The first mononuclear η^8-coordinated pentalene complex: synthesis and molecular structure of $[Ta\{\eta^8\text{-}C_8H_4(SiMe_3)_2\text{-}1,4\}Cl_3]$

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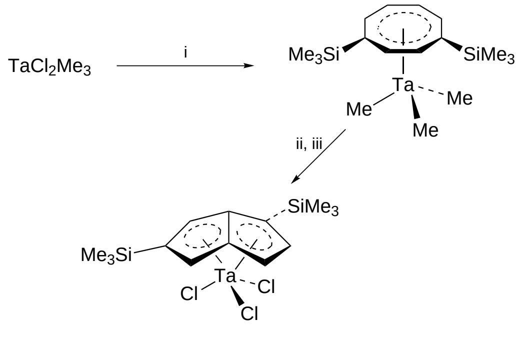
Treatment of $[TaCl_2Me_3]$ with $Li_2(cot'')$ (cot″ = 1,4-bis(trimethylsilyl)cyclooctatetraene] affords $[Ta(\eta\text{-}cot'')Me_3]$, which reacts with $[NHPr^i{}_2Et]Cl$ in dichloromethane to yield the complex $[Ta\{\eta^8\text{-}C_8H_4(SiMe_3)_2\text{-}1,4\}Cl_3]$; X-ray crystallography shows the latter to contain a pentalene ligand bound through all eight carbons to a single tantalum centre.

Transition-metal complexes derived from pentalene, or its dianion, are somewhat rare, and presently known examples fall into two categories: (*a*) binuclear systems which contain the planar pentalene dianion *e.g.* $[M_2(\eta^5,\eta^5\text{-}C_8H_6)_2]$ (M = Co, Ni),[1] $[(\eta^3\text{-}C_3H_5)Ni(\eta^5,\eta^5\text{-}C_8H_6)Ni(\eta^3\text{-}C_3H_5)]$[2] and $[(\eta^5\text{-}C_5Me_5)M(\eta^5,\eta^5\text{-}C_8H_6)M(\eta^5\text{-}C_5Me_5)]$ (M = Fe, Co, Ni);[3] (*b*) binuclear systems in which two metal carbonyl fragments are bound to the five-membered rings of a folded pentalene ring system, formed by *in situ* elimination of dihydrogen from a cyclooctatetraene ligand, *e.g.* $[\{Ru(MMe_3)(CO)_2)\}_2(\eta^5,\eta^5\text{-}C_8H_6)]$ (M = Si, Ge), $[Ru_3(CO)_8(\eta^5,\eta^5\text{-}C_8H_6)]$ and $[Ru_3(CO)_8\{\eta^5,\eta^5\text{-}C_8H_4(SiMe_3)_2\text{-}1,4\}]$.[4]

Recently, we have been exploring the chemistry of group 4 metal complexes incorporating the cot″ ligand [cot″ = 1,4-bis(trimethylsilyl)cyclooctatetraene] and were interested in extending this work to the group 5 elements.[5] Here we report the surprising conversion of an η^8-cot″ ligand into an η^8-pentalene ligand on a single tantalum centre.

Attempts to prepare a complex of the type $[Ta(\eta\text{-}cot'')Cl_3]$ starting from $TaCl_5$, as an entry into mono-cot″ tantalum chemistry, were uniformly unsuccessful, persistently producing brown intractable solids. As an alternative starting material, dark purple $[Ta(\eta\text{-}cot'')Me_3]$ **1** was prepared from the reaction between $Li_2(cot'')$ and $[TaCl_2Me_3]$ in hexane at −78 °C (Scheme 1) in 70% yield,† in an analogous fashion to that described by Schrock and coworkers for the synthesis of $[Ta(\eta\text{-}cot)Me_3]$.[6] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** show the typical resonances for a planar η^8-cot″ ring and the Ta–Me groups.‡

In an attempt to prepare $[Ta(\eta\text{-}cot'')Cl_3]$, the complex $[Ta(\eta\text{-}cot'')Me_3]$ was treated with 3 equiv. of $[NHPr^i{}_2Et]Cl$ in CH_2Cl_2; however, after work up air-sensitive red needles of the pentalene complex $[Ta\{\eta^8\text{-}C_8H_4(SiMe_3)_2\text{-}1,4\}Cl_3]$ **2** (Scheme 1) were obtained in 10% yield.§



Scheme 1 i, $Li_2[(cot'')(thf)_x]$, *n*-pentane; ii, 3 $[NHPr^i{}_2Et]Cl$, CH_2Cl_2; iii, vacuum sublimation (10^{-5} mbar, 140 °C)

The ^1H NMR spectrum of **2** exhibits four downfield signals (δ 6.51–5.32) attributable to four distinct ring proton environments and two upfield singlets (δ 0.4 and 0.3) assignable to two distinct trimethylsilyl groups. The $^{13}C\{^1H\}$ NMR spectrum shows ten resonances, eight of which are at low field and as such can be attributed to the carbon ring framework, whilst those carbons associated with the trimethylsilyl substituents are identified by two singlets at δ −0.2 and −0.7.¶

Single crystals of **2**, suitable for X-ray diffraction studies,‖ were grown by vapour-phase diffusion in an evacuated sealed tube at 160 °C. The molecular structure of **2**, as shown in Fig. 1, shows the complex to contain the first example of a pentalene ligand η^8-coordinated to a single metal centre. The pentalene ring in **2** is folded about the bridgehead [C(2)–C(6)] bond, with a fold angle of 33°; in the metal–metal bonded binuclear complex $[\{Ru(GeMe_3)(CO)_2\}_2(\eta^5,\eta^5\text{-}C_8H_6)]$ the fold angle is 9°.[7] The tantalum–ring carbon distances of **2** range from 2.182(13), for the bridgehead carbons to 2.583(13) Å for the ‘wingtip’ carbons, and may be compared to the tantalum–ring carbon distances in $[Ta(cot'')Me_3]$ **1** which lie between 2.424(6) and 2.488(5) Å.[8] The pentalene ring C–C bond lengths in **2** range from 1.36(2) [C(7)–C(8)] to 1.48(2) [C(1)–C(2)] Å with a bridgehead [C(2)–C(6)] bond length of 1.47(2) Å. In the planar pentalene ring system found in $[(\eta^5\text{-}C_5Me_5)Fe(\eta^5,\eta^5\text{-}C_8H_6)Fe(\eta^5\text{-}C_5Me_5)]$, the ring C–C distances lie between 1.464(5) (for the bridgehead) and 1.408(5) Å. For the folded (9°) ligand in $[\{Ru(GeMe_3)(CO)_2\}_2(\eta^5,\eta^5\text{-}C_8H_6)]$,[6] the ring C–C distances range from 1.32(5) to 1.51(4) with a bridgehead C–C distance of 1.43(5) Å. The Ta–Cl bond lengths in **2** range from 2.362(3) to 2.386(3) Å and can be compared to the Ta–Cl

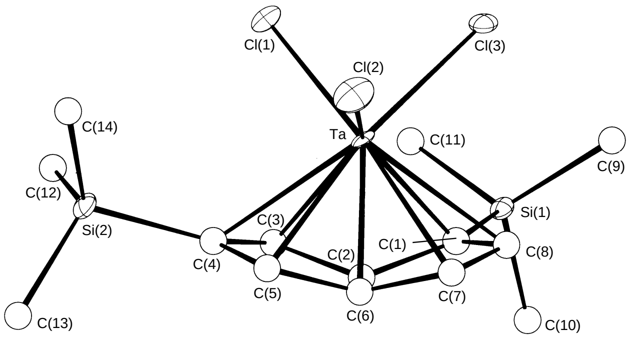


Fig. 1 CAMERON[12] representation of the crystal structure of **2**. Selected bond lengths (Å) and angles (°): Ta–C(1) 2.351(12), Ta–C(2) 2.182(13), Ta–C(3) 2.358(12), Ta–C(4) 2.583(12), Ta–C(5) 2.469 (13), Ta–C(6) 2.217(12), Ta–C(7) 2.488(13), Ta–C(8) 2.539(13), Ta–Cl(1) 2.362(3), Ta–Cl(2) 2.374(4), Ta–Cl(3) 2.386 (3), C(1)–C(2) 1.48(2), C(2)–C(6) 1.47(2), C(2)–C(3) 1.40(2), C(3)–C(4) 1.43(2), C(4)–C(5) 1.41(2), C(5)–C(6) 1.43(2), C(6)–C(7) 1.43(2), C(7)–C(8) 1.36(2), C(8)–C(1) 1.45(2); C(1)–C(2)–C(3) 129.8(11), C(2)–C(3)–C(4) 109.7(11), C(4)–C(5)–C(6) 108.9(12), C(7)–C(6)–C(2) 108.2(10), C(8)–C(7)–C(6) 107.8 (11), C(8)–C(1)–C(2) 104.0 (10), C(3)–C(2)–C(6) 106.8(11), C(6)–C(2)–C(1) 106.7(10), C(5)–C(4)–C(3) 107.8 (11), C(7)–C(6)–C(5) 133.8(12), C(5)–C(6)–C(2) 106.7(11), C(1)–C(8)–C(1) 113.0(11).

distance of 2.387(11) Å in $[\mathrm{Ta}(\eta^5\text{-}\mathrm{C}_5\mathrm{Me}_5)\mathrm{Me}_2\mathrm{Cl}_2]$.[9] Further comparisons are difficult due to the lack of other, related compounds.

Attempts are currently underway to study the mechanism of this reaction and to improve the yield of **2**; the latter promises to be a versatile precursor to monopentalene tantalum chemistry.

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Footnotes and References

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† *Preparation of* $[\mathrm{Ta}(\eta\text{-cot}'')\mathrm{Me}_3]$ **1**: to a pentane (40 ml) solution of $[\mathrm{TaCl}_2\mathrm{Me}_3]$ (0.25 g, 0.84 mmol) at -40 °C was added a pentane (40 ml) suspension of $[\mathrm{Li}_2(\mathrm{cot}'')]$ (0.284 g, 0.9 mmol) dropwise over a period of 45 min during which the reaction mixture darkened to brown. Once the addition was complete, the brown suspension was stirred at -40 °C for 60 min before being warmed to room temp. and left to stir overnight. Filtration through Celite on a frit, and concentration and cooling of the red filtrate to -30 °C yielded **1** as purple crystals (0.28 g, yield = 70%).

‡ *NMR and mass spectral data* for complex **1**. ^{1}H NMR ($\mathrm{C}_6\mathrm{D}_6$, 298 K); δ 6.39 (2 H, m, CH ring), 6.33 (2 H, s, CH ring), 5.95 (2 H, m, CH ring), 0.67 (9 H, s, TaMe), 0.49 (18 H, s, SiMe_3). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C}_7\mathrm{D}_8$, 298 K); δ 102.82 (CH ring), 100.62 (CH ring), 96.96 (CH ring), 93.84 ($C\mathrm{SiMe}_3$ ring), 65.55 (TaMe), 0.36 (SiMe_3). Mass spectrum (EI). m/z 459 ($[\mathrm{M}]^+ - \mathrm{Me}$, 50%).

§ *Preparation of* $[\mathrm{Ta}\{\eta^8\text{-}\mathrm{C}_8\mathrm{H}_4(\mathrm{SiMe}_3)_2\text{-}1,4\}\mathrm{Cl}_3]$ **2**: to a solid mixture of $[\mathrm{Ta}(\mathrm{cot}'')\mathrm{Me}_3]$ (0.195 g, 0.41 mmol) and $[\mathrm{NHPr}^i{}_2\mathrm{Et}]\mathrm{Cl}$ (0.204 g, 1.23 mmol) in a sublimer tube was added $\mathrm{CH}_2\mathrm{Cl}_2$ (*ca.* 20 ml) at room temp. After the mixture was allowed to stir for 15 min, the solvent was removed *in vacuo*. The residue was then sublimed at 140 °C (10^{-5} mbar) to afford a red solid. Recrystallisation of this solid from pentane–diethyl ether (9 : 1) produced long red needle crystals of **2** (0.022 g, yield = 10%). Microanalysis: Calc.: C, 31.50; H, 4.15. Found: C, 31.89; H, 4.24%.

¶ *NMR and mass spectral data* for complex **2**: ^{1}H NMR ($\mathrm{CD}_2\mathrm{Cl}_2$, 298 K): δ 6.51 (1 H, d, J_{HH} 4.3, CH ring), 5.86 (1 H, d, J_{HH} 0.9, CH ring), 5.68 (1 H, dd, J_{HH} 4.3, 0.9, CH ring), 5.32 (1 H, s, CH ring), 0.4 (9 H, s, SiMe_3), 0.3 (9 H, s, SiMe_3). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD}_2\mathrm{Cl}_2$, 298 K); δ 142.7 (C ring), 139.4 (CH ring), 133.0 (C ring), 126.0 (CH ring), 118.0 (CH ring), 112.3 (CH ring), 107.5 ($C\mathrm{SiMe}_3$), 106.3 ($C\mathrm{SiMe}_3$), -0.2 (SiMe_3), -0.7 (SiMe_3). Mass spectrum (EI). m/z 534 ($[\mathrm{M}]^+$, 23%).

‖ *Crystal data*: $\mathrm{C}_{14}\mathrm{H}_{22}\mathrm{Cl}_3\mathrm{Si}_2\mathrm{Ta}$, $M = 533.80$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.206(2)$, $b = 11.245(4)$, $c = 12.233(4)$ Å, $\alpha = 88.85(3)$, $\beta = 75.08(3)$, $\gamma = 83.69(3)$°, $U = 952.0(5)$ Å^3, $Z = 2$, $D_c = 1.86$ cm^{-3}, $F(000) = 516$. Monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 63.1$ cm^{-1}, $T = 173$ K. Data were collected on an Enraf–Nonius CAD 4 diffractometer in the θ–2θ mode using a crystal of *ca.* $0.4 \times 0.2 \times 0.05$ mm. A total of 3341 unique reflections were measured for $2 < \theta < 25°$ and $+h, \pm k, \pm l$, and used in the refinement based on F^2 using SHELXL-93.[10] The structure was solved by direct methods using SHELXS-86[11] and Ta, Cl, Si atoms were refined anisotropically by full-matrix lest-squares methods. Hydrogen atoms were included in the riding mode with $U_{\mathrm{iso}} = 1.2$ or 1.5 U_{eq}(C) for the methyl groups. An absorption correction (ψ scan, $T_{\max} = 1.00$, $T_{\min} = 0.58$) was applied. The final residuals were $R_1 = 0.068$ [for 2948 reflections with $I > 2\sigma(I)$] and $wR_2 = 0.179$ (for all data). CCDC 182/530.

1 T. J. Katz and N. Acton, *J. Am. Chem. Soc.*, 1972, **94**, 3281; T. J. Katz, N. Acton and J. McGinnis, *J. Am. Chem. Soc.*, 1972, **94**, 6205.

2 A. Miyake and A. Kanai, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 801.

3 E. E. Bunel, L. Valle, N. L. Jones, P. J. Carroll, C. Barra, M. Gonzalez, N. Munoz, G. Visconti, A. Aizman and J. M. Manriquez, *J. Am. Chem. Soc.*, 1988, **110**, 6597.

4 S. A. R. Knox and F. G. A. Stone, *Acc. Chem. Res.*, 1974, **7**, 321.

5 N. C. Burton, F. G. N. Cloke, P. B. Hitchcock, H. C. de Lemosand and A. A. Sameh, *J. Chem. Soc., Chem. Commun.*, 1989, 1462; F. G. N. Cloke, P. B. Hitchcock and S. C. P. Joseph, *J. Chem. Soc., Chem. Commun.*, 1994, 1207; F. G. N. Cloke, P. B. Hitchcock, N. Kaltsoyannis, S. C. P. Joseph, A. McCamley and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1994, 2867; C. J. Cardin, F. G. N. Cloke, P. B. Hitchcock and S. C. P. Joseph, *Organometallics*, 1995, **14**, 3556; Q. A. Abbasali, F. G. N. Cloke, P. B. Hitchcock, S. C. P. Joseph and D. Peron, *J. Mol. Catal.*, submitted.

6 A. D. English, L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, 1976, **98**, 903.

7 J. A. K. Howard and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1978, 412.

8 S. C. P. Joseph, D.Phil. Thesis, University of Sussex, 1994.

9 M. Gomez, G. Jimenez, P. Royo and J. M. Selas, *J. Organomet. Chem.*, 1992, **439**, 147.

10 G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

11 G. M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, 1986.

12 D. J. Watkin and L. J. Pearce, CAMERON, An Interactive Graphics Editor, University of Oxford, 1993.

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