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# THE SYNTHESIS, CHARACTERIZATION AND X-RAY STRUCTURE OF *ANTI*-$W_2(GePh_3)_2(NMe_2)_4$

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**Abstract**—The reaction between $LiGePh_3$ and $W_2Cl_2(NMe_2)_4$ in toluene–THF produces $W_2(GePh_3)_2(NMe_2)_4$ in high yield (69%). The product is air-stable, decomposes at 209°C and is soluble in aromatic hydrocarbon solvents. The $^1H$ NMR spectrum reveals only an *anti*-isomer with $T_c = 115°C$, $\Delta G^\dagger = 74$ kJ mol$^{-1}$ for amide rotation. The X-ray structure is consistent with the $^1H$ NMR spectrum and reveals a central *anti*-ethane-like $W_2N_4Ge_2$ core with bond lengths and angles: $W \equiv W = 2.2970(9)$ Å, $W—Ge = 2.625(1)$ Å, $W—N = 1.95(av)$ Å, $W—W—Ge = 95.89(3)°$. The compound crystallized in the $P2_1/n$ space group with the cell parameters $a = 19.770(6)$, $b = 11.685(2)$, $c = 9.326(2)$ Å, $\beta = 99.74(1)°$, $Z = 2$, $V = 2123.3$ Å$^3$, $d_c = 1.802$ g cm$^{-3}$ at $-172°C$.

There are a number of germanides of the chromium triad, especially for metal centres supported with carbonyl and cyclopentadiene ligands.[1] Despite this very few have been structurally characterized. To our knowledge no dimetallic compounds of this triad containing a metal to germanium bond is known. Previously compounds of the type $M_2(R)_2(NMe_2)_4$ [$M = Mo, W$; $R = Cl$, $Si(SiMe_3)_3$, $Sn(SnMe_3)_3$, $SeC_6H_2Me_3$, $SC_6H_2Me_3$, $OCPh_3$] have been synthesized, normally by metathesis reactions involving LiR and the substitutionally labile $M_2Cl_2(NMe_2)_4$ compounds.[2–4] Here we report the reaction of $LiGePh_3$ with $W_2Cl_2(NMe_2)_4$ to produce the first group VI dimetallic germanyl $M_2(GePh_3)_2(NMe_2)_4$. This species could be considered as an example of a heteropolyatomic germanium-containing metal oligomer.

## RESULTS AND DISCUSSION

### *Preparation*

Reaction of $W_2Cl_2(NMe_2)_4$ with $LiGePh_3$ proceeds in a toluene–THF solution to produce $W_2(GePh_3)_2(NMe_2)_4$ in high yield (69%), eq. (1):

$$W_2Cl_2(NMe_2)_4 + 2LiGePh_3 \longrightarrow 2LiCl + W_2(GePh_3)_2(NMe_2)_4. \quad (1)$$

The reaction proceeds quite rapidly in that seemingly all the LiCl is immediately precipitated on mixing the reagents. Filtering the solution to remove the LiCl and allowing the filtrate to stand at room temperature yielded orange crystals of $W_2(GePh_3)_2(NMe_2)_4$. These crystals were suitable for an X-ray determination as noted below. The compound is air-stable and soluble in aromatic hydrocarbon solvents (0.2 g/25 cm$^3$ toluene). It thermally decomposes at 208–209°C but seems relatively inert to hydrolysis either by 6 N $HNO_3$ or EtOH/KOH (6 N) solutions. These physical properties are probably attributable to the steric shielding provided by the $GePh_3$ ligands, which limits access to the metal centres.

### *Characterization*

$W_2(GePh_3)_2(NMe_2)_4$ had the expected dimethylamide and phenyl ring vibrations in the IR. No assignable M—Ge stretches were seen in the region 4000–200 cm$^{-1}$ [W—Ge = 190 cm$^{-1}$].[5] The $^1H$ NMR spectrum of $W_2(GePh_3)_2(NMe_2)_4$ in $C_6D_6$ is consistent with only the *anti*-rotamer being present in solution. All the dimethylamide ligands are equivalent (related by symmetry elements $\sigma$ and $C_2$) but the methyl groups on each dimethylamide ligand are different, being either proximal or distal to the $M \equiv M$ bond. A difference in chemical shift of 1.55 ppm between these groups is attributable to the diamagnetic anisotropy produced by the M—M triple bond. Variable temperature $^1H$ NMR spectra in $C_6D_5CD_3$ show extreme broadening at 105°C (Fig. 1) ($\Delta\nu = 465$ Hz) and give an estimated coales-

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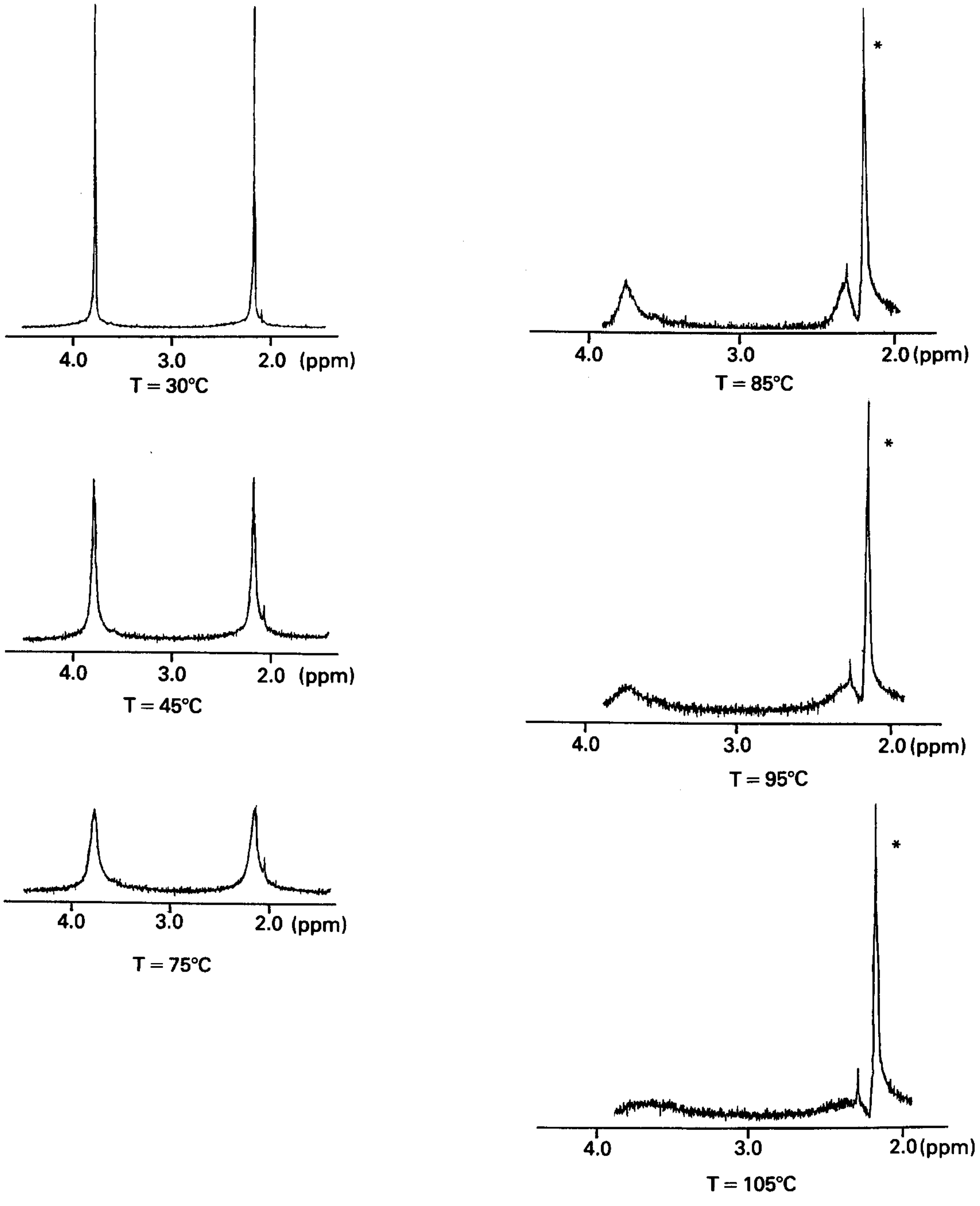

Fig. 1. Variable temperature $^1$H NMR spectra recorded in toluene-$d_8$ at 300 MHz showing the dimethylamide resonances of *anti*-$W_2(GePh_3)_2(NMe_2)_4$. * Residual protio toluene.

cence temperature of 115°C at 300 MHz for free rotation about the M—N bond of a dimethylamide ligand. This is amongst the highest $T_c$ values recorded for M—$NMe_2$ rotation in $M_2R_2(NMe_2)_4$ complexes[2,3] and is consistent with the large steric pressure of the $GePh_3$ ligands. Cooling a sample of $W_2(GePh_3)_2(NMe_2)_4$ to $-40$°C does not reveal any other dimethylamide environments.

*Solid-state molecular structure*

The molecular crystal structure of $W_2(GePh_3)_2(NMe_2)_4$ found in the solid state (X-ray) is shown in Fig. 2, looking perpendicular to the W—W vector, and a parallel view is shown in Fig. 3. The structure reveals an "ethane-like" staggered conformation with the $GePh_3$ ligands disposed in

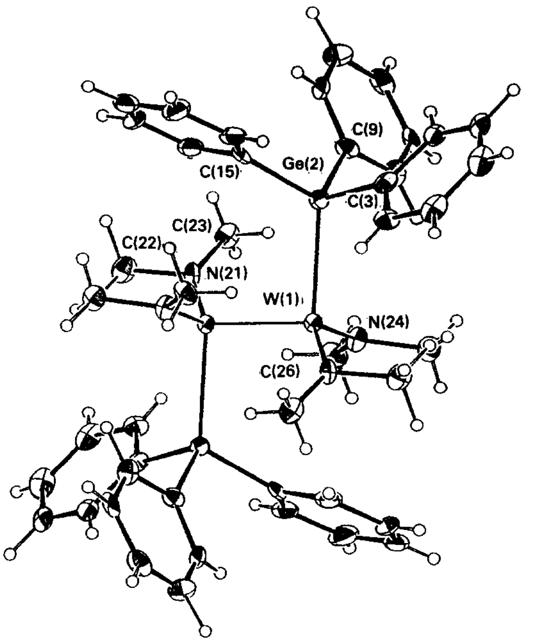

Fig. 2. An ORTEP view of the centrosymmetric $W_2(GePh_3)_2(NMe_2)_4$ giving the atom numbering scheme used in the tables.

an *anti*-configuration. The molecule has a crystallographically imposed centre of inversion.

The W—W distance of 2.2970(9) Å is typical for a W—W triple bond, and considerably shorter than the W—Ge distance of 2.625(1) Å. This later distance is shorter[2] than the corresponding Mo—Sn distance in $Mo_2\{Sn(SnMe_3)_3\}_2(NMe_2)_4$, 2.77 Å, and shorter than the Mo—Si distance in $Mo_2\{Si(SiMe_3)_3\}_2(NMe_2)_4$, 2.67 Å. It is also shorter than the sum of covalent radii of tungsten and germanium. The angles subtended at tungsten reveal the steric pressure of the $GePh_3$ ligand across the M—M bond. Most notable is the enlarged N—W—N angle, 124°, relative to the Ge—W—N angles, 109(av)° (Table 1).

The M—N distance of 1.95(av) Å is consistent with other dimethylamide tungsten distances in $W_2R_2(NMe_2)_4$ complexes, and together with the planarity at nitrogen is indicative of a strong M—N $d\pi$–$p\pi$ interaction.[7]

The observed *anti*-configuration is expected on steric grounds to be more stable than the *gauche* configuration in the presence of the large $GePh_3$ groups. Indeed the large "propeller-like" phenyl rings would seem to preclude the *gauche* conformation even in solution and provide a hydrophobic shield for the $NMe_2$ ligands. Presumably it is this shielding that makes the compound inert to air, acid and alcoholic alkaline solutions.

## EXPERIMENTAL

General procedures and the preparation of $W_2Cl_2(NMe_2)_4$ have been reported.[8]

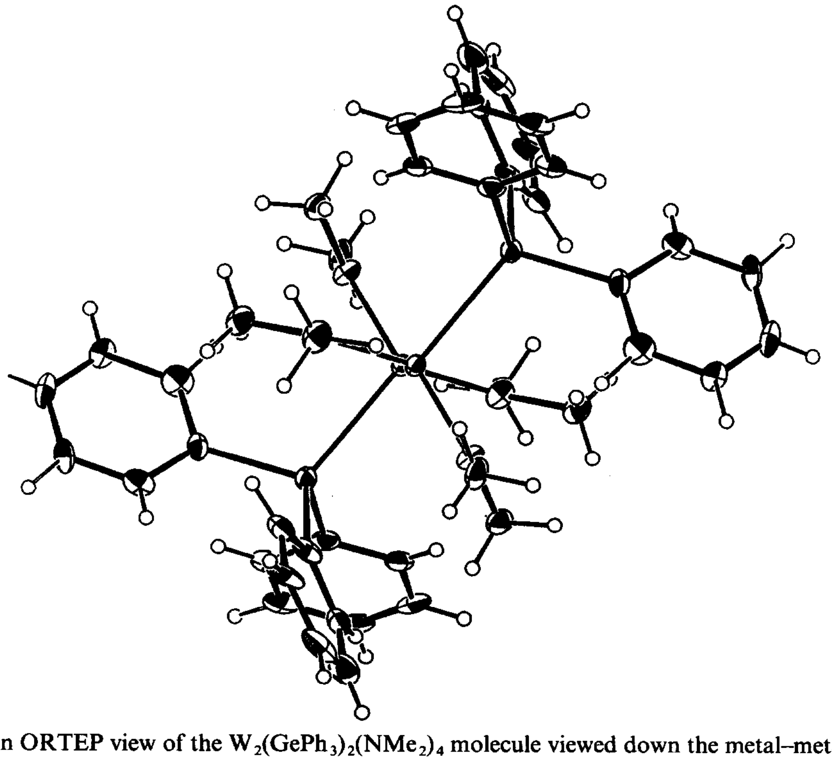

Fig. 3. An ORTEP view of the $W_2(GePh_3)_2(NMe_2)_4$ molecule viewed down the metal–metal bond.

Table 1. Selected bond distances (Å) and angles (°) in $W_2(GePh_3)_2(NMe_2)_4$

| | | | |
|---|---|---|---|
| W(1)—W(1) | 2.2970(9) | Ge(2)—C(15) | 1.971(10) |
| W(1)—Ge(2) | 2.625(1) | N(21)—C(22) | 1.471(13) |
| W(1)—N(21) | 1.954(8) | N(21)—C(23) | 1.447(13) |
| W(1)—N(24) | 1.945(7) | N(24)—C(25) | 1.457(12) |
| Ge(2)—C(3) | 1.990(9) | N(24)—C(26) | 1.469(13) |
| Ge(2)—C(9) | 1.976(9) | | |
| W(1)′—W(1)—N(21) | 106.82(21) | W(1)—N(21)—C(22) | 112.3(6) |
| W(1)′—W(1)—N(24) | 106.99(22) | W(1)—N(21)—C(23) | 137.9(6) |
| W(1)′—W(1)—Ge(2) | 95.89(6) | C(22)—N(21)—C(23) | 109.3(8) |
| Ge(2)—W(1)—N(21) | 110.4(2) | W(1)—N(24)—C(25) | 135.4(6) |
| Ge(2)—W(1)—N(24) | 108.3(2) | W(1)—N(24)—C(26) | 116.0(6) |
| N(21)—W(1)—N(24) | 124.5(3) | C(25)—N(24)—C(26) | 107.9(8) |
| C(3)—Ge(2)—C(9) | 106.1(4) | Ge(2)—C(3)—C(4) | 120.7(7) |
| C(3)—Ge(2)—C(15) | 104.3(4) | Ge(2)—C(3)—C(8) | 121.5(7) |
| C(9)—Ge(2)—C(15) | 103.9(4) | | |

### *Preparation of* $W_2(GePh_3)_2(NMe_2)_4$

Triphenylgermanium chloride (0.500 g, 1.47 mmol) was dissolved in THF (5 $cm^3$) and added over 10 min to a stirred lithium suspension (0.060 g, 8.6 mmol) in THF (5 $cm^3$). This mixture was stirred for 5 h to generate a yellow solution and a white precipitate. The $LiGePh_3$ solution was filtered through a fine porosity frit and added to a solution of $W_2Cl_2(NMe_2)_4$ (0.405 g, 0.75 mmol) in toluene (15 $cm^3$) at room temperature to produce an immediate white precipitate. The reaction solution was allowed to stand for 5 min then filtered through a celite/glass frit. The filtrate was allowed to stand at room temperature for 12 h and deposited orange crystals which were collected by decanting the solvent and washing with hexane (10 $cm^3$), toluene (10 $cm^3$) and diethyl ether (10 $cm^3$). These were suitable for X-ray crystallography as described below. Yield: 0.47 g, 0.40 mmol, 53%. Cooling the filtrate to −20°C produced a further small crop, 0.19 g, 0.16 mmol; combined yield: 69%.

Found: C, 46.3; H, 4.6; N, 4.8. Calc: C, 45.8; H, 4.7; N, 4.7%. The crystals were air-stable for over a week at room temperature and had a decomposition point of 208–209°C. $^1H$ NMR at room temperature in $C_6D_6$: $\delta$ 7.61 (m, 12H), 7.20 (m, 18H), 3.73 (s, 12H), 2.18 (s, 12H). VT: $^1H$ NMR $T_c = 115°C$ (estimated), $\Delta\nu = 465$ Hz, $\Delta G^{\dagger} = 74$ kJ $mol^{-1}$ in $C_6D_5CD_3$. IR data (KBr pellet, $cm^{-1}$): 3040m, 2980m, 2940m, 2845s, 2800m, 2750m, 1560m, 1470m, 1450?, 1435s, 1420vs, 1380w, 1290m, 1250m, 1230s, 1173m, 1150w, 1125m, 1085w, 1070s, 1015s, 985w, 955w, 935vs, 920vs, 840m, 805m, 725vs, 685vs, 655w, 600w, 540m, 460s, 360w, 300s, 290s.

### *Crystallographic determination*

A suitable crystal was located and transferred to the goniostat using standard inert atmosphere handling techniques, employed by the Indiana University Molecular Structure Center, and cooled to −172°C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$). Subsequent solution and refinement of the structure confirmed this choice.

Data were collected by using a continuous $\theta$–$2\theta$ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated sigmas in the usual manner. The structure was solved by a combination of direct methods (MULTAN 78) and Fourier techniques. Data were corrected for absorption, based on well-defined crystal faces. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined (full-matrix least-squares) isotropically and non-hydrogen atoms anisotropically in the final cycles (see Table 2 for crystallographic data).

A final difference Fourier was featureless, with the largest peak being 0.45 e/$Å^3$.

Atomic coordinates have been deposited with the Director, Crystallographic Data Center, Cambridge.

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Table 2. Summary of crystallographic data

| | |
|---|---|
| Empirical formula | $W_2C_{44}H_{54}N_4Ge_2$ |
| Colour of crystal | Orange |
| Crystal dimensions (mm) | 0.124 × 0.22 × 0.22 |
| Space group | $P2_1/n$ |
| Cell dimensions | |
| Temperature (°C) | −172 |
| $a$ (Å) | 19.770(6) |
| $b$ (Å) | 11.685(2) |
| $c$ (Å) | 9.326(2) |
| $\beta$ (°) | 99.74(1) |
| $Z$ (molecules/cell) | 2 |
| Volume ($Å^3$) | 2123.30 |
| Calculated density (g $cm^{-3}$) | 1.802 |
| Wavelength (Å) | 0.71069 |
| Molecular weight | 1151.82 |
| Linear absorption coefficient ($cm^{-1}$) | 69.349 |
| Detector to sample distance (cm) | 22.5 |
| Sample to source distance (cm) | 23.5 |
| Average omega scan width at half height | 0.25 |
| Scan speed (° $min^{-1}$) | 8.0 |
| Scan width (° + dispersion) | 2.0 |
| Individual background (s) | 4 |
| Aperture size (mm) | 3.0 × 4.0 |
| $2\theta$ range (°) | $6 \leqslant \theta \leqslant 45$ |
| Total number of reflections collected | 3598 |
| Number of unique intensities | 2762 |
| Number with $F > 0.0$ | 2563 |
| Number with $F > 2.33\sigma(F)$ | 2380 |
| Number of variables | 342 |
| $R(F)$ | 0.0356 |
| $R_w(F)$ | 0.0330 |
| Goodness-of-fit for the last cycle | 1.030 |
| Maximum delta/sigma for last cycle | 0.23 |

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