

Iridium(III) Hydrides derived from an Iridium(I) Substrate by Oxidative Addition and Cyclometallation of Germanium(II) Bis(trimethylsilyl)amide; X-Ray Structures of

$[\{\text{CH}_2\text{Me}_2\text{SiN(R)(NR}_2\text{)Ge}\}\text{H}(\mu\text{-Cl})_2\{\text{Ge(NR}_2\text{)N(R)SiMe}_2\text{CH}_2\}\text{IrH}\{\text{Ge(NR}_2\text{)}_2\}]$ and $[\text{Ir}\{\text{GeCl(NR}_2\text{)N(R)SiMe}_2\text{CH}_2\}(\text{CO})_2\text{H}\{\text{Ge(NR}_2\text{)}_2\}]$ ($\text{R} = \text{SiMe}_3$)[†]

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Treatment of $[\{\text{Ir}(\eta\text{-C}_8\text{H}_{14})_2(\mu\text{-Cl})\}_2]$ with $\text{Ge(NR}_2)_2$ in $n\text{-C}_6\text{H}_{14}$ at 20 °C ($\text{C}_8\text{H}_{14} = \text{cyclo-octene}$, $\text{R} = \text{SiMe}_3$) in the absence or presence of CO leads to $[\{\text{CH}_2\text{Me}_2\text{SiN(R)(NR}_2\text{)Ge}\}\text{H}(\mu\text{-Cl})_2\{\text{Ge(NR}_2\text{)N(R)SiMe}_2\text{CH}_2\}\text{IrH}\{\text{Ge(NR}_2\text{)}_2\}]$ (**1**) or $[\text{Ir}\{\text{GeCl(NR}_2\text{)N(R)SiMe}_2\text{CH}_2\}(\text{CO})_2\text{H}\{\text{Ge(NR}_2\text{)}_2\}]$ (**2**), respectively; the Ir–Ge distances in (**1**) and (**2**) range from 2.325(3) to 2.470(3) Å.

The bivalent group 14 (Ölander numbering) metal amides $\text{M}'(\text{NR}_2)_2$ ($\text{M}' = \text{Ge}$ or Sn , $\text{R} = \text{SiMe}_3$) are proving to have an extensive transition metal (M) chemistry, behaving in one of the following ways: (a) as terminal¹ or bridging² 2-electron ligands; (b) as substrates for insertion into M–X bonds (*e.g.*, $\text{X} = \text{Cl}$ or Me);^{1,3} (c) as reducing agents;⁴ and (d) as *N*-centred nucleophiles with respect to transition metal hydrides.¹

We now report a novel type of behaviour, whereby $\text{Ge(NR}_2)_2$ acts as a reagent HA for oxidative addition to a low oxidation state transition metal complex $[\text{M}(\text{L}_n)\text{X}]$. Two classes of such reactions have been discovered: leading to either $[\text{M}(\text{H})\text{A}(\text{L}_m)]$ or $[\text{M}(\text{H})(\text{A-X})(\text{L}_m)]$.

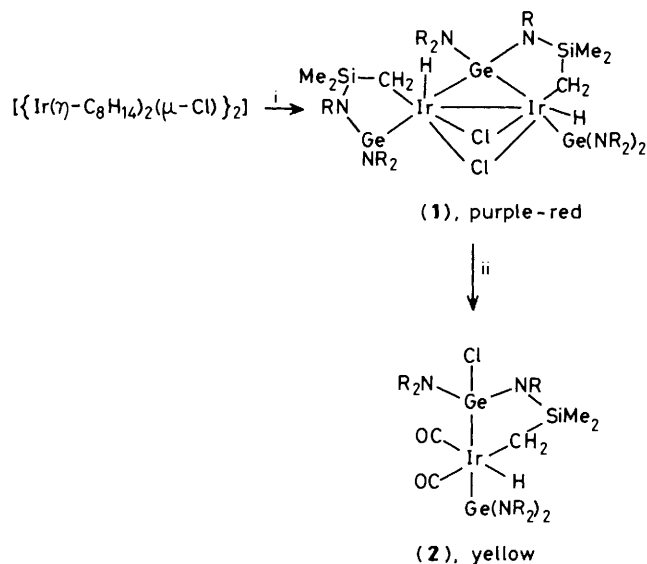
Reaction of $[\{\text{Ir}(\eta\text{-C}_8\text{H}_{14})_2(\mu\text{-Cl})\}_2]$ ($\text{C}_8\text{H}_{14} = \text{cyclo-octene}$) with $4\text{Ge(NR}_2)_2$ afforded (i in Scheme 1) the binuclear hydrido-iridium(III) complex (**1**), *via* oxidative insertion of each Ir^I centre into a C–H bond of $\text{Ge(NR}_2)_2$. Features of note include: (a) the remarkably mild reaction conditions leading to complex (**1**) (i in Scheme 1); (b) the contrast with the

corresponding Rh–Sn reaction which yielded $[(\text{Rh}(\mu\text{-Cl})\{\text{Sn}(\text{NR}_2)_2\}_2)_2]$, or $[\text{Rh}(\eta\text{-C}_8\text{H}_{14})(\eta\text{-PhMe})\{\text{SnCl}(\text{NR}_2)_2\}]$ in PhMe ;³ (c) the novel hybrid ligand $:\text{Ge}(\text{NR}_2)\text{N}(\text{R})\text{SiMe}_2\text{CH}_2^-$ (**3**) which has both an alkyl and a germylene (germanediyl) centre; and (d) the demonstration that the new ligand (**3**) is capable of acting in either a chelating or a bridging mode, see (**1**) and Figure 1.

Cleavage of the binuclear complex (**1**) by CO in the presence of one equivalent of $\text{Ge(NR}_2)_2$ led to the mononuclear hydrido-Ir^{III} complex (**2**). This reaction (ii in Scheme 1) demonstrates, *inter alia*, the considerable nucleophilicity of the $\text{Ge(NR}_2)_2$ ligand; thus complex (**2**) still contains a terminally bound $\text{Ge(NR}_2)_2$, which is not displaced by excess of CO. Also noteworthy is the new dianionic hybrid ligand $-\text{GeCl}(\text{NR}_2)\text{N}(\text{R})\text{SiMe}_2\text{CH}_2^-$ (**4**), formally generated by Cl^- migration from Ir to the Ge atom of ligand (**3**).

Complexes (**1**) and (**2**) are of further interest as (a) rare examples of iridium complexes derived from cyclometallated ligands which are other than *N*-, *P*-, or *C*-centred (*cf.*, ref. 5), and (b) the first iridium complexes having $\text{Ge(NR}_2)_2$ ligands. Other examples of cyclometallated complexes derived from

[†] No reprints available.



Scheme 1. R = SiMe₃. C₈H₁₄ = cyclo-octene. Reagents and conditions; i, 4Ge(NR₂)₂, n-C₆H₁₄, 20 °C; ii, Ge(NR₂)₂, CO, 1 atm, n-C₆H₁₄, 20 °C. Characterisation: ¹H n.m.r. [two inequivalent IrH at δ -21.8 and -24.1 for (1), and a single IrH at δ -9.96 for (2)], i.r., and X-ray [Figures 1 (1) and 2 (2)].

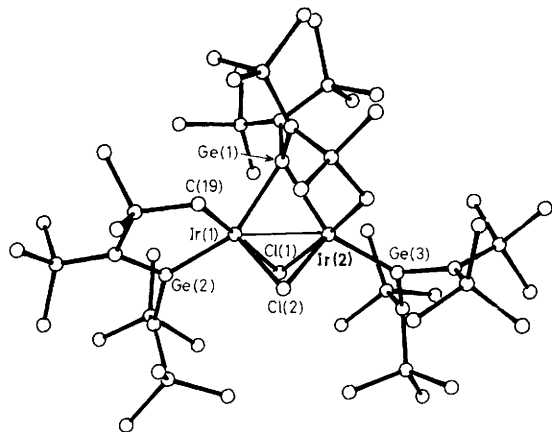


Figure 1. The molecular structure and atom numbering scheme for $[\{\overline{\text{CH}_2\text{Me}_2\text{Si}(\text{R})(\text{NR}_2)\text{Ge}}\}\text{Ir}(\mu\text{-Cl})_2\{\overline{\text{Ge}(\text{NR}_2)\text{N}(\text{R})\text{SiMe}_2\text{CH}_2}\}\text{IrH}\{\text{Ge}(\text{NR}_2)_2\}]$ (R = SiMe₃) (1). Selected bond lengths (Å) and angles (°) are: Ir(1)–Ge(1) 2.466(2), Ir(1)–Ge(2) 2.325(3), Ir(1)–Cl(1) 2.442(5), Ir(1)–Cl(2) 2.485(8), Ir(1)–C(19) 2.11(2), Ir(2)–Ge(1) 2.470(3), Ir(2)–Ge(3) 2.331(3), Ir(2)–Cl(1) 2.462(7), Ir(2)–Cl(2) 2.467(5), Ir(2)–C(1) 2.15(2), Ir(1)–Ir(2) 2.723(1); Ir(1)–Ge(1)–Ir(2) 66.96(2), Ir(1)–Cl(1)–Ir(2) 67.4(2), Ir(1)–Cl(2)–Ir(2) 66.7(2).

–NR₂ are $[\text{MCp}_2\{\text{N}(\text{SiMe}_3)\text{SiMe}_2\text{CH}_2\}]$ [MCp₂ = Ti(η-C₅H₅)₂⁶ or U(η-C₅Me₅)₂⁷], but their formation is unlikely to have involved oxidative insertion into a trimethylsilyl C–H bond.

X-Ray quality crystals of each of the complexes (1) and (2) were grown from n-hexane at –30 °C. The X-ray structures of

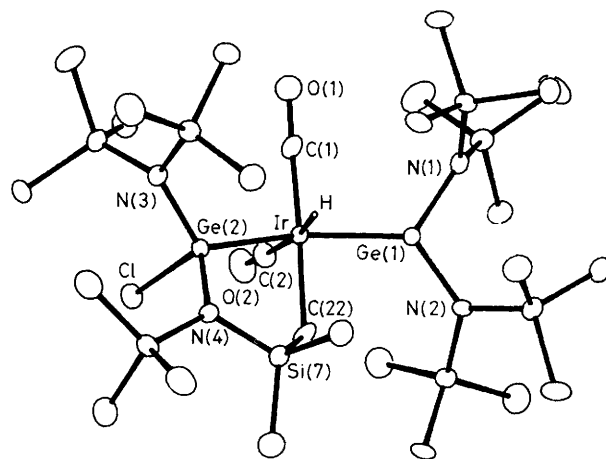


Figure 2. The molecular structure and atom numbering scheme for $[\text{Ir}\{\overline{\text{GeCl}(\text{NR}_2)\text{N}(\text{R})\text{SiMe}_2\text{CH}_2}\}(\text{CO})_2\text{H}\{\text{Ge}(\text{NR}_2)_2\}]$ (R = SiMe₃) (2). Selected bond lengths (Å) and angles (°) are: Ir–Ge(1) 2.418(1), Ir–Ge(2) 2.460(1), Ir–C(1) 1.84(1), Ir–C(2) 1.92(1), Ir–C(22) 2.12(1), Ir–H 1.72(8); Ge(1)–Ir–Ge(2) 158.55(4), N(1)–Ge(1)–N(2) 109.5(4), N(3)–Ge(2)–N(4) 113.0(3), N(3)–Ge(2)–Cl 104.4(3), N(4)–Ge(2)–Cl 100.8(3).

complexes (1) and (2) are illustrated in Figures 1 and 2, respectively.‡

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References

- M. F. Lappert and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1985, 51.
- G. K. Campbell, P. B. Hitchcock, M. F. Lappert, and M. C. Misra, *J. Organomet. Chem.*, 1985, **289**, C1.
- S. M. Hawkins, P. B. Hitchcock, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1985, 1592.
- T. A. K. Al-Allaf, C. Eaborn, P. B. Hitchcock, M. F. Lappert, and A. Pidcock, *J. Chem. Soc., Chem. Commun.*, 1985, 548.
- G. J. Leigh and R. L. Richards in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, Vol. 5, Section 36.2.1.6; P. B. Hitchcock, M. F. Lappert, and P. Terreros, *J. Organomet. Chem.*, 1982, **239**, C26; L. Dahlenburg and A. Yardimcioglu, *ibid.*, 1985, **291**, 371.
- C. R. Bennett and D. C. Bradley, *J. Chem. Soc., Chem. Commun.*, 1974, 29.
- S. J. Simpson, H. W. Turner, and R. A. Andersen, *Inorg. Chem.*, 1981, **20**, 2991.

‡ Crystal data for (1) [and (2) in square brackets]: *M* = 1635.4 [1070.4]; triclinic [triclinic], space group *P* $\bar{1}$ [*P* $\bar{1}$], *a* = 11.940(2) [11.240(1)], *b* = 17.651(4) [14.621(1)], *c* = 19.682(4) [15.974(1)] Å; α = 70.41(2) [72.91(1)], β = 84.12(2) [81.53(1)], γ = 71.40(2) [76.64(1)]°, *U* = 3703.7 [2432.4] Å³; *Z* = 2 [2]; *D*_c = 1.47 [1.46] g cm⁻³; μ(Mo-Kα) = 50.5 [42.1] cm⁻¹; 5129 [5023] reflections with *I* > σ(*I*), collected on an Enraf–Nonius CAD4 diffractometer; *R* = 0.061 [0.038]; *R*_w = 0.080 [0.069]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.