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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 Ru(GeCl$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)L (**1**) and Ru(GeCl$_3$)(η^5-C$_9$H$_7$)(PPh$_3$)L (**2**) [L = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**) and PPh(OEt)$_2$ (**c**)] were prepared by allowing chloro compounds RuCl(η^5-C$_5$H$_5$)(PPh$_3$)L and RuCl(η^5-C$_9$H$_7$)(PPh$_3$)L to react with an excess of GeCl$_2\cdot$dioxane in ethanol. Treatment of trichlorogermyl complexes **1** and **2** with LiAlH$_4$ in THF yielded trihydridogermyl derivatives Ru(GeH$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)L (**3**) and Ru(GeH$_3$)(η^5-C$_9$H$_7$)(PPh$_3$)L (**4**). Instead, reaction of trichlorogermyl complexes **1** and **2** with NaBH$_4$ in ethanol afforded triethoxygermyl complexes Ru[Ge(OEt)$_3$](η^5-C$_5$H$_5$)(PPh$_3$)L (**5**) and Ru[Ge(OEt)$_3$](η^5-C$_9$H$_7$)(PPh$_3$)L (**6**). Trichlorogermyl complexes with the tris(pyrazolyl)borate ligand M(GeCl$_3$)(Tp)(PPh$_3$)L [M = Ru (**7**), Os (**10**)] were prepared by reacting chloro compounds MCl(Tp)(PPh$_3$)L with an excess of GeCl$_2\cdot$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 M(GeH$_3$)(Tp)(PPh$_3$)L (**8**, **12**) and triethoxygermyl derivatives M[Ge(OEt)$_3$](Tp)(PPh$_3$)L (**9**, **11**). The complexes were characterised by IR and multinuclear NMR spectroscopy and by X-ray crystal structure determination of **3a**.

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 [GeR$_2$GeR$_2$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- [M]–GeH$_3$ and organogermyl [M]–GeR$_3$ (R = Me, OEt, PhC$\equiv$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 MCl(η^5-C$_5$H$_5$)PPh$_3$L, MCl(η^5-C$_9$H$_7$)PPh$_3$L, and MCl(Tp)PPh$_3$L [M = Ru, Os; Tp = tris(pyrazolyl)borate; L = 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. RuCl$_3\cdot$3H$_2$O and OsO$_4$ were obtained from Pressure Chemical Co. (USA) and used as received. Phosphonite PPh(OEt)$_2$ was prepared by the method of Rabinowitz and Pellon [9], while P(OMe)$_3$ and P(OEt)$_3$ were obtained from Sigma–Aldrich Co. (USA) and purified by distillation under nitrogen. GeCl$_2\cdot$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.

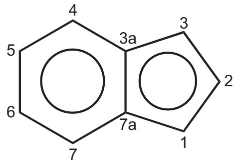
Infrared spectra were recorded on a Perkin–Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between −90 and +30 °C, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ 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 RuCl(η^5-C_5H_5)(PPh_3)L, RuCl(Tp)(PPh_3)L, OsCl(Tp)(PPh_3)L [L = P(OMe)$_3$, P(OEt)$_3$, PPh(OEt)$_2$] [11a] and RuCl(η^5-C_9H_7)(PPh_3)$_2$ [11b] were prepared following the methods previously reported.

2.2.1. *RuCl(η^5-C_9H_7)(PPh_3)L [L = P(OMe)$_3$, P(OEt)$_3$]*

An excess of the appropriate phosphite L (6.0 mmol) was added to a solution of RuCl(η^5-C_9H_7)(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, CH_3), 3.42 (s br, 2H, H1 + H3 Ind) ppm. $^{31}P\{^1H\}$ 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 $C_{30}H_{31}ClO_3P_2Ru$ (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, CH_2), 3.36 (s br, 2H, H1 + H3 Ind), 1.10 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 147.5, δ_B 49.4, J_{AB} = 76.5. Anal. Calcd for $C_{33}H_{37}ClO_3P_2Ru$ (680.12): C, 58.28; H, 5.48; Cl, 5.21. Found: C, 58.43; H, 5.37; Cl, 5.39%

2.2.2. *Ru($GeCl_3$)(Cp)(PPh_3)L (**1**) and Ru($GeCl_3$)(η^5-C_9H_7)(PPh_3)L (**2**) [L = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**)]*

In a 25-mL three-necked round-bottomed flask were placed solid samples of the appropriate complex RuCl(Cp)(PPh_3)L or RuCl(η^5-C_9H_7)(PPh_3)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, CH_3, J_{PH} = 12.0 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 149.85, δ_B 51.1, J_{AB} = 61.0. $C_{26}H_{29}Cl_3GeO_3P_2Ru$ (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, CH_2), 1.15 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 154.0, δ_B 60.55, J_{AB} = 61.5. $C_{29}H_{35}Cl_3GeO_3P_2Ru$ (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, CH_2), 1.37 and 1.13 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 167.2, δ_B 49.6, J_{AB} = 52.2. $C_{33}H_{35}Cl_3GeO_2P_2Ru$ (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, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 146.8, δ_B 50.2, J_{AB} = 60.8. $C_{30}H_{31}Cl_3GeO_3P_2Ru$ (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, CH_2), 1.20 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 141.6, δ_B 49.7, J_{AB} = 60.8. $C_{33}H_{37}Cl_3GeO_3P_2Ru$ (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. *Ru(GeH_3)(Cp)(PPh_3)L (**3**) and Ru(GeH_3)(η^5-C_9H_7)(PPh_3)L (**4**) [L = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**)]*

In a 50-mL three-necked round-bottomed flask were placed solid samples of the appropriate complex Ru($GeCl_3$)(Cp)(PPh_3)L (**1**) and Ru($GeCl_3$)(η^5-C_9H_7)(PPh_3)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) ν_{Ge-H}: 1949, 1924 (m) cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 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_{AX} = 3.2, J_{BX} = 1.2 (3H, GeH_3), 3.14 (d, 9H, CH_3, J_{PH} = 12.0). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 162.4, δ_B 61.8, J_{AB} = 61.5. $C_{26}H_{32}GeO_3P_2Ru$ (628.19): calcd. C 49.71, H 5.13; found C 49,58, H 5.26%.

3b: IR (KBr pellet) ν_{Ge-H}: 1915 (m br) cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 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, CH_2), ABX_3, δ_X 3.26, J_{AX} = 3.1, J_{BX} = 1.3 (3H, GeH_3), 0.98 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 157.5, δ_B 61.6, J_{AB} = 60.7. $C_{29}H_{38}GeO_3P_2Ru$ (670.27): calcd. C 51.97, H 5.71; found C 52.14, H 5.80%.

3c: IR (KBr pellet) ν_{Ge-H}: 1945, 1918 (m) cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 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, CH_2), ABX_3, δ_X 3.30, J_{AX} = 2.95, J_{BX} = 1.6 (3H, GeH_3), 1.14, 0.96 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 175.4, δ_B 58.8, J_{AB} = 47.3. $C_{33}H_{38}GeO_2P_2Ru$ (702.31): calcd. C 56.44, H 5.45; found C 56.26, H 5.57%.

4a: IR (KBr pellet) ν_{Ge-H}: 1921 (m br) cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 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_{AX} = 3.7, J_{BX} = 0.6 (3H, GeH_3), 3.18 (d, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 159.2, δ_B 60.0, J_{AB} = 55.0. $C_{30}H_{34}GeO_3P_2Ru$ (678.25): calcd. C 53.13, H 5.05; found C 53.01, H 5.16%.

4b: IR (KBr pellet) ν_{Ge-H}: 1931 (m br) cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: 7.70–6.95 (m, 15H, Ph), 7.83 (t m, 2H, H5 + H6 Ind), 6.32 (d, 2H, H4 + H7 Ind), 5.24 (m, 1H, H2 Ind), 4.90 (m, 1H, H3 Ind), 4.47 (m, 1H, H1 Ind), 3.67 (m, 6H, CH_2), ABX_3, δ_x 3.22, $J_{Ax} = 3.7$, $J_{Bx} = 0.95$ (3H, GeH_3), 0.99 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 153.3, δ_B 59.4, $J_{AB} = 55.9$. $C_{33}H_{40}GeO_3P_2Ru$ (720.33): calcd. C 55.02, H 5.60; found C 55.18, H 5.46%.

2.2.4. *Ru[Ge(OEt)$_3$](Cp)(PPh$_3$)L (**5**) and Ru[Ge(OEt)$_3$](η^5-C$_9$H$_7$)(PPh$_3$)L (**6**) [L = P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**)]*

In a 50-mL three-necked round-bottomed flask were placed solid samples of the appropriate complex $Ru(GeCl_3)(Cp)(PPh_3)L$ (**1**) or $Ru(GeCl_3)(\eta^5\text{-}C_9H_7)(PPh_3)L$ (**2**) (1.38 mmol), an excess of $NaBH_4$ (8 mmol, 0.30 g), and 20 mL of ethanol. The reaction mixture was stirred at room temperature for 30 min and then the solvent was removed under reduced pressure. The solid obtained was extracted with three 10-mL portions of toluene using a cellulose column for the filtration. The extracts were evaporated to dryness to leave an oil which was triturated with ethanol (3 mL). A yellow solid slowly separated out, which was filtered and dried under vacuum; yield 65%.

5b: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.78, 7.07 (m, 15H, Ph), 4.70 (d, 5H, Cp), 4.04 (m, 6H, CH_2 phos), 3.82 and 3.63 (q, 6H, CH_2 GeOEt), 1.27 and 1.24 (t, 9H, CH_3 phos), 1.02 (t, 9H, CH_3 GeOEt). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 155.3, δ_B 58.1, $J_{AB} = 60.5$. $C_{35}H_{50}GeO_6P_2Ru$ (802.43): calcd. C 52.39, H 6.28; found C 52.21, H 6.16%.

5c: ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: 7.40–6.98 (m, 20H, Ph), 4.61 (s, 5H, Cp), 4.24, 3.92, 3.66 and 3.41 (m, 4H, CH_2 phos), 4.09 and 4.05 (q, 6H, CH_2 GeOEt), 1.31 (t, 9H, CH_3 GeOEt), 1.21 and 1.20 (t, 6H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 175.4, δ_B 55.4, $J_{AB} = 47.4$. $C_{39}H_{50}GeO_5P_2Ru$ (834.47): calcd. C 56.13, H 6.04; found C 56.31, H 5.93%.

6b: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.34–6.49 (m, 15H, Ph), 6.79 (t m, 2H, H5 + H6 Ind), 6.04 (d, 2H, H4 + H7 Ind), 5.88 (m, 1H, H2 Ind), 5.03 (s br, 1H, H3 Ind), 4.61 (br, 1H, H1 Ind), 3.85 (m, 6H, CH_2 phos), 3.69 (q, 6H, CH_2 GeOEt), 1.20 (t, 9H, CH_3 GeOEt), 1.03 (t, 9H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 150.6, δ_B 54.4, $J_{AB} = 53.5$. $C_{39}H_{52}GeO_6P_2Ru$ (852.48): calcd. C 54.95, H 6.15; found C 54.78, H 6.09%.

2.2.5. *Ru(GeCl$_3$)(Tp)(PPh$_3$)L (**7**) [P = P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**)]*

In a 50-mL three-necked round-bottomed flask were placed solid samples of the appropriate complex $RuCl(Tp)(PPh_3)L$ (0.37 mmol), an excess of $GeCl_2\cdot$dioxane (1.1 mmol, 0.25 g), and 10 mL of ethanol. The reaction mixture was refluxed for 90 min and the solvent was removed under reduced pressure to give a solid, which was triturated with ethanol (2 mL), filtered and crystallised from CH_2Cl_2 and ethanol; yield 65%.

7b: IR (KBr pellet) ν_{B-H}: 2459 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.39–5.69 (m, 9H, Tp), 7.45–7.17 (m, 15H, Ph), 3.57 (m, 6H, CH_2), 1.11 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 132.6, δ_B 51.8, $J_{AB} = 51.5$. $C_{33}H_{40}BCl_3GeN_6O_3P_2Ru$ (921.54): calcd. C 43.01, H 4.38, Cl 11.54, N 9.12; found C 43.22, H 4.49, Cl 11.40, N 8.99%.

7c: IR (KBr pellet) ν_{B-H}: 2460 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.95–5.41 (m, 9H, Tp), 7.38–6.98 (m, 20H, Ph), 4.95, 4.12 and 3.87 (m, 4H, CH_2), 1.21 and 1.18 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 166.3, δ_B 52.45, $J_{AB} = 47.0$. $C_{37}H_{40}BCl_3GeN_6O_2P_2Ru$ (953.58): calcd. C 46.60, H 4.23, Cl 11.15, N 8.81; found C 46.42, H 4.35, Cl 11.01, N 8.94%.

2.2.6. *Ru(GeH$_3$)(Tp)(PPh$_3$)L (**8**) [P = P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**)]*

In a 50-mL three-necked round-bottomed flask were placed solid samples of the appropriate complex $Ru(GeCl_3)(Tp)(PPh_3)L$ (**7**) (0.21 mmol), an excess of $LiAlH_4$ (4.2 mmol, 0.16 g), and 20 mL of THF. The reaction mixture was stirred at room temperature for 80 min and then the solvent was removed under reduced pressure giving a brown solid. The complex was extracted from the solid 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 (2 mL). A yellow solid slowly separated out, which was filtered and dried under vacuum; yield 35%.

8b: IR (KBr pellet) ν_{B-H}: 2454 (w); ν_{Ge-H}: 1922 (m br) cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: 8.29–5.60 (m, 9H, Tp), 7.64–6.74 (m, 15H, Ph), 3.38 and 3.30 (m, 6H, CH_2), 3.32 (s, 3H, GeH_3), 0.90 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 147.4, δ_B 59.35, $J_{AB} = 55.0$. $C_{33}H_{43}BGeN_6O_3P_2Ru$ (818.20): calcd. C 48.44, H 5.30, N 10.27; found C 48.28, H 5.42, N 10.11%.

8c: IR (KBr pellet) ν_{B-H}: 2459 (w), ν_{Ge-H}: 1935, 1915 (m) cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: 8.38–5.53 (m, 9H, Tp), 7.35–6.95 (m, 20H, Ph), 3.78 and 3.40 (m, 4H, CH_2), 3.23 (s, 3H, GeH_3), 1.01 and 0.90 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 182.4, δ_B 65.0, $J_{AB} = 46.2$. $C_{37}H_{43}BGeN_6O_2P_2Ru$ (850.24): calcd. C 52.27, H 5.10, N 9.88; found C 52.43, H 5.20, N 9.74%.

2.2.7. *Ru[Ge(OEt)$_3$](Tp)(PPh$_3$)[P(OEt)$_3$] (**9b**)*

In a 50-mL three-necked round-bottomed flask were placed 0.2 g (0.21 mmol) of the complex $Ru(GeCl_3)(Tp)(PPh_3)[P(OEt)_3]$ (**7b**), an excess of $NaBH_4$ (4.34 mmol, 0.16 g), and 20 mL of ethanol. The reaction mixture was refluxed for 10 min and then the solvent was removed under reduced pressure. The complex was extracted from the solid obtained with three 10-mL portions of toluene using a cellulose column (3 cm) for filtration. The extracts were evaporated to dryness to give an oil which was triturated with ethanol (2 mL). A yellow solid slowly separated out, which was filtered and dried under vacuum; yield 40%.

IR (KBr pellet) ν_{B-H}: 2460 (w) cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C) δ: 9.10–5.50 (m, 9H, Tp), 7.32–6.98 (m, 15H, Ph), 3.89 and 3.81 (q, 6H, CH_2 GeOEt), 3.45 (m, 6H, CH_2 phos), 1.24 (t, 9H, CH_3 GeOEt), 0.97 (t, 9H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 144.3, δ_B 57.1, $J_{AB} = 53.4$. $C_{39}H_{55}BGeN_6O_6P_2Ru$ (950.36): calcd. C 49.29, H 5.83, N 8.84; found C 49.10, H 5.74, N 8.97%.

2.2.8. *Os(GeCl$_3$)(Tp)(PPh$_3$)L (10) [L = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**)]*

In a 50-mL three-necked round-bottomed flask were placed solid samples of the complex $OsCl(Tp)(PPh_3)L$ (0.23 mmol), an excess of $GeCl_2\cdot$dioxane (0.46 mmol, 107 mg), and 30 mL of 1,2-dichloroethane. The reaction mixture was refluxed for 1 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (2 mL) until a white solid separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 70%.

10a: IR (KBr pellet) ν_{B-H}: 2482 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.24–5.62 (m, 9H, Tp), 7.31–7.18 (m, 15H, Ph), 3.33 (d, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 75.3, δ_B 8.9, $J_{AB} = 30.3$. $C_{30}H_{34}BCl_3GeN_6O_3OsP_2$ (968.62): calcd. C 37.20, H 3.54, Cl 10.98, N 8.68; found C 37.08, H 3.67, Cl 11.16, N 8.55%.

10b: IR (KBr pellet) ν_{B-H}: 2487 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.40–5.56 (m, 9H, Tp), 7.65–7.16 (m, 15H, Ph), 3.56 (m, 6H, CH_2), 1.10 (t, 9H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 72.4, δ_B 7.7, $J_{AB} = 29.3$. $C_{33}H_{40}BCl_3GeN_6O_3OsP_2$ (1010.70): calcd. C 39.22, H 3.99, Cl 10.52, N 8.32; found C 30.39, H 4.10, Cl 10.38, N 8.44%.

10c: IR (KBr pellet) ν_{B-H}: 2482 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.27–5.64 (m, 9H, Tp), 7.48–7.20 (m, 20H, Ph), 4.36, 3.96, 3.67 and 3.28 (m, 4H, CH_2), 1.37 and 1.10 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB, δ_A 129.9, δ_B −2.23, $J_{AB} = 24.3$. $C_{37}H_{40}BCl_3GeN_6O_2OsP_2$ (1042.74): calcd. C 42.62, H 3.87, Cl 10.20, N 8.06; found C 42.47, H 3.76, Cl 10.33, N 7.95%.

2.2.9. *Os[Ge(OEt)$_3$](Tp)(PPh$_3$)L (**11**) [L = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**)]*

An excess of $NaBH_4$ (2.4 mmol, 91 mg) in ethanol (20 mL) was added to a suspension of the appropriate $Os(GeCl_3)(Tp)(PPh_3)L$ (**10**) (0.12 mmol) in ethanol (10 mL) and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure to give a solid from which the complex was extracted with three 10-mL portions of toluene using a cellulose column (3 cm) for filtration. The extracts were evaporated to dryness to give an oil which was triturated with ethanol (2 mL). A white solid slowly separated out from the resulting solution, which was filtered and dried under vacuum; yield 55%.

11a: IR (KBr pellet) ν_{B-H}: 2464 (m) cm^{-1}. ^{1}H NMR ($CD_3C_6D_5$, 25 °C) δ: 8.82–5.51 (m, 9H, Tp), 7.59–7.00 (m, 15H, Ph), 3.84 (q) and 3.76 (q) (6H, CH_2), 3.11 (d, 9H, CH_3 phos), 1.23 (t, 9H, CH_3 GeOEt). ^{31}P{^{1}H} NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 86.3, δ_B 12.1, J_{AB} = 30.5. $C_{36}H_{49}BGeN_6O_6OsP_2$ (997.44): calcd. C 43.35, H 4.95, N 8.43; found C 43.43, H 5.07, N 8.30%.

11b: IR (KBr pellet) ν_{B-H}: 2459 (m) cm^{-1}. ^{1}H NMR ($CD_3C_6D_5$, 25 °C) δ: 9.19–5.45 (m, 9H, Tp), 7.63–6.97 (m, 15H, Ph), 3.90 (q) and 3.82 (q) (6H, CH_2 GeOEt), 3.46 (m, 6H, CH_2 phos), 1.24 (t, 9H, CH_3 phos), 0.98 (t, 9H, CH_3 GeOEt). ^{31}P{^{1}H} NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 82.8, δ_B 11.2, J_{AB} = 29.5. $C_{39}H_{55}BGeN_6O_6OsP_2$ (1039.52): calcd. C 45.06, H 5.33, N 8.08; found C 44.92, H 5.24, N 8.21%.

2.2.10. *Os(GeH$_3$)(Tp)(PPh$_3$)[P(OMe)$_3$] (**12a**)*

In a 50-mL three-necked round-bottomed flask were placed a solid sample of complex $Os(GeCl_3)(Tp)(PPh_3)[P(OMe)_3]$ (**10a**) (100 mg, 0.1 mmol), an excess of $NaBH_4$ (2 mmol, 76 mg), and 20 mL of ethanol. The reaction mixture was refluxed for 30 min and then the solvent was removed under reduced pressure. The complex was extracted from the solid obtained with three 10-mL portions of toluene using a cellulose column (3 cm) for filtration. Extracts were evaporated to dryness and the oil obtained was triturated with ethanol (2 mL). A white solid slowly separated out, which was filtered and dried under vacuum; yield 40%.

IR (KBr pellet) ν_{B-H}: 2476 (m); ν_{Ge-H}: 1955 (m br) cm^{-1}. ^{1}H NMR ($CD_3C_6D_5$, 25 °C) δ: 8.82–5.50 (m, 9H, Tp), 7.60–7.02 (m, 15H, Ph), 3.52 (dd br, 3H, GeH_3), 3.11 (d br, 9H, CH_3). ^{31}P{^{1}H} NMR ($CD_3C_6D_5$, 25 °C) δ: AB, δ_A 88.75, δ_B 10.95, J_{AB} = 29.1. $C_{30}H_{37}BGeN_6O_3OsP_2$ (865.28): calcd. C 41.64, H 4.31, N 9.71; found C 41.78, H 4.19, N 9.62%.

2.3. *Crystal structure determination of Ru(GeH$_3$)(Cp)(PPh$_3$)[P(OMe)$_3$] (**3a**)*

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART [12] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [13] for integration of intensity of reflections and scaling, and SADABS [14] for empirical absorption correction. The crystallographic treatment of the compounds was performed with the Oscail program [15]. The structures were solved by direct methods and refined by a full-matrix least-squares based on F^2 [16]. Hydrogen atoms were included in idealised positions and refined, except those bound to the germanium atoms, that were found in the electronic density map and refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 1.

3. Results and discussion

3.1. *Cyclopentadienyl and indenyl complexes*

Half-sandwich trichlorogermyl complexes of the types $Ru(GeCl_3)(\eta^5\text{-}C_5H_5)(PPh_3)L$ (**1**) and $Ru(GeCl_3)(\eta^5\text{-}C_9H_7)(PPh_3)L$ (**2**) were prepared by reacting chloro complexes $RuCl(\eta^5\text{-}C_5H_5)(PPh_3)L$ and $RuCl(\eta^5\text{-}C_9H_7)(PPh_3)L$ with $GeCl_2\cdot$dioxane in ethanol, as shown in Scheme 1.

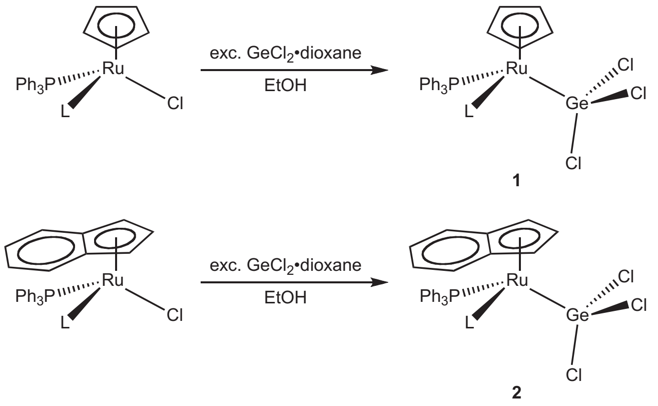
Table 1
Crystal data and structure refinement for **3a**.

Empirical formula	$C_{26}H_{32}O_3P_2GeRu$
Formula weight	628.12
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 17.932(3) Å
	b = 10.0667(14) Å
	c = 16.375(2) Å
	β = 114.508(2)°
Volume	2689.6(7) Å^3
Z	4
Density (calculated)	1.551 Mg/m^3
Absorption coefficient	1.823 mm^{-1}
F(000)	1272
Crystal size	0.33 × 0.12 × 0.10 mm
θ range for data collection	1.25–25.02°
Index ranges	$-21 \leq h \leq 21$
	$-11 \leq k \leq 11$
	$-19 \leq l \leq 19$
Reflections collected	19,979
Independent reflections	4742 [R(int) = 0.0446]
Reflections observed (>2σ)	3330
Data Completeness	0.999
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6609
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4742/0/312
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0489$ $wR_2 = 0.1201$
R indices (all data)	$R_1 = 0.0797$ $wR_2 = 0.1440$
Largest diff. peak and hole	1.267 and −1.018 eÅ^{-3}

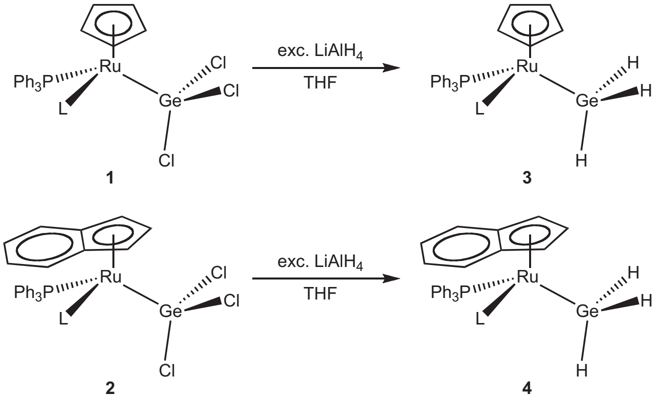
The reaction proceeded with the insertion of $GeCl_2$ into the Ru–Cl bond to afford trichlorogermyl derivatives **1** and **2**, which were isolated in good yield and characterised.

Trichlorogermyl derivatives **1** and **2** were reacted with hydride-transfer reagents such as $LiAlH_4$ and $NaBH_4$, to test whether substitution of the germanium-bonded chlorides with H$^-$ would occur, affording trihydridogermyl [Ru]–GeH_3 derivatives. The results showed that both Cp and indenyl complexes **1** and **2** react with $LiAlH_4$ in THF to yield hydridogermyl derivatives $Ru(GeH_3)(\eta^5\text{-}C_5H_5)(PPh_3)L$ (**3**) and $Ru(GeH_3)(\eta^5\text{-}C_9H_7)(PPh_3)L$ (**4**), which were separated in good yield and characterised (Scheme 2).

Surprisingly, the reaction of trichlorogermyl complexes **1** and **2** with $NaBH_4$ in ethanol did not give trihydridogermyl complexes **3** and **4**, but proceeded with the formation of triethoxygermyl



Scheme 1. L = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**).

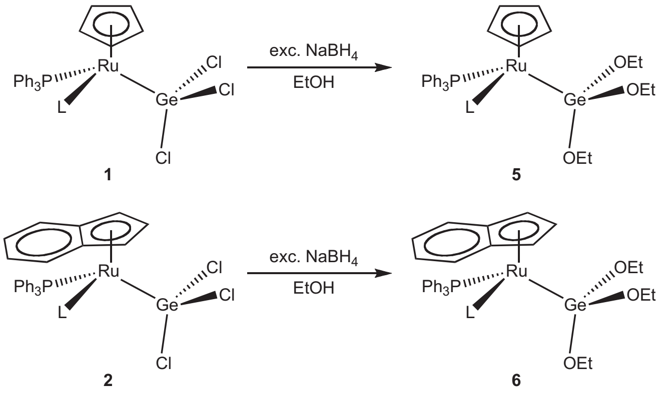


Scheme 2. L = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**).

derivatives Ru[Ge(OEt)$_3$](η^5-C_5H_5)(PPh$_3$)L (**5b**, **5c**) and Ru[Ge(OEt)$_3$](η^5-C_9H_7)(PPh$_3$)L (**6b**), as shown in Scheme 3.

The reaction proceeded with apparent substitution of the three Ge—bonded chlorides with OEt$^-$, giving triethoxygermyl derivatives **5b**, **5c** and **6b**, which were isolated in good yield and characterised. The formation of triethoxygermyl species in this reaction was not completely unexpected, both because of the known oxophilic nature of germanium [1–3], which forms stable OR and OH derivatives, and the precedent of rhenium complexes Re[Ge(OEt)$_3$](CO)$_n$P$_{5-n}$ [7]. However, we found that [Ru]—GeH$_3$ species are very stable in ethanol and that NaBH$_4$ does not therefore produce [Ru]—GeH$_3$ in the reaction with [Ru]—GeCl$_3$ complexes **1** and **2**, but probably favours a different reaction of chlorogermyl with ethanol, yielding the final [Ru]—Ge(OEt)$_3$ species **5b**, **5c** and **6b**.

Comparison between the reactivity of known half-sandwich stannyl complexes [Ru]—SnCl$_3$ [11a] and our germyl complexes [Ru]—GeCl$_3$ towards group-13 tetrahydrides BH$_4^-$ and AlH$_4^-$ can only be made for cyclopentadienyl derivatives Ru(ECl$_3$)(η^5-C_5H_5)(PPh$_3$)L (E = Sn, Ge), and highlights the fact that trihydrido species [Ru]—EH$_3$ were prepared with both Sn and Ge elements. However, although tin trihydrido SnH$_3$ was obtained only with NaBH$_4$, the preparation of trihydridogermyl GeH$_3$ requires LiAlH$_4$ as reagent in the reaction of [Ru]—GeCl$_3$. Instead, the reaction of trichlorogermyl compounds with NaBH$_4$ appears to be interesting, since it reveals a new reaction by the GeCl$_3$ ligand, affording triethoxygermyl derivatives [Ru]—Ge(OEt)$_3$. It is worth noting that, although a number of germyl complexes of Ru and Os have been reported in the literature, none of them contains trihydridogermyl as ligand. The use of mixed-ligand half-sandwich fragments Ru(η^5-C_5H_5)(PPh$_3$)L and Ru(η^5-C_9H_7)(PPh$_3$)L allowed the easy preparation not only of [Ru]—GeCl$_3$ and [Ru]—Ge(OEt)$_3$ complexes, but also of the first trihydridogermyl derivatives of ruthenium.



Scheme 3. L = P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**).

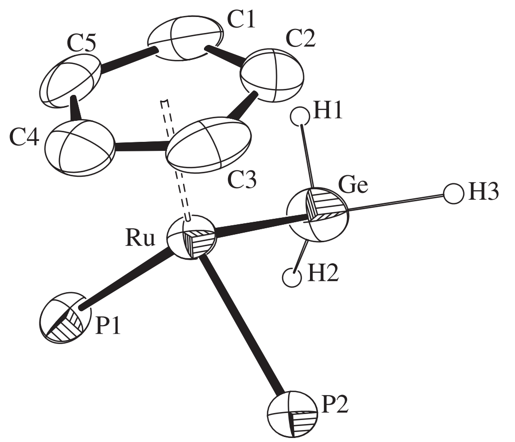


Fig. 1. ORTEP view (30% probability level) of compound **3a**. Only the hydrogen atoms bonded to the germanium atom were drawn. [P1] represents a P(OMe)$_3$ and [P2] a PPh$_3$.

The new germyl complexes **1**–**6** were isolated as yellow (**1**–**4**) or white (**5**, **6**) solids, stable in air and in solution of common organic solvents, where they behave as non-electrolytes. Their formulation is supported by analytical and spectroscopic (IR, NMR) data and by X-ray crystal structure determination of Ru(GeH$_3$)(η^5-C_5H_5)(PPh$_3$)[P(OMe)$_3$] (**3a**), the ORTEP of which is shown in Fig. 1.

The complex consists of a ruthenium atom in a half-sandwich piano-stool structure, coordinated by a η^5-cyclopentadienyl ligand having one trihydridogermyl ligand and two phosphine ligands, one PPh$_3$ and one P(OMe)$_3$, as the legs. Selected bond lengths and angles are shown in Table 2. The overall geometry of the complex is well-known to be octahedral and is marked by near 90° values for angles P—Ru—P and Ge—Ru—P, between 89.11(5) and 95.98(7)°. The usual η^5-coordination mode of the Cp ligand (with a Ru—centroid distance of 1.9056(5) Å) shows Ru—C bond distances between 2.230(7) and 2.263(7) Å, the longer one corresponding to that trans to the germyl ligand. These values are in the usual range for RuCp moieties: for example, a Ru—Cp distance of 1.889 Å in Ru(Cp)(SnClMe$_2$)[P(OEt)$_3$](PPh$_3$) [11a]. The Ru—P bond distances [2.193(2) Å for Ru—P(OMe)$_3$ and 2.294(2) Å for Ru—PPh$_3$] are also similar to those previously found: for example, 2.2239(5) and 2.3113(4) in Ru(Cp)Cl[P(OMe)$_3$](PPh$_3$) [17]. The Ru—Ge bond distance is 2.4421(9) Å. To the best of our knowledge, there is no crystallographically characterised trihydridogermanium ligand coordinated to a ruthenium atom, although other metal complexes are known [18]. The CSD (Cambridge Structural Database) [19] was used to find scarce mononuclear complexes of ruthenium with terminal R$_3$Ge ligands, but they show comparable values for this

Table 2
Selected bond lengths [Å] and angles [°] for **3a**.

Ru—CT01	1.9056(5)	Ru—P(1)	2.1933(19)
Ru—P(2)	2.2945(16)	Ru—Ge	2.4421(9)
Ru—C(1)	2.232(7)	Ru—C(2)	2.230(7)
Ru—C(3)	2.247(7)	Ru—C(4)	2.263(7)
Ru—C(5)	2.242(7)	Ge—H(1)	1.36(9)
Ge—H(2)	1.42(9)	Ge—H(3)	1.71(12)
CT01—Ru—P(1)	125.46(5)	CT01—Ru—P(2)	126.88(5)
CT01—Ru—Ge	117.70(3)	P(1)—Ru—Ge	91.50(6)
P(2)—Ru—Ge	89.11(5)	P(1)—Ru—P(2)	95.98(7)
Ru—Ge—H(1)	109(4)	Ru—Ge—H(2)	116(4)
Ru—Ge—H(3)	109(4)	H(1)—Ge—H(2)	99(5)
H(1)—Ge—H(3)	98(5)	H(2)—Ge—H(3)	122(5)

distance, *i.e.*, R = Cl, Ru–Ge bond average of 2.44 Å [20]; R = Me, Ru–Ge bond distance of 2.4455(4) Å [21]; R = Ph, Ru–Ge bond distances of 2.5498(2) Å to 2.5751(2) Å [22].

The GeH_3 moiety shows a tetrahedral arrangement, but the limitations of X-ray diffractometry for hydrogen atoms in the proximity of heavy metals is well-known, so these geometric parameters do not require further comment.

The ^1H NMR spectra of trichlorogermyl complexes $Ru(GeCl_3)(\eta^5\text{-}C_5H_5)(PPh_3)L$ (**1**) and $Ru(GeCl_3)(\eta^5\text{-}C_9H_7)(PPh_3)L$ (**2**) showed the signals characteristic of Cp or indenyl ligands and the phosphine groups, whereas the $^{31}P\{^1H\}$ spectra were AB multiplets, fitting the proposed formulation for the complexes.

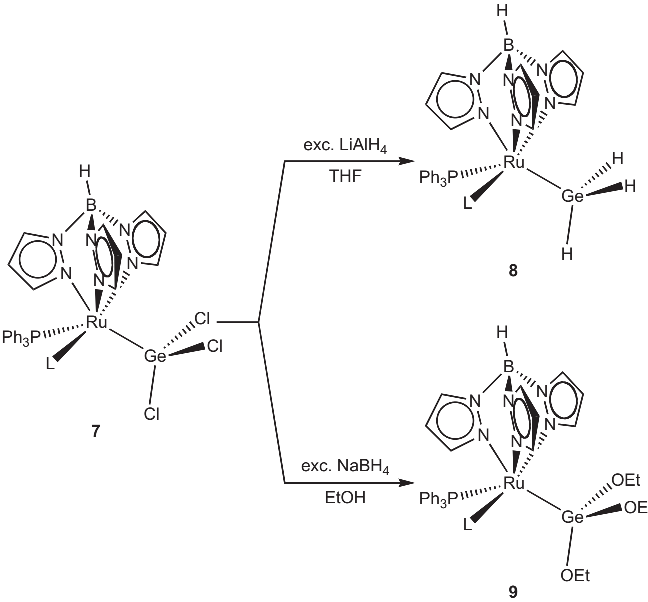
The IR spectra of trihydridogermyl derivatives $Ru(GeH_3)(\eta^5\text{-}C_5H_5)(PPh_3)L$ (**3**) and $Ru(GeH_3)(\eta^5\text{-}C_9H_7)(PPh_3)L$ (**4**) showed two bands of medium intensity at 1949–1915 cm^{-1}, attributed to the ν_{GeH} of the GeH_3 group. However, the presence of this ligand was confirmed by the ^1H NMR spectra, which showed a doublet of doublets at 3.30–3.21 ppm, simulated with the parameters reported in the Experimental section and due to the resonance of the GeH_3 group. The multiplicity of signals is due to coupling with the two non-equivalent ^{31}P nuclei of the phosphines. The spectra also show the signals of the $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_9H_7$ and phosphine ligands; the ^{31}P NMR spectra appeared as AB multiplets, fitting the proposed formulation.

Besides the signals of the Cp, indenyl and phosphine ligands, the ^1H NMR spectra of triethoxygermyl complexes $Ru[Ge(OEt)_3](\eta^5\text{-}C_5H_5)(PPh_3)L$ (**5b**, **5c**) and $Ru[Ge(OEt)_3](\eta^5\text{-}C_9H_7)(PPh_3)L$ (**6b**) showed one quartet at 4.09–3.63 ppm and one triplet at 1.31–1.02 ppm, which were correlated with each other in a COSY experiment and attributed to the ethoxy group of the $Ge(OEt)_3$ ligand. The ^{31}P NMR spectra appeared as AB multiplets, matching the proposed formulation for the complexes.

3.2. *Tris(pyrazolyl)borate complexes*

The results obtained with half-sandwich cyclopentadienyl and indenyl fragments prompted us to extend study to a comparable ligand such as tris(pyrazolyl)borate (Tp), to test whether it too can stabilise trihydridogermyl derivatives. Results showed that the mixed-ligand chloro complexes $RuCl(Tp)(PPh_3)L$ did react with $GeCl_2\cdot$dioxane to give trichlorogermyl derivatives $Ru(GeCl_3)(Tp)(PPh_3)L$ (**7**), which were isolated in good yield and characterised (Scheme 4).

Also in this case, the reaction proceeded with insertion of the $GeCl_2$ into the Ru–Cl bond to afford trichlorogermyl derivative **7**. The reactivity of these [Ru]–$GeCl_3$ compounds towards hydride-transfer reagents such as $LiAlH_4$ and $NaBH_4$ were studied, and the results showed that, like the related half-sandwich compounds **1** and **2**, the reaction proceeded with both reagents, but only with $LiAlH_4$ in THF did trihydridogermyl complexes $Ru(GeH_3)(Tp)(PPh_3)L$ (**8b**, **8c**) form (Scheme 5). Instead, with $NaBH_4$ in ethanol, the reaction of trichlorogermyl [Ru]–$GeCl_3$ (**7b**, **7c**) afforded triethoxygermyl derivatives $Ru[Ge(OEt)_3](Tp)(PPh_3)L$ (**9b**), which were isolated in good yield and characterised (Scheme 5).



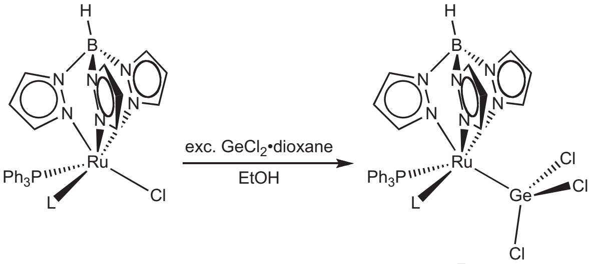
Scheme 5. L = $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**).

These reactions on Ru–Tp fragments are interesting, because they allowed the preparation of the first germyl complexes stabilised by tris(pyrazolyl)borate as supporting ligand. We therefore extended these studies to the related Os–Tp derivatives, and found that mixed-ligand chloro complexes with PPh_3 and phosphites $OsCl(Tp)(PPh_3)L$ did react with an excess of $GeCl_2\cdot$dioxane to give trichlorogermyl derivatives $Os(GeCl_3)(Tp)(PPh_3)L$ (**10**), as shown in Scheme 6.

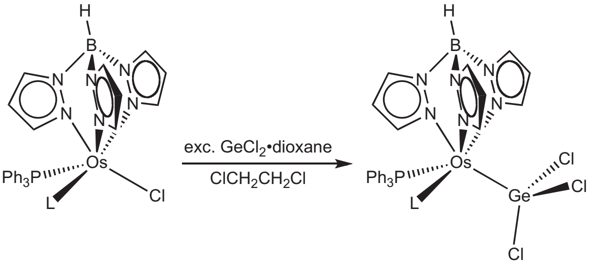
The reaction is similar to that of ruthenium, with insertion of $GeCl_2$ into the Os–Cl bond, yielding the [Os]–$GeCl_3$ derivatives.

Surprisingly, different behaviour was shown by osmium complex (**10**) towards the hydride agents $LiAlH_4$ and $NaBH_4$ with respect to the related ruthenium derivative $Ru(GeCl_3)(Tp)(PPh_3)L$ (**7b**, **7c**).

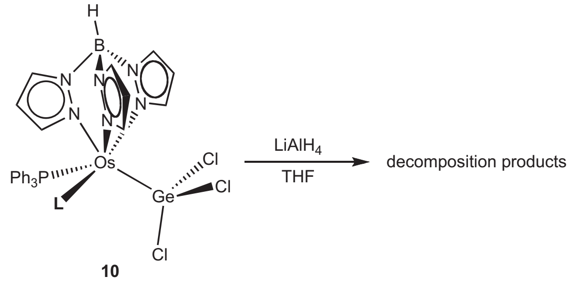
Schemes 7 and 8 summarise the results and show that only the reaction with $NaBH_4$ of complexes $Os(GeCl_3)(Tp)(PPh_3)[P(OR)_3]$ (R = Me, Et) gave stable and isolable germyl derivatives. In fact, although the reaction of [Os]–$GeCl_3$ (**10**) with $LiAlH_4$ in THF did not yield any species containing a germyl ligand (Scheme 7), the reaction with $NaBH_4$ depended on both the nature of the phosphite ligand and the experimental conditions (Scheme 8). In particular, trimethylphosphite complex $Os(GeCl_3)(Tp)(PPh_3)[P(OMe)_3]$ (**10a**) reacted with $NaBH_4$ in ethanol at room temperature to give the triethoxygermyl derivative $Os[Ge(OEt)_3](Tp)(PPh_3)[P(OMe)_3]$ (**11a**),



Scheme 4. L = $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**).

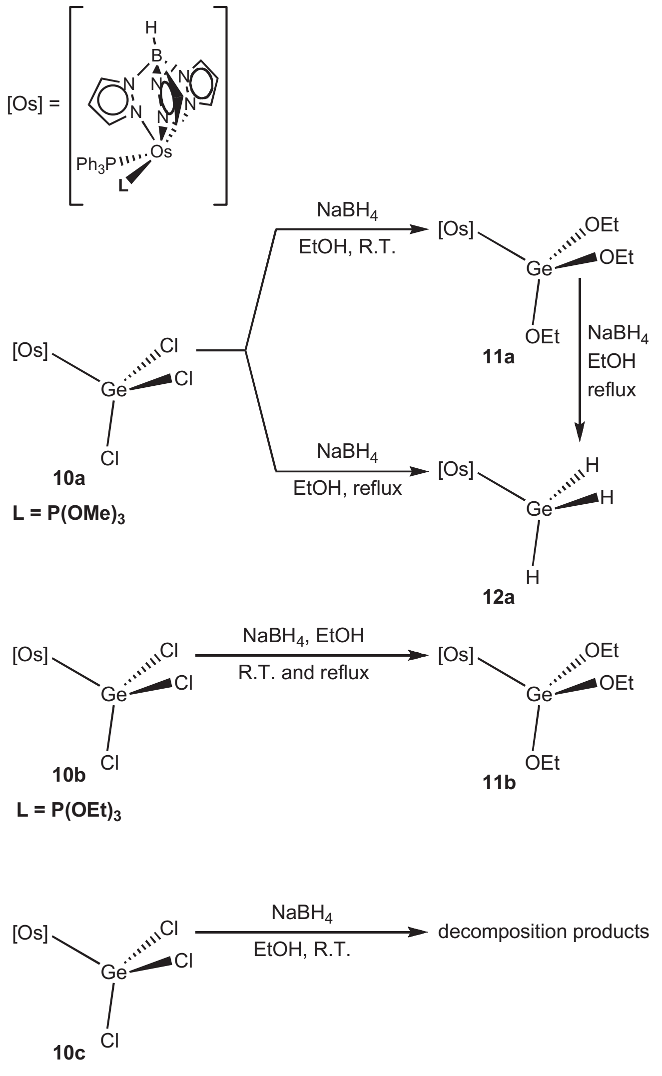


Scheme 6. L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**).



Scheme 7. L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**).

whereas the trihydridogermyl derivative $Os(GeH_3)(Tp)(PPh_3)[P(OMe)_3]$ (**12a**) formed in refluxing conditions. Conversely, the related triethylphosphite complex $Os(GeCl_3)(Tp)(PPh_3)[P(OEt)_3]$ (**10b**) in any conditions, *i.e.*, at room temperature or refluxing, exclusively gave the triethoxygermyl derivative $Os[Ge(OEt)_3](Tp)(PPh_3)[P(OEt)_3]$ (**11b**) in the reaction with $NaBH_4$ in ethanol. Lastly, only decomposition products were obtained from the same reaction of $Os(GeCl_3)(Tp)(PPh_3)[PPh(OEt)_2]$ (**10c**).



Scheme 8.

These results were rather surprising, and indicated that the first product of the reaction of $[Os]-GeCl_3$ (**10**) with $NaBH_4$ in ethanol is triethoxygermyl derivative $[Os]-Ge(OEt)_3$ (**11a**, **11b**) which, in the case of $P(OMe)_3$, can further react with $NaBH_4$ to afford trihydridogermyl $[Os]-GeH_3$ (**12a**) as final product. Indeed, the trihydridogermyl complex **12a** was also formed by reacting $[Os]-Ge(OEt)_3$ (**11a**) with $NaBH_4$ in refluxing ethanol. Comparison between the properties of the germyl complexes of Ru and Os containing Tp as supporting ligand also showed that the trihydridogermyl species $[M]-GeH_3$ forms much more easily with Ru than with Os, and that the single species of the latter, $Os(GeH_3)(Tp)(PPh_3)[P(OMe)_3]$ (**12a**), can only be obtained with $P(OMe)_3$ in the reaction with $NaBH_4$.

The reluctance of osmium to give stable GeH_3 derivatives was also shown by the reaction of trichlorogermyl compounds $[M]-GeCl_3$ with $LiAlH_4$ which, in all conditions, gave decomposition products with osmium, although stable trihydridogermyl derivatives $[M]-GeH_3$ were obtained in the case of ruthenium. The only property common to both metals was the easy formation of the triethoxygermyl derivative $[M]-Ge(OEt)_3$, which could be obtained with both $P(OEt)_3$ and $P(OMe)_3$ ligands.

All germyl complexes stabilised by the Tp ligand – $M(GeCl_3)(Tp)(PPh_3)L$ (**7**, **10**), $M[Ge(OEt)_3](Tp)(PPh_3)L$ (**9**, **11**) and $M(GeH_3)(Tp)(PPh_3)L$ (**8**, **12**) – were isolated as white or pale-yellow solids, stable in air and in solution of common organic solvents, where they behave as non-electrolytes. Their formulations were confirmed by analytical data, mainly chlorine for $[M]-GeCl_3$ species, and by infrared and NMR spectra.

In particular, the IR spectra of trichlorogermyl complexes $M(GeCl_3)(Tp)(PPh_3)L$ (**7**, **10**) showed a medium-intensity band at 2460–2440 cm^{-1}, attributed to the ν_{BH} of the Tp ligand, the presence of which was further confirmed by ^1H NMR spectra, which showed the characteristic signals of the hydrogen atoms of the pyrazolate group. In the proton spectra, the resonances associated with the phosphine ligands also appeared, whereas the ^{31}P spectra showed an AB quartet, indicating the presence of two magnetically non-equivalent phosphorus nuclei, matching the proposed formulation for the compounds.

The IR spectra of trihydridogermyl complexes $M(GeH_3)(Tp)(PPh_3)L$ (**8**, **12**) (M = Ru **8**, Os **12**) showed not only the absorption of supporting ligands but also two medium-intensity bands at 1955–1915 cm^{-1}, attributed to the ν_{GeH} of the GeH_3 group. However, support for the presence of the trihydridogermyl ligand came from the ^1H NMR spectra, which showed a slightly broad singlet at 3.32–3.23 ppm for **8** and 3.52 ppm for **12a**, due to coupling of the germyl hydrides with the phosphorus nuclei of the phosphines. The ^{31}P NMR spectra were AB multiplets, fitting the proposed formulations for the complexes.

The ^1H NMR spectra of triethoxygermyl derivatives $M[Ge(OEt)_3](Tp)(PPh_3)L$ (**9**, **11**) showed not only the signals of the Tp, PPh_3 and phosphite supporting ligands but also a quartet between 3.90 and 3.76 ppm and a triplet at 1.23–1.24 ppm, attributed to the ethoxy groups of the $Ge(OEt)_3$ ligand. This attribution was supported by a COSY experiment, which showed a correlation between methylene and the methyl protons of the OCH_2CH_3 groups. For all triethoxygermyl complexes **9**, **11**, the ^{31}P NMR spectra appeared as AB multiplets, matching the proposed formulation.

4. Conclusions

This paper reports that both half-sandwich fragments with cyclopentadienyl and indenyl ligands $Ru(\eta^5-C_5H_5)(PPh_3)L$ and $Ru(\eta^5-C_9H_7)(PPh_3)L$ (L = phosphite) can stabilise trichlorogermyl complexes $[Ru]-GeCl_3$. Their reaction with group 13 hydrides, which afforded trihydridogermyl derivatives $[Ru]-GeH_3$ with $LiAlH_4$, was interesting, whereas triethoxygermyl complexes [Ru]–

$Ge(OEt)_3$ were only obtained with $NaBH_4$ in ethanol. The tris(pyrazolylborate) ligand (Tp) can also stabilise trichlorogermyl derivatives $M(GeCl_3)(Tp)(PPh_3)L$ for both Ru and Os, the reactivity of which with $LiAlH_4$ and $NaBH_4$ allowed both trihydridogermyl $M(GeH_3)(Tp)(PPh_3)L$ and triethoxygermyl complexes $M[Ge(OEt)_3](Tp)(PPh_3)L$ to be achieved.

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Appendix A. Supplementary material

CCDC 941586 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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