

Synthesis of Triscyclopentadienyl(triphenylgermyl)uranium and Facile Isonitrile Insertion into the Uranium–Germanium Bond

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The uranium–germanium bonded complex $(\text{cp})_3\text{UGePh}_3$ (**1**) ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$) has been prepared from $(\text{cp})_3\text{UCl}$ and KGePh_3 and fully characterized; it reacts readily with 2,6-dimethylphenyl isocyanide $[(\text{Xyl})\text{NC}]$ to give the carbamoyl insertion product $(\text{cp})_3\text{U}[\text{C}(\text{GePh}_3)=\text{N}(\text{Xyl})]$ (**2**), the dynamic ^1H n.m.r. behaviour of which is described.

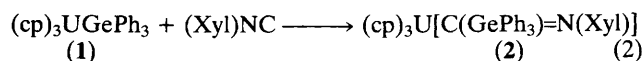
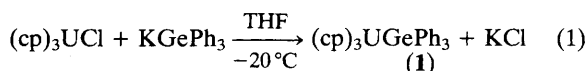
A large number of heterobimetallic complexes¹ containing direct metal–metal bonds have been described and their theoretical and practical importance is well documented. While many examples of bimetallic compounds of the d transition series metals have been reported in the last two decades, only recently have similar compounds involving 5f elements, containing in particular Th–Ru,^{2a} Th–Pt,^{2b} and U–Sn³ bonds, been prepared and structurally characterized.

Herein we report the synthesis and characterization of $(\text{cp})_3\text{UGePh}_3$ (**1**) ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$) and the insertion of xylyl isonitrile $[(\text{Xyl})\text{NC}]$ into the U–Ge bond to give the $(\text{cp})_3\text{U}[\text{C}(\text{GePh}_3)=\text{N}(\text{Xyl})]$ derivative (**2**).

Complex (**1**) was isolated (80% yield) as a dark red powder from the reaction of $(\text{cp})_3\text{UCl}$ and KGePh_3 in tetrahydrofuran (THF) (equation 1)[†] after filtration of the brown solution and removal of the solvent. Complex (**1**) is inert towards CO (1 atm., room temp.); however, it dissolves in toluene to give a green solution which reacts at room temperature with 2,6-dimethylphenyl isocyanide (1 equiv.), turning red in 2–3 h and providing (**2**) almost quantitatively according to equation (2). Complexes (**1**) and (**2**) are thermally stable and air sensitive; they are soluble in toluene, benzene, and THF [in which (**1**) slowly decomposes at room temperature] and insoluble in n-hexane [(**1**) also in Et_2O]. The proposed formulations for (**1**) and (**2**) are based on their satisfactory elemental analyses and are consistent with their i.r. and ^1H

n.m.r. spectra.[‡] In particular (**2**) shows a new i.r. band [with respect to (**1**)] at 1520 cm^{-1} attributable to $\nu(\text{C}=\text{N})$,⁴ which matches well with C–N stretching frequencies of structurally characterized η^2 -isonitrile insertion products.⁵ In this case it is probably indicative of the η^2 mode of ligation of the $-\text{C}(\text{GePh}_3)=\text{N}(\text{Xyl})$ moiety to the uranium atom [structure (A)].

The ^1H n.m.r. spectra of both compounds show large isotropic shifts typical for paramagnetic organometallic U^{IV} compounds. Insertion of $(\text{Xyl})\text{NC}$ into the U–Ge bond of (**1**) dramatically shifts the signals of the phenyl protons allowing their unequivocal assignment by double resonance experiments. The signal of the cyclopentadienyl protons of (**2**) appears as a broad singlet at room temperature, upfield of those of (**1**), but it is split into two singlets at low temperature (Figure 1). The non-equivalence of the cp groups can be imputed to a restricted rotation of the $-\text{C}(\text{GePh}_3)=\text{NXyl}$ ligand about the axis connecting the uranium atom with the midpoint of the C=N bond. In fact, assuming a tetrahedral geometry around the uranium atom with the cp centroids and the midpoint of the C=N bond as the vertices, the absence of free rotation makes the three cp groups no longer magnetically equivalent as represented in Figure 2. The barrier to rotation can be estimated at the coalescence temperature (-23°C). The isotropic shifts of the cp resonances were found to obey an approximate Curie relationship below the coalescence tem-



[†] KGePh_3 was freshly prepared from Ph_6Ge_2 and K in THF and added dropwise to a cooled $(\text{cp})_3\text{UCl}$ solution. After 2 h stirring the solution was warmed to room temperature and stirred for a further 5 h.

[‡] Spectroscopic data for (**1**): ^1H n.m.r. (C_6D_6 , 27°C , $\text{C}_6\text{D}_5\text{H}$ as internal standard, relative to Me_4Si), δ -3.7 (s, 15H, cp), -8.5 (d, 6H, *o*-PhH), and 4.1 (m, 9H, *m*- and *p*-PhH); m/z 304 (GePh_3^+), 610 (Ge_2Ph_6^+), 368 (cp_2U^+), 227 (GePh_2^+), M^+ not observed; i.r. (Nujol, KBr disc), ν_{max} 2190, 2110, 1570, 1070, 1010, 790, 730, 700, 440 cm^{-1} . Compound (**2**): ^1H n.m.r. (C_6D_6 , 27°C), δ -11.6 (br. s, 15H, cp), -29.4 (s, 6H, Me), 24.3 (d, 6H, *o*-PhH), 11.8 (t, 6H, *m*-PhH), 9.8 (t, 3H, *p*-PhH), 0.4 (t, 1H, *p*-XylH), -2.2 (d, 2H, *m*-XylH); m/z 435 [$(\text{Ph}_3\text{GeC}=\text{NXyl})^+$], 433 (cp_3U^+), 304 (GePh_3^+), 227 (GePh_2^+), M^+ not observed; i.r. (Nujol, KBr disc), ν_{max} 1560, 1520, 1190, 1160, 1090, 1020, 780, 740, 700, and 470 cm^{-1} .

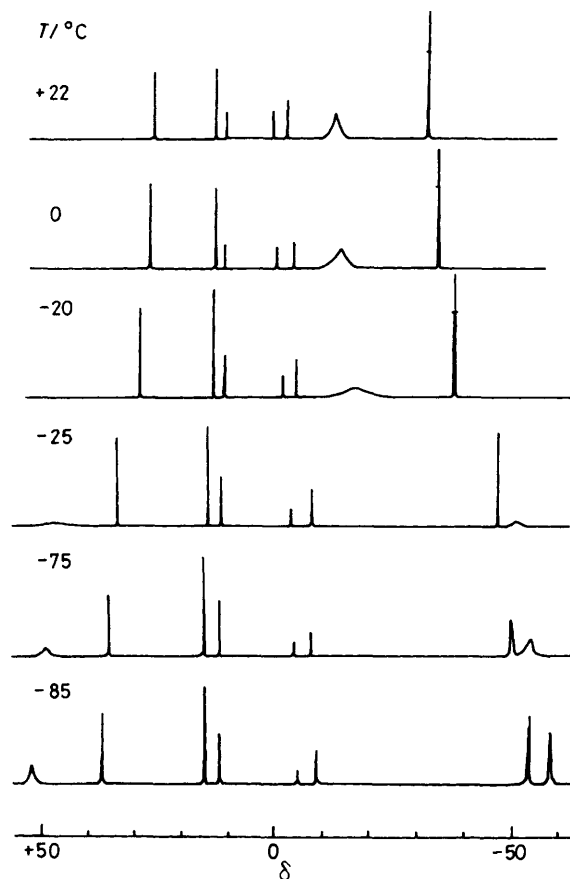


Figure 1. Variable temperature Fourier transform ^1H n.m.r. spectra (80 MHz) of $(\text{cp})_3\text{U}[\text{C}(\text{GePh}_3)=\text{NXyl}]$ in $[\text{}^2\text{H}_8]\text{toluene}$. The absolute vertical scale may vary somewhat from spectrum to spectrum.

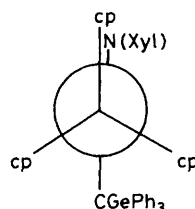
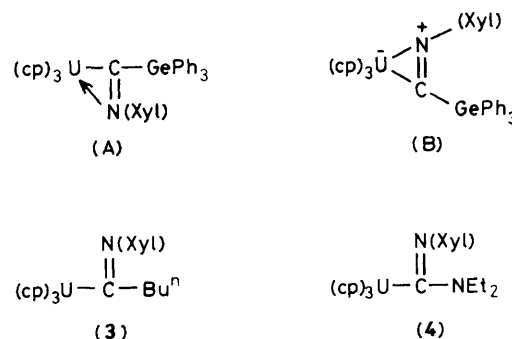


Figure 2

perature and an extrapolation of a least-squares fit to these data yields $\Delta\delta$ 7046 Hz and τ_c 6.39×10^{-5} at this temperature.

The activation energy ΔG^\ddagger ,^{6§} for the process was estimated to be 40.8 ± 3 kJ mol⁻¹. This value, even though smaller, compares with energetic barriers to analogous process in other insertion products.⁷ It is noteworthy that this phenomenon [*i.e.* magnetic non-equivalence of the three cp groups in $(\text{cp})_3\text{UX}$ compounds] has been observed thus far almost exclusively⁸ when X is a ligand obtained by insertion of xyl isonitrile into the U-C⁷ and U-N⁵ bonds. Unfortunately no crystals suitable for an X-ray structural characterization of (2) have been obtained; however its i.r. spectrum and its dynamic



^1H n.m.r. behaviour are reminiscent of the previously described compounds (3)⁷ and (4),^{5b} indicating that an electronic formulation such as (B) (in which the $(\text{Xyl})\text{N}=\text{CGePh}_3$ moiety is bonded to the uranium atom in such a strong fashion that the free rotation about the axis is hampered) may significantly contribute to the structure of (2).

In conclusion, the data reported give further proof of the possibility of the formation of U-metal compounds and show that the reactivity of $(\text{cp})_3\text{UGePh}_3$ towards xyl isonitrile is similar to that previously observed with compounds containing U-N and U-C bonds leading in our case to a η^2 -germyl carbamoyl derivative. This reaction, which represents one of the very few examples of isonitrile insertion into metal-metal bonds,⁹ confirms the interesting predicted reactivity of these bimetallic compounds.^{1a}

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§ $\delta_a = 11.08 \times 10^3 T^{-1} + 2.91$
 $\delta_b = -8.46 \times 10^3 T^{-1} + 2.76$
 $\tau_c^{-1} = (KT/h) \exp(-\Delta G^\ddagger/RT)$