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Facile Transmetalation Reactions of Macrocyclic ($C_{22}H_{22}N_4$) Complexes of Germanium(II), Tin(II), and Lead(II)[1]

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In a previous communication, we described the synthesis of group 14 macrocyclic complexes of the general type M(tmtaa) (M = Ge(**1**), Sn (**2**); tmtaa = dibenzotetramethyltetraaza[14]-annulene).[2] Both complexes adopt unusual[3] square pyramidal M(II) geometries in which the Ge(II) and Sn(II) centers reside 0.909(4) and 1.15(1) Å respectively above the N_4 plane of the saddle-shaped macrocycle. We have now succeeded in preparing the congeneric Pb(II) compound Pb(tmtaa) (**3**) by an analogous synthetic route, which, on the basis of spectroscopic data,[4] can be assigned a structure similar to those of the Ge(II) and Sn(II) complexes but with the Pb atom presumably raised >1.15 Å above the N_4 plane.

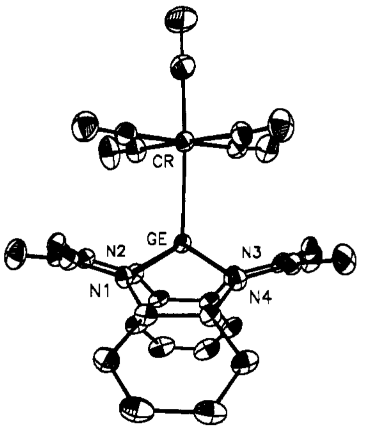

Figure 1. View of the crystal structure (ORTEP) of **4**. Important bond distances (Å) and angles (deg): Cr–Ge = 2.500(2), Ge–N(1) = 2.012(7), Ge–N(2) = 2.028(7), Ge–N(3) = 2.002(7), Ge–N(4) = 2.042(6); N(1)–Ge–N(2) = 82.9(3), N(2)–Ge–N(3) = 78.7(3), N(3)–Ge–N(4) = 83.0(3), N(1)–Ge–N(4) = 78.6(3).

The availability of a M lone pair in M(tmtaa) compounds enables them to function as electron donor ligands and thus to provide access to unusual intermetallic derivatives. We have performed an X-ray analysis[5] on (tmtaa)GeCr(CO)$_5$ (**4**), the first such complex, which was prepared via the reaction of **1** with (THF)Cr(CO)$_5$.[2] The local geometries around chromium and germanium are octahedral and square pyramidal, respectively, and the equatorial Cr(CO)$_4$ and GeN$_4$ moieties are arranged in an eclipsed fashion (Figure 1). The major change in the Ge(tmtaa) molecule as it undergoes complexation is shortening of the average Ge–N bond distance from 2.107(4) to 2.021(7) Å. Typically, the Ge–N bond distance in N_2Ge(II) systems is ~1.87 Å while N→Ge donor–acceptor bonds are ~2.12 Å in length.[6] The observed Ge–N bond distance in **4** is therefore close to that expected on the basis of two σ and two donor–acceptor bonds. There are very few Ge(II)–Cr(O) bond distances in the literature. In terms of available X-ray structural data, the compound most

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(1) Dedicated to Professor Hans Bock on the occasion of his 65th birthday.

(2) Atwood, D. A.; Atwood, V. O.; Cowley, A. H.; Atwood, J. L.; Román, E. *Inorg. Chem.* **1992**, *31*, 3871.

(3) For Sn(II) and Pb(II) phthalocyanine and porphyrin complexes, see: Barbe, J.-M.; Ratti, C.; Richard, P.; Lecomte, C.; Gerardin, R.; Guilard, R. *Inorg. Chem.* **1990**, *29*, 4126 and references therein.

(4) **3**: mp 168–173 °C. Anal. Calcd for $C_{22}H_{22}N_4Pb$: C, 48.08; H, 4.03. Found: C, 47.82; H. 3.85. HRMS (EI, 70 eV): calcd for $C_{22}H_{22}N_4Pb$ (M^+), *m/e* 550.161 088; found, *m/e* 550.160 647. ^1H NMR (300.15 MHz, C_6D_6, 295 K, TMS external): δ 6.89 (m, 8 H, C_6H_4), 4.69 (s, 2 H, CH), 1.87 (s, 12 H, CH_3). **5**: mp 213–128 °C (dec). Anal. Calcd for $C_{25}H_{22}CrN_4O_3$: C, 62.76; H, 4.63. Found: C, 63.25; H, 3.92. HRMS (EI, 70 eV): calcd for $C_{22}H_{22}CrN_4$ (M^+ – 3CO), *m/e* 394.124 957; found, *m/e* 394.124 634. IR (Nujol mull): ν_{CO} 1988, 2003 cm^{-1}. ^1H NMR (300.15 MHz, C_6D_6, 295 K, TMS external): δ 6.82 (m, 8H, C_6H_4), 4.25 (s, 2 H, CH), 1.57 (s, 12 H, CH_3). **6**: mp 225–228 °C (dec). Anal. Calcd for $C_{23}H_{25}A1N_4$: C, 71.86; H, 6.55. Found: C, 71.01; H, 7.06. HRMS (EI, 70 eV): calcd for $C_{22}H_{22}A1N_4$ (M^+ – CH_3), *m/e* 369.165 988; found, *m/e* 369.166 05. ^1H NMR (300.15 MHz, C_6D_6, 295 K, TMS external): δ 6.90 (s, 8 H, C_6H_4), 4.76 (m, 2 H, CH), 1.97 (s, 12 H, CH_3), 0.69 (s, 3H, A1CH_3).

(5) Crystal data for **4** ($C_{27}H_{22}CrGeN_4O_5$): triclinic, $P\bar{1}$, with a = 10.631 (2) Å, b = 11.270 (3) Å, c = 12.707 (3) Å, α = 66.49 (2)°, β = 81.84 (2)°, γ = 89.12 (2)°, V = 1380.5 (6) Å^3, Z = 2, d_{calcd} = 1.47 g cm^{-3}, μ(Mo Kα) 15.08 cm^{-1}. A total of 3289 independent reflections was collected at 298 K on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated radiation (0.710 69 Å) in the $\theta/2\theta$ scan mode. Of these, 2428 reflections were considered observed ($I > 6.0\sigma(I)$). The Ge and Cr atoms were found from a Patterson search. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions and refined using fixed isotropic thermal parameters. The structure was refined to final R and R_w values of 0.508 and 0.0607, respectively.

(6) See, for example: Pfeiffer, J.; Mariggele, W.; Notemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245.

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similar to **4** is $(MesS)_2GeCr(CO)_5$ (Mes = mesityl) in which this bond distance is 2.367(2) Å and for which a bond order of 1.5 was estimated.[7] The Ge–Cr bond distance in **4** is somewhat longer (2.500(2) Å) but still shorter than the sum of the covalent radii for Ge[8] and Cr[9] (2.69 Å). The CO stretching frequencies for **4** (2050, 1967, 1951 cm^{-1}) are very similar to those reported for $(Ph_2N)_2GeCr(CO)_5$ (2066, 1960, 1955 cm^{-1}).[10]

Interestingly, the reaction of the lead analogue **3** with $(THF)Cr(CO)_5$ (in THF solution at 25 °C) results in transmetalation rather than intermetallic complex formation (eq 1). It has not proved possible to determine the X-ray crystal structure of the resulting $Cr(CO)_3(tmtaa)$ (**5**). The identification of **5** therefore rests on analytical and spectroscopic data.[4] The highest *m/e* peak in either the EIor CI (CH_4) mass spectrum of **5** occurs at 394. The assignment of this peak to $M^+ - 3CO$ was confirmed by an HRMS experiment, which revealed peaks of the appropriate isotopic ratios that correspond to $C_{22}H_{22}N_4Cr$. The presence of the $Cr(CO)_3$ moiety was indicated by the detection of IR bands at 2003 (A_1) and 1988 (E) cm^{-1}. The equivalence of the aryl, methine, and methyl resonances in the ^1H NMR[4] is indicative of a symmetrical attachment of the $Cr(CO)_3$ and tmtaa units.

$$\underset{\mathbf{3}}{Pb(tmtaa)} + (THF)Cr(CO)_5 \rightarrow \underset{\mathbf{5}}{Cr(CO)_3(tmtaa)} + Pb(O) + 2CO \quad (1)$$

In order to expand the scope of the transmetalation reactions, compounds **1–3** were treated with $AlMe_3$ in toluene solution. In each case transmetalation took place at ambient temperature and in virtually quantitative yield (eq 2). Compound **6** was identified on the basis of elemental analysis, NMR and mass spectroscopy,[4] and independent synthesis. Analysis of the highest *m/e* peaks in the HRMS revealed that the isotopic distribution corresponds to $C_{22}H_{22}N_4Al$ ($M^+ - CH_3$). The presence of the Al–Me moiety was evident from a peak at δ 0.69 in the ^1H NMR spectrum. Moreover, the ^1H NMR spectrum is (a) very similar to that reported for the analogous Al–Et compound reported by Goedken et al.[11] and (b) indicative of a square pyramidal N_4Al unit with an axial Me group. Independent synthesis of **6** (95% yield) was achieved by treatment of H_2tmtaa with an excess of $AlMe_3$ in toluene at −78 °C.

$$M(tmtaa) + AlMe_3 \rightarrow \underset{\mathbf{6}}{Al(tmtaa)Me} + \text{“}MMe_2\text{”} \quad (2)$$

$$M = Ge(\mathbf{1}), Sn(\mathbf{2}), Pb(\mathbf{3})$$

In summary, we have demonstrated novel examples of transmetalation reactions for tmtaa complexes.[12] This transmetalation approach appears to be a useful method for the synthesis of new main group and transition complexes featuring the tmtaa ligand.

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Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **4** (4 pages). Ordering information is given on any current masthead page.

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(7) Jutzi, P.; Steiner, W.; König, E.; Huttner, G.; Frank, A.; Schubert, U. *Chem. Ber.* **1978**, *111*, 606.

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(11) Goedken, V. L.; Ito, H.; Tio, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1453.

(12) For an excellent review of the synthesis and reactivity of transition metal tmtaa complexes, see: Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 2553.