



Preparation and reactivity of germyl complexes of ruthenium and osmium stabilised by cyclopentadienyl, indenyl and tris(pyrazolyl) borate fragments

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ABSTRACT

Half-sandwich trichlorogermyl complexes $\text{Ru}(\text{GeCl}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{L}$ (**1**) and $\text{Ru}(\text{GeCl}_3)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)\text{L}$ (**2**) [$\text{L} = \text{P}(\text{OMe})_3$ (**a**), $\text{P}(\text{OEt})_3$ (**b**) and $\text{PPh}(\text{OEt})_2$ (**c**)] were prepared by allowing chloro compounds $\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{L}$ and $\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)\text{L}$ to react with an excess of $\text{GeCl}_2 \cdot \text{dioxane}$ in ethanol. Treatment of trichlorogermyl complexes **1** and **2** with LiAlH_4 in THF yielded trihydridogermyl derivatives $\text{Ru}(\text{GeH}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{L}$ (**3**) and $\text{Ru}(\text{GeH}_3)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)\text{L}$ (**4**). Instead, reaction of trichlorogermyl complexes **1** and **2** with NaBH_4 in ethanol afforded triethoxygermyl complexes $\text{Ru}[\text{Ge}(\text{OEt})_3](\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{L}$ (**5**) and $\text{Ru}[\text{Ge}(\text{OEt})_3](\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)\text{L}$ (**6**). Trichlorogermyl complexes with the tris(pyrazolyl)borate ligand $\text{M}(\text{GeCl}_3)(\text{Tp})(\text{PPh}_3)\text{L}$ [$\text{M} = \text{Ru}$ (**7**), Os (**10**)] were prepared by reacting chloro compounds $\text{MCl}(\text{Tp})(\text{PPh}_3)\text{L}$ with an excess of $\text{GeCl}_2 \cdot \text{dioxane}$. Depending on metal centre, nature of phosphite and experimental conditions, the reaction of trichlorogermyl complexes **7** and **10** with LiAlH_4 or NaBH_4 afforded trihydridogermyl $\text{M}(\text{GeH}_3)(\text{Tp})(\text{PPh}_3)\text{L}$ (**8**, **12**) and triethoxygermyl derivatives $\text{M}[\text{Ge}(\text{OEt})_3](\text{Tp})(\text{PPh}_3)\text{L}$ (**9**, **11**). The complexes were characterised by IR and multinuclear NMR spectroscopy and by X-ray crystal structure determination of **3a**.

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1. Introduction

The chemistry of transition metal complexes containing trichlorogermyl GeCl_3 or triorganogermyl GeR_3 as ligands has been extensively studied over several decades [1–3], both from a fundamental point of view and because these complexes are regarded as intermediates in a number of transition metal-catalysed transformations of group-14 element compounds [4,5]. A number of germyl complexes of several metals have thus been prepared, containing both mononuclear GeCl_3 and GeR_3 and polynuclear [$\text{GeR}_2\text{GeR}_2\text{GeR}_2$] germyl groups, but relatively few have been reported with trihydridogermyl GeH_3 as ligand [6].

We are interested in the synthesis and reactivity of germyl complexes of transition metals and have recently reported [7,8] the synthesis and reactivity of trihydrido- $[\text{M}]-\text{GeH}_3$ and organogermyl $[\text{M}]-\text{GeR}_3$ ($\text{R} = \text{Me}, \text{OEt}, \text{PhC}\equiv\text{C}$) derivatives of Mn and Re, and the preparation of osmium complexes containing an oxo-germanium cluster as ligand. We have now extended these

studies to both half-sandwich and tris(pyrazolyl)borate complexes of the iron triad of the types $\text{MCl}(\eta^5\text{-C}_5\text{H}_5)\text{PPh}_3\text{L}$, $\text{MCl}(\eta^5\text{-C}_9\text{H}_7)\text{PPh}_3\text{L}$, and $\text{MCl}(\text{Tp})\text{PPh}_3\text{L}$ [$\text{M} = \text{Ru}, \text{Os}$; $\text{Tp} = \text{tris}(\text{pyrazolyl})\text{borate}$; $\text{L} = \text{phosphite}$] and this paper reports the preparation and characterisation of new germyl complexes, including the first trihydridogermyl derivatives of ruthenium and osmium.

2. Experimental section

2.1. General comments

All synthetic work was carried out in an appropriate inert atmosphere (Ar, N_2) using standard Schlenk techniques or an inert atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under nitrogen at -25°C . All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and OsO_4 were obtained from Pressure Chemical Co. (USA) and used as received. Phosphonite $\text{PPh}(\text{OEt})_2$ was prepared by the method of Rabinowitz and Pellon [9], while $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OEt})_3$ were obtained from Sigma–Aldrich Co. (USA) and purified by distillation under nitrogen. $\text{GeCl}_2 \cdot \text{dioxane}$, NaBH_4 , and LiAlH_4

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were also obtained from Sigma–Aldrich Co. (USA) and used as received. Other reagents were purchased from commercial sources in the highest available purity and used as received.

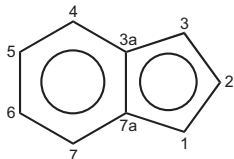
Infrared spectra were recorded on a Perkin–Elmer Spectrum–One FT–IR spectrophotometer. NMR spectra (^1H , ^{13}C , ^{31}P) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between -90 and $+30$ °C, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane; $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are reported with respect to external 85% H_3PO_4 , with downfield shifts considered positive. The iNMR software package [10] was used to treat NMR data. The conductivity values of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C were measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze del Farmaco, University of Padova (Italy).

2.2. Synthesis of complexes

The compounds $\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}$, $\text{RuCl}(\text{Tp})(\text{PPh}_3)_2\text{L}$, $\text{OsCl}(\text{Tp})(\text{PPh}_3)_2\text{L}$ [$\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$] [11a] and $\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2$ [11b] were prepared following the methods previously reported.

2.2.1. $\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2\text{L}$ [$\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$]

An excess of the appropriate phosphite L (6.0 mmol) was added to a solution of $\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2$ (1.29 mmol, 1.0 g) in THF (30 mL) and the reaction mixture was refluxed for 30 min. The solvent was removed under reduced pressure to give an oil, which was treated with the appropriate alcohol ROH (10 mL). The resulting solution was stirred for about 1 h and then cooled to -25 °C. After some days, an orange solid separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 75%.



L = P(OMe)₃: ^1H NMR (CD_2Cl_2 , 25 °C) δ : 7.65–7.25 (m, 15H, Ph), 6.91 (t m, 2H, H5 + H6 Ind), 6.61 (d, 2H, H4 + H7 Ind), 5.26 (m, 1H, H2 Ind), 3.46 (d, 9H, CH₃), 3.42 (s br, 2H, H1 + H3 Ind) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C) δ : AB spin syst, δ_A 152.7, δ_B 49.0, $J_{AB} = 75.3$ Hz. Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{ClO}_3\text{P}_2\text{Ru}$ (638.04): C, 56.47; H, 4.90; Cl, 5.56. Found: C, 56.66; H, 4.81; Cl, 5.70%.

L = P(OEt)₃: ^1H NMR (CD_2Cl_2 , 25 °C) δ : 7.50–7.25 (m, 15H, Ph), 6.85 (t m, 2H, H5 + H6 Ind), 6.62 (d, 2H, H4 + H7 Ind), 5.23 (m br, 1H, H2 Ind), 3.83 (m, 6H, CH₂), 3.36 (s br, 2H, H1 + H3 Ind), 1.10 (t, 9H, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C) δ : AB, δ_A 147.5, δ_B 49.4, $J_{AB} = 76.5$. Anal. Calcd for $\text{C}_{33}\text{H}_{37}\text{ClO}_3\text{P}_2\text{Ru}$ (680.12): C, 58.28; H, 5.48; Cl, 5.21. Found: C, 58.43; H, 5.37; Cl, 5.39%.

2.2.2. $\text{Ru}(\text{GeCl}_3)(\text{Cp})(\text{PPh}_3)_2\text{L}$ (**1**) and $\text{Ru}(\text{GeCl}_3)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2\text{L}$ (**2**) [$\text{L} = \text{P}(\text{OMe})_3$ (**a**), $\text{P}(\text{OEt})_3$ (**b**), $\text{PPh}(\text{OEt})_2$ (**c**)]

In a 25-mL three-necked round-bottomed flask were placed solid samples of the appropriate complex $\text{RuCl}(\text{Cp})(\text{PPh}_3)_2\text{L}$ or $\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2\text{L}$ (1.3 mmol), an excess of GeCl_2 -dioxane (4.14 mmol, 0.96 g), and 10 mL of ethanol. The reaction mixture was refluxed for 1 h and then the solvent was removed under reduced pressure to give an oily product, which was triturated with ethanol (2 mL). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 80%.

1a: ^1H NMR (CD_2Cl_2 , 25 °C) δ : 7.48–7.27 (m, 15H, Ph), 4.76 (s, 5H, Cp), 3.49 ppm (d, 9H, CH₃, $J_{\text{PH}} = 12.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ,

25 °C) δ : AB, δ_A 149.85, δ_B 51.1, $J_{AB} = 61.0$. $\text{C}_{26}\text{H}_{29}\text{Cl}_3\text{GeO}_3\text{P}_2\text{Ru}$ (731.52): calcd. C 42.69, H 4.00, Cl 14.54; found C 42.85, H 4.17, Cl 14.69%.

1b: ^1H NMR (CD_2Cl_2 , 25 °C) δ : 7.50–7.18 (m, 15H, Ph), 4.72 (s, 5H, Cp), 3.88 and 3.84 (m, 6H, CH₂), 1.15 (t, 9H, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C) δ : AB, δ_A 154.0, δ_B 60.55, $J_{AB} = 61.5$. $\text{C}_{29}\text{H}_{35}\text{Cl}_3\text{GeO}_3\text{P}_2\text{Ru}$ (773.60): calcd. C 45.02, H 4.56, Cl 13.75; found C 44.80, H 4.66, Cl 13.60%.

1c: ^1H NMR (CD_2Cl_2 , 25 °C) δ : 7.42–7.10 (m, 20H, Ph), 4.92 (s, 5H, Cp), 4.13, 3.87, 3.65 and 3.55 (m, 4H, CH₂), 1.37 and 1.13 (t, 6H, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C) δ : AB, δ_A 167.2, δ_B 49.6, $J_{AB} = 52.2$. $\text{C}_{33}\text{H}_{35}\text{Cl}_3\text{GeO}_2\text{P}_2\text{Ru}$ (805.65): calcd. C 49.20, H 4.38, Cl 13.20; found C 49.42, H 4.51, Cl 13.39%.

2a: ^1H NMR (CD_2Cl_2 , 25 °C) δ : 7.76–7.00 (m, 15H, Ph), 6.75 (t, 2H, H5 + H6 Ind), 6.17 (d, 2H, H4 + H7), 5.42 (t, 1H, H2 Ind), 5.40 (br, 1H, H3 Ind), 3.51 (d, 9H, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C) δ : AB, δ_A 146.8, δ_B 50.2, $J_{AB} = 60.8$. $\text{C}_{30}\text{H}_{31}\text{Cl}_3\text{GeO}_3\text{P}_2\text{Ru}$ (781.58): calcd. C 46.10, H 4.00, Cl 13.61; found C 45.87, H 4.12, Cl 13.41%.

2b: ^1H NMR (CD_2Cl_2 , 25 °C) δ : 7.74–6.97 (m, 15H, Ph), 6.82 (t m, 2H, H5 + H6 Ind), 6.05 (d, 2H, H4 + H7 Ind), 5.46 (m, 1H, H2 Ind), 5.36 (br, 1H, H3 Ind), 4.48 (br, 1H, H1 Ind), 3.87 (m, 6H, CH₂), 1.20 (t, 9H, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C) δ : AB, δ_A 141.6, δ_B 49.7, $J_{AB} = 60.8$. $\text{C}_{33}\text{H}_{37}\text{Cl}_3\text{GeO}_3\text{P}_2\text{Ru}$ (823.66): calcd. C 48.12, H 4.53, Cl 12.91; found C 48.34, H 4.39, Cl 12.70%.

2.2.3. $\text{Ru}(\text{GeH}_3)(\text{Cp})(\text{PPh}_3)_2\text{L}$ (**3**) and $\text{Ru}(\text{GeH}_3)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2\text{L}$ (**4**) [$\text{L} = \text{P}(\text{OMe})_3$ (**a**), $\text{P}(\text{OEt})_3$ (**b**), $\text{PPh}(\text{OEt})_2$ (**c**)]

In a 50-mL three-necked round-bottomed flask were placed solid samples of the appropriate complex $\text{Ru}(\text{GeCl}_3)(\text{Cp})(\text{PPh}_3)_2\text{L}$ (**1**) and $\text{Ru}(\text{GeCl}_3)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2\text{L}$ (**2**) (0.4 mmol), an excess of LiAlH_4 (8 mmol, 0.30 g), and 20 mL of THF. The reaction mixture was stirred at room temperature for 1 h and then the solvent was removed under reduced pressure leaving a solid from which the complex was extracted with three 10-mL portions of toluene using a cellulose column (3 cm) for filtration. Extracts were evaporated to dryness to give an oil which was triturated with ethanol (3 mL). A yellow solid separated out, which was filtered and dried under vacuum; yield 70%.

3a: IR (KBr pellet) $\nu_{\text{Ge-H}}$: 1949, 1924 (m) cm^{-1} . ^1H NMR ($\text{CD}_3\text{C}_6\text{D}_5$, 25 °C) δ : 7.58, 7.30 and 7.04 (m, 15H, Ph), 4.52 (s, 5H, Cp), ABX_3 spin syst, δ_x 3.25, $J_{\text{Ax}} = 3.2$, $J_{\text{Bx}} = 1.2$ (3H, GeH₃), 3.14 (d, 9H, CH₃, $J_{\text{PH}} = 12.0$). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CD}_3\text{C}_6\text{D}_5$, 25 °C) δ : AB, δ_A 162.4, δ_B 61.8, $J_{AB} = 61.5$. $\text{C}_{26}\text{H}_{32}\text{GeO}_3\text{P}_2\text{Ru}$ (628.19): calcd. C 49.71, H 5.13; found C 49.58, H 5.26%.

3b: IR (KBr pellet) $\nu_{\text{Ge-H}}$: 1915 (m br) cm^{-1} . ^1H NMR ($\text{CD}_3\text{C}_6\text{D}_5$, 25 °C) δ : 7.60, 7.29 and 7.02 (m, 15H, Ph), 4.52 (s, 5H, Cp), 3.69 and 3.54 (m, 6H, CH₂), ABX_3 , δ_x 3.26, $J_{\text{Ax}} = 3.1$, $J_{\text{Bx}} = 1.3$ (3H, GeH₃), 0.98 (t, 9H, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CD}_3\text{C}_6\text{D}_5$, 25 °C) δ : AB, δ_A 157.5, δ_B 61.6, $J_{AB} = 60.7$. $\text{C}_{29}\text{H}_{38}\text{GeO}_3\text{P}_2\text{Ru}$ (670.27): calcd. C 51.97, H 5.71; found C 52.14, H 5.80%.

3c: IR (KBr pellet) $\nu_{\text{Ge-H}}$: 1945, 1918 (m) cm^{-1} . ^1H NMR ($\text{CD}_3\text{C}_6\text{D}_5$, 25 °C) δ : 7.38 and 7.01 (m, 20H, Ph), 4.37 (s, 5H, Cp), 3.87, 3.52 and 3.25 (m, 4H, CH₂), ABX_3 , δ_x 3.30, $J_{\text{Ax}} = 2.95$, $J_{\text{Bx}} = 1.6$ (3H, GeH₃), 1.14, 0.96 (t, 6H, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CD}_3\text{C}_6\text{D}_5$, 25 °C) δ : AB, δ_A 175.4, δ_B 58.8, $J_{AB} = 47.3$. $\text{C}_{33}\text{H}_{38}\text{GeO}_2\text{P}_2\text{Ru}$ (702.31): calcd. C 56.44, H 5.45; found C 56.26, H 5.57%.

4a: IR (KBr pellet) $\nu_{\text{Ge-H}}$: 1921 (m br) cm^{-1} . ^1H NMR ($\text{CD}_3\text{C}_6\text{D}_5$, 25 °C) δ : 7.25–6.95 (m, 15H, Ph), 6.84 (m, 2H, H5 + H6 Ind), 6.42 (d, 2H, H4 + H7 Ind), 5.18 (m br, 1H, H2 Ind), 4.88 (s br, 1H, H3 Ind), 4.48 (s br, 1H, H1 Ind), ABX_3 , δ_x 3.21, $J_{\text{Ax}} = 3.7$, $J_{\text{Bx}} = 0.6$ (3H, GeH₃), 3.18 (d, 9H, CH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C) δ : AB, δ_A 159.2, δ_B 60.0, $J_{AB} = 55.0$. $\text{C}_{30}\text{H}_{34}\text{GeO}_3\text{P}_2\text{Ru}$ (678.25): calcd. C 53.13, H 5.05; found C 53.01, H 5.16%.

4b: IR (KBr pellet) $\nu_{\text{Ge-H}}$: 1931 (m br) cm^{-1} . ^1H NMR ($\text{CD}_3\text{C}_6\text{D}_5$, 25 °C) δ : 7.70–6.95 (m, 15H, Ph), 7.83 (t m, 2H, H5 + H6 Ind), 6.32 (d,

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