Synthesis of  $\text{L}^2(\text{OTf})\text{Ge}$  (**3**).** A toluene solution (10 mL) of  $\text{L}^2\text{GeCl}$  (189 mg, 0.53 mmol) was slowly added to a suspension of  $\text{AgOTf}$  (136 mg, 0.53 mmol) in toluene (10 mL). The reaction mixture was then stirred at room temperature in the absence of light for 1 h and filtered. The volatile materials were removed under reduced pressure to yield **3** as a yellow solid (75% yield, 188 mg). Mp: 146–155 °C (dec). IR: ( $\text{CHCl}_3$ )  $\nu$  1378.7 (OTf); ( $\text{C}_6\text{D}_6$ )  $\nu$  1367.7 (OTf); ( $\text{C}_5\text{H}_5\text{N}$ )  $\nu$  1367.4, 1271.7 (OTf)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.44 (s, 6H,  $\text{CH}_3$ ), 4.98 (s, 1H, CH), 6.95–7.42 (m, 10H,  $\text{C}_6\text{H}_5$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.07 (s, 6H,  $\text{CH}_3$ ), 5.66 (s, 1H, CH), 7.33–7.39 (m, 10H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  23.88 (s,  $\text{CH}_3$ ), 103.45 (s, CH), 119.8 (s,  $\text{CF}_3$ ), 129.49 (s, *m*-aryl-C), 129.96 (s, *p*-aryl-C), 131.02 (s, *o*-aryl-C), 142.44 (s,  $\text{C}_{\text{ipso}}$ ), 168.82 (s, C–N).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  –2.03 (s,  $\text{CF}_3$ ). MS:  $m/z$  472 [ $\text{M}]^+$ , 323 [ $\text{M} - \text{OTf}]^+$ . Anal.

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Calcd for  $C_{18}F_3H_{17}N_2O_3SGe$  (470.996): C, 45.90; H, 3.64; N, 5.95. Found: C, 45.95; H, 3.70; N, 5.92.

**Synthesis of  $L^2GaCl$  (**7**).** A dichloromethane solution (5 mL) of  $L^2GeCl$  (**4**) (421 mg, 1.17 mmol) was added to a suspension of  $GaCl_3$  (206 mg, 1.18 mmol) in dichloromethane (5 mL) at  $-78^\circ C$ . The reaction mixture was warmed to room temperature for 2 h. After filtration and removal of the solvent under reduced pressure, **7** was obtained as a yellow solid (50% yield, 228 mg). Mp:  $165-170^\circ C$  (dec).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.92 (s, 6H,  $CH_3$ ), 5.10 (s, 1H, CH), 7.12–7.42 (m, 10H,  $C_6H_5$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  23.66 (s,  $CH_3$ ), 97.19 (s, CH), 126.26 (s, *m*-aryl-C), 127.21 (s, *p*-aryl-C), 129.47 (s, *o*-aryl-C), 142.93 (s,  $C_{ipso}$ ), 170.09 (s, C–N).  $^{71}Ga$  NMR ( $CDCl_3$ ):  $\delta$  245.8. MS: (EI)  $m/z$  390  $[M]^+$ . Anal. Calcd for  $C_{17}H_{17}N_2GaCl_2$  (389.95): C, 52.36; H, 4.39; N, 7.19. Found: C, 52.26; H, 4.40; N, 7.25.

**Synthesis of  $L^2In$  (**8**).** A dichloromethane solution (8 mL) of  $L^2GeCl$  (**4**) (352 mg, 0.98 mmol) was added to a suspension of  $InI_3$  (486 mg, 0.98 mmol) in dichloromethane (8 mL) at  $-78^\circ C$ . The reaction mixture was warmed to room temperature for 2 h. After filtration and removal of the solvent under reduced pressure, **8** was obtained as a yellow solid (52% yield, 315 mg). Crystallization from toluene at room temperature gave yellow crystals of **8**. Mp:  $136-138^\circ C$  (dec).  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  1.48 (s, 6H,  $CH_3$ ), 4.55 (s, 1H, CH), 7.03–7.11 (m, 10H,  $C_6H_5$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  24.03 (s,  $CH_3$ ), 97.62 (s, CH), 125.44 (s, *m*-aryl-C), 126.06 (s, *p*-aryl-C), 129.64 (s, *o*-aryl-C), 146.02 (s,  $C_{ipso}$ ), 169.56 (s, C–N). MS:  $m/z$  618,  $[M]^+$ , 491  $[M - I]^+$ . Anal. Calcd for  $C_{17}H_{17}N_2InI_2$  (617.926): C, 33.04; H, 2.77; N, 4.53. Found: C, 32.97; H, 2.65; N, 4.51.

**Reaction of  $L^2(Cl)GeW(CO)_5$  (**1**) with  $NaBPh_4$ .** A dichloromethane solution (10 mL) of  $L^2(Cl)GeW(CO)_5$  (257 mg, 0.377 mmol) was added to a suspension of  $NaB(Ph)_4$  (129 mg, 0.377 mmol) in dichloromethane (5 mL) at room temperature. The reaction mixture was refluxed during 1 day and then filtered. The volatile materials were removed under reduced pressure to obtain a yellow solid (290 mg). The  $^1H$  NMR and mass spectra of the crude product showed the presence of **9** and **10** in addition to minor unidentified products.  $^1H$  NMR and MS data for **9** and **10** were extracted from spectra of the mixture.

**9:**  $L^2(Ph)GeW(CO)_5$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.98 (s, 6H,  $CH_3$ ), 5.30 (s, 1H, CH), 7.18–7.69 (m, 15H,  $C_6H_5$ ). MS:  $m/z$  722  $[M]^+$ , 694  $[M - CO]^+$ , 638  $[M - 3CO]^+$ , 582  $[M - 5CO]^+$ .

**10:**  $L^2(B(Ph)_2O)GeW(CO)_5$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.99 (s, 6H,  $CH_3$ ), 5.31 (s, 1H, CH), 7.20–7.76 (m, 20H,  $C_6H_5$ ). MS:  $m/z$  826  $[M]^+$ , 742  $[M - 3CO]^+$ , 686  $[M - 5CO]^+$ .

**Reaction of  $L^2(Cl)GeW(CO)_5$  (**1**) with  $AgPF_6$ .** A dichloromethane solution (10 mL) of  $L^2(Cl)GeW(CO)_5$  (**1**) (350 mg, 0.513 mmol) was added to a suspension of  $AgPF_6$  (130 mg, 0.513 mmol) in dichloromethane (5 mL) at room temperature and in the absence of light. The reaction mixture was stirred for 1 h at room temperature and then filtered. **11** crystallized as yellow needles after the solution stood at room temperature for 2 days. The volatile materials in the remaining solution were removed under reduced pressure to yield a yellow solid crude product (180 mg), the  $^1H$ ,  $^{19}F$ , and  $^{31}P$  NMR and mass spectra of which indicated it to consist of ca. 2:3 molar mixture of **11** and **12** in addition to minor unidentified products.

**11:**  $(L^2H_2)^+(PF_6)^-$ .  $^{31}P$  NMR ( $CD_3CN$ ): 143.6 (hept,  $^1J_{PF} = 707$  Hz).  $^{19}F$  NMR ( $CD_3CN$ ):  $\delta$  7.81 (d,  $^1J_{FP} = 707$  Hz).  $^1H$  NMR (80.13 MHz,  $CD_3CN$ ):  $\delta$  2.54 (s, 6H,  $CH_3$ ), 5.54 (s, 1H, CH), 7.07–7.49 (m, 10H,  $C_6H_5$ ), 8.93 (s, 2H, NH).

**12:**  $L^2GeOP(O)F_2$ .  $^{31}P$  NMR ( $CD_3CN$ ):  $-22.1$  (t,  $^1J_{PF} = 978$  Hz).  $^{19}F$  NMR ( $CD_3CN$ ):  $\delta -0.54$  (d,  $^1J_{FP} = 979$  Hz).  $^1H$  NMR ( $CD_3CN$ ):  $\delta$  2.01 (s, 6H,  $CH_3$ ), 5.63 (s, 1H, CH), 7.04–7.46 (m, 10H,  $C_6H_5$ ). MS:  $m/z$  424  $[M]^+$ .

**Synthesis of  $[L^2(Cl)Ge]_2W(CO)_4$  (**13**).** (a) A mixture of  $L^2-GeCl$  (**4**) (998 mg, 2.79 mmol) and  $W(CO)_6$  (490 mg, 1.40 mmol) in tetrahydrofuran (60 mL) was irradiated for 4 h. CO was eliminated by bubbling of argon in the reaction mixture for 15 min. The volatile materials were removed under reduced pressure; subsequent addition of pentane and filtration afforded crude **13** as a yellow solid (70% yield, 992 mg). Recrystallization from chloroform at room temperature gave yellow crystals of **13**.

(b) A  $C_6D_6$  solution (2 mL) of  $L^2(Cl)GeW(CO)_5$  (**1**) (50 mg, 0.07 mmol) was irradiated for 3 h. The solution turned maroon, and a black solid appeared. After filtration, the solution was determined to be a mixture of **1** (65%) and **13** (35%).

**13:** Mp:  $190-205^\circ C$  (dec). IR ( $CHCl_3$ ):  $\nu$  1897.8  $cm^{-1}$  (CO).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.88 (s, 12H,  $CH_3$ ), 5.38 (s, 2H, CH), 7.22–7.42 (m, 20H,  $C_6H_5$ ).  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  1.45 (s, 12H,  $CH_3$ ), 4.96 (s, 2H, CH), 7.20–7.48 (m, 20H,  $C_6H_5$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  24.81 (s,  $CH_3$ ), 101.11 (s, CH), 127.73 (s, *m*-aryl-C), 129.49 (s, *p*-aryl-C), 129.72 (s, *o*-aryl-C), 143.18 (s,  $C_{ipso}$ ), 166.82 (s, C–N), 200.96 (s, CO). MS:  $m/z$  358  $[M - L^2Ge(Cl) - W(CO)_4]^+$ . Anal. Calcd for  $C_{38}H_{34}N_4O_4Cl_2Ge_2W$  (1010.62): C, 45.16; H, 3.39; N, 5.54. Found: C, 45.20; H, 3.42; N, 5.62.

**Reaction of  $[L^2(Cl)Ge]_2W(CO)_4$  with  $AgOTf$ .** A toluene suspension (10 mL) of  $(L^2(Cl)Ge)_2W(CO)_4$  (**13**) (177 mg, 0.18 mmol) was added to a suspension of  $AgOTf$  (93 mg, 0.36 mmol) in toluene (10 mL). The reaction mixture was then stirred at room temperature for 1 h and filtered. The brown precipitate was dissolved in DMSO ( $AgCl$  precipitate), and the solution was analyzed by  $^1H$  NMR and IR spectroscopy (52% yield, 116 mg). IR: ( $d_6$ -DMSO)  $\nu$  1271.4 (OTf), 1370.5 (OTf), 1904.4 (CO)  $cm^{-1}$ .  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.03 (s, 6H,  $CH_3$ ), 2.30 (s, 6H,  $CH_3$ ), 5.57 (s, 1H, CH), 5.92 (s, 1H, CH), 7.07–7.50 (m, 20H,  $C_6H_5$ ). MS: (EI)  $m/z$  472  $[M - L^2Ge(OTf)W(CO)_4]^+$ .

**X-ray Crystal Structure Determination of Compounds **2**, **8**, and **13**.** Crystal data for **2**, **8**, and **13** are presented in Table 1. All data were collected at low temperatures ( $-80^\circ C$ ) on a Bruker-AXS CCD 1000 diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods by means of SHELXS-97<sup>32</sup> and refined with all data on  $F^2$  by means of SHELXL-97.<sup>33</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model.

**Acknowledgment.** A.C. and V.L. acknowledge the Conseil Régional d'Aquitaine for financial support for V.L.

**Supporting Information Available:** CIF files for the structures reported in this paper.  $^1H$ ,  $^{13}C\{^1H\}$ , and  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ ) and IR data for compounds **2**, **3**, and **13**. Cartesian coordinates and total natural charge of compounds **1'**, **2'**, and **2''**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM050214V

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