$(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{CH}_2\text{CH}_2\text{CMe}_3)_2(\eta^2\text{-CHPMe}_2)$: a Stable Sixteen Electron Long-chain Di-alkyl Compound of Tantalum

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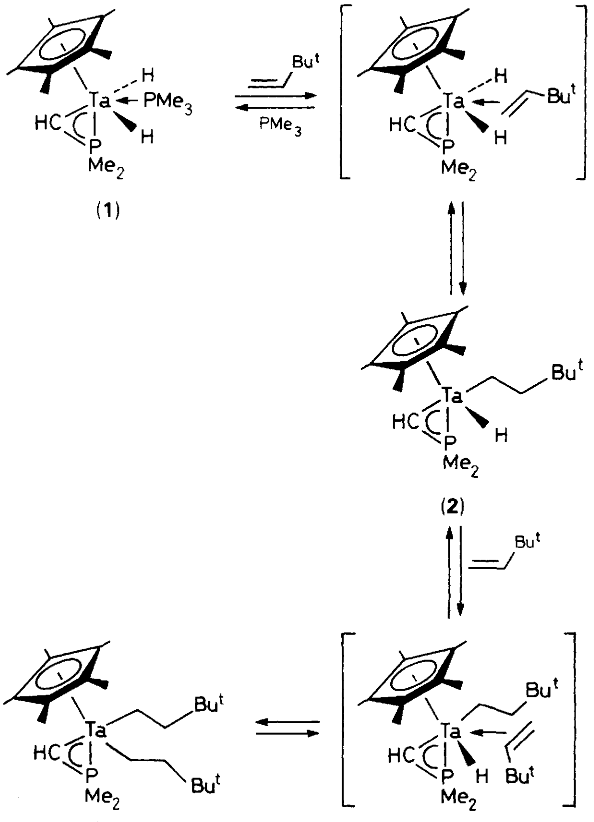
Neohexene inserts into the Ta–H bonds of $(\text{C}_5\text{Me}_5)\text{Ta}(\text{H})_2(\eta^2\text{-CHPMe}_2)(\text{PMe}_3)$ (**1**) to give the co-ordinatively unsaturated neohexyl hydride $(\text{C}_5\text{Me}_5)\text{Ta}(\text{H})(\text{CH}_2\text{CH}_2\text{CMe}_3)(\eta^2\text{-CHPMe}_2)$ (**2**) followed by the bis(neohexyl) compound $(\text{C}_5\text{Me}_5)\text{Ta}(\text{CH}_2\text{CH}_2\text{CMe}_3)_2(\eta^2\text{-CHPMe}_2)$ (**3**) whose *X*-ray structure is reported: the stability of these long-chain tantalum alkyls may be understood by comparison with pseudo-isoelectronic Group 4 metallocenes.

The vast majority of co-ordinatively unsaturated transition metal alkyl complexes possessing β-hydrogens, and especially homoleptic alkyls, are unstable due to the propensity for β-elimination and subsequent loss of alkene.[1] For the heavier Group 5 metals, the only stable long-chain alkyls are saturated eighteen electron metallocene derivatives of the type $\text{Cp}_2\text{M(L)R}$ (M = Nb, Ta; Cp = C_5H_5; R = Et, Pr^n, L = CO, isocyanide)[2] or $\text{Cp}_2\text{M(O)R}$ (R = Bu^n)[3] in which β-elimination is prevented by strong binding of small π-acid ligands or an oxo group, respectively. Co-ordinatively unsaturated long-chain metallocene dialkyls and chloroalkyls, however, are reasonably stable for zirconium and hafnium[4] due to the electronic and steric constraints of the Cp_2M moiety which prevent the M–C–C–H fragment from achieving a *syn* co-planar arrangement for elimination. Attempts to prepare the analogous seventeen electron niobium and tantalum derivatives by metathesis of the chloride groups of $\text{Cp}'_2\text{MCl}_2$ [M = Ta, Cp′ = Cp, (C_5Me_5); M = Nb, Cp′ = Cp] with excess Grignard reagent invariably lead to the eighteen electron hydrido-alkene complexes, $\text{Cp}'_2\text{M(H)(CH}_2\text{=CHR)}$[5] (R = H, Me) arising by reduction and metathesis followed by β-elimination.



Scheme 1

Here, we describe neohexene insertions into the Ta–H bonds of (**1**) to give rare examples of stable, co-ordinatively unsaturated long-chain alkyl complexes of tantalum. The stability of these formally d^0 tantalum alkyls[6] may be attributed to a similar combination of steric and electronic constraints that exist in Group 4 metallocene alkyls.[6c,7]

Treatment of (**1**)[8] with excess ethylene affords an intractable mixture of tantalum ethyl, homologated alkyl species, and free alkenes (detected by NMR spectroscopy). However, when (**1**) is reacted with an excess of the sterically demanding alkene $\text{CH}_2\text{=CHBu}^t$ (neohexene), sequential insertions into the Ta–H bonds may be observed according to Scheme 1. The intermediate alkene adducts are not observable since the metal–alkene interactions are weak in these formally d^0 Ta^V compounds. Also, PMe_3 is ejected from the metal co-ordination sphere upon generation of the alkyl ligand, presumably due to the increased steric congestion. The mono-neohexyl-

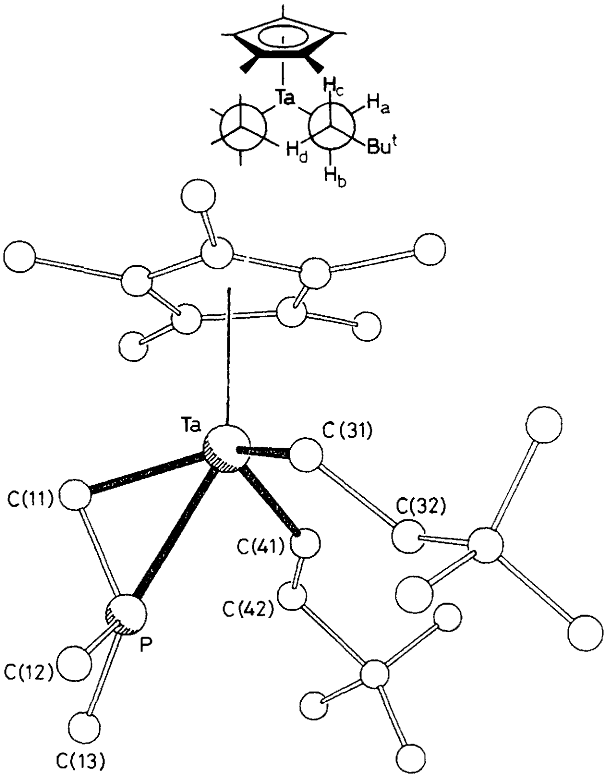


Figure 1. (Top) Newman projection, and (bottom) molecular structure of (**3**), with important atoms labelled. Only the major disorder component of atom C(42) is shown. Key dimensions: Ta–P 2.501(2), Ta–C(11) 1.983(13), P–C(11) 1.715(13), Ta–C(31) 2.242(11), Ta–C(41) 2.184(16), C(31)–C(32) 1.542(22) Å; P–Ta–C(11) 43.1(4), Ta–C(11)–P 84.8(6), Ta–P–C(11) 52.1(4), C(31)–Ta–C(41) 112.9(7)°.

hydride (**2**) is observable by NMR spectroscopy† but reacts with neohexene at a comparable rate to its formation to give the bis(neohexyl) complex (**3**) which may be isolated as a colourless, crystalline solid in 66% yield after crystallization from light petroleum. Satisfactory elemental analysis has been obtained and further characterization is provided by IR and NMR spectroscopies and mass spectrometry† and a single crystal *X*-ray diffraction‡ study. The 250 MHz ^{1}H NMR spectrum reveals diastereotopic α- and β-methylene hydrogens at δ 0.64/0.20 and 1.53/1.35, respectively. Difference NOE experiments indicate a conformationally rigid (Ta–CH_2) bond since irradiation of the C_5Me_5 hydrogens results in a 2.5% enhancement of the α-CH_2 signal at δ 0.20 whilst having no effect upon its diastereotopic partner at δ 0.64. Conversely, irradiation of the PMe_2 methyl resonance at δ 1.62 enhances the signal at δ 0.64 by 2.5% but leaves the δ 0.20 resonance unaltered. These experiments facilitate the assignments of H_a and H_b as shown in the Newman projection. Neither NOE experiment had any effect upon the β-CH_2 hydrogens H_c and H_d; however, irradiation of the (C_5Me_5) ring methyl groups results in a strong enhancement (8.5%) of the metallacycle methine hydrogen confirming that the CH terminus projects towards the (C_5Me_5) ring. Colourless prisms of (**3**) may be obtained upon prolonged cooling at −35 °C of a saturated light petroleum solution. The molecular structure is illustrated in Figure 1 and important distances are shown in the Figure caption. The co-ordination sphere of (**3**) consists of a η^5-co-ordinated C_5Me_5 ligand, a 3-membered Ta(η^2-$CHPMe_2$) metallacycle, which is essentially unperturbed from the parent complex (**1**),[8] and two neohexyl ligands. One of the neohexyl groups is disordered at the β-carbon C(42) which exists with approximately equal probabilities (55 : 45) in two sites; the discussion is therefore confined to the non-disordered neohexyl ligand. The Ta–C_α distance of 2.242(11) Å lies within the range of tantalum–carbon single bonds in Ta^V alkyl complexes (typically 2.2—2.3 Å[12]). The neohexyl ligand adopts a staggered conformation with the bulky metal fragment and t-butyl groups lying *anti*-periplanar [the dihedral angle between the planes defined by Ta–C(31)–C(32) and C(31)–C(32)–C(33) is 3.8°].

Inert atmosphere solutions of (**3**) in aromatic or aliphatic hydrocarbons are stable to decomposition over several weeks at room temperature, decomposing only slowly at 50 °C to liberate both neohexene and neohexane (^{1}H NMR). The stability of (**3**) to β-elimination may be attributed primarily to the inter-ligand steric interactions which prevent the M–C–C–H unit from readily interacting with the metal LUMO and achieving a *syn* co-planar arrangement suitable for elimination. The same explanation may also account for the absence (by NMR and IR spectroscopies and *X*-ray crystallography) of any agostic interactions involving the α- or β-alkyl hydrogens.

The analogy between half-sandwich tantalum compounds containing the η^2-$CHPMe_2$ ligand and bent metallocenes of the Group 4 metals is also apparent in reactions of (**1**) with other substrates. These studies will form subjects of future reports.

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† *Selected NMR data* for (**2**): ^{1}H NMR (C_6D_6, 250 MHz, 298 K) δ 8.71 (d, 1H, $^2J_{PH}$ 2.0 Hz, C*H*PMe_2), 4.74 (d, 1H, $^2J_{PH}$ 12.0 Hz, M–H), 2.05 (s, 15H, C_5*Me*$_5$), 1.52 (d, 3H, $^2J_{PH}$ 9.6 Hz, PMe_2), 1.37 (d, 3H, $^2J_{PH}$ 10.2 Hz, PMe_2), 1.04 (s, 9H, CMe_3), CH_2 resonances obscured by methylenes of (**3**). For (**3**): ^{1}H NMR (C_6D_6 250 MHz, 298 K) δ 9.05 (s, 1H, C*H*PMe_2), 1.79 (s, 15H, C_5*Me*$_5$), 1.62 (d, 6H, $^2J^{PH}$ 8.9 Hz, CHP*Me*$_2$), 1.53 (ddd, 2H, $^3J_{H_bH_d}$ 4.1, $^3J_{H_aH_d}$ = $^2J_{H_cH_d}$ 13.6 Hz, H_d), 1.35 (ddd, 2H, $^3J_{H_aH_c}$ 4.0, $^3J_{H_bH_c}$ = $^2J_{H_cH_d}$ 13.6 Hz, H_c), 1.00 (s, 18H, CMe_3), 0.64 (dddd, 2H, $^3J_{PH_b}$ 10.8, $^3J_{H_bH_d}$ 4.1, $^3J_{H_bH_c}$ 13.6, $^2J_{H_aH_b}$ 12.2 Hz, H_b), 0.20 (dddd, 2H, $^3J_{PH_a}$ 9.9, $^3J_{H_aH_c}$ 4.0, $^3J_{H_aH_d}$ 13.6, $^2J_{H_aH_b}$ 12.2 Hz, H_a); ^{13}C NMR (C_6D_6, 62.9 MHz, 298 K) δ 204.9 (dd, $^1J_{CH}$ 166.9, $^1J_{CP}$ 58.9, *C*HMe_2), 112.5 (s, *C*$_5$Me$_5$), 53.9 (t, $^1J_{CH}$ 116.8, *C*$H_2CH_2Bu^t$), 44.7 (t, $^1J_{CH}$ 124.6, $CH_2CH_2Bu^t$), 34.02 [s, *C*(Me)$_3$], 15.8 [qd, $^1J_{CH}$ 125.4, $^1J_{CP}$ 17.5, P(*C*H$_3$)$_2$], 29.6 [q, $^1J_{CH}$ 123.9, C(*C*H$_3$)$_3$], 11.0 [q, $^1J_{CH}$ 126.9, C$_5$(*C*H$_3$)$_5$]; ^{31}P{^{1}H} NMR (C_6D_6, 101 MHz, 298 K) δ −46.85 (s, $CHPMe_2$).

‡ *Crystal data* for $C_{25}H_{48}PTa$: M = 560.6, monoclinic, $P2_1/c$, a = 17.663(2), b = 10.401(2), c = 16.776(3) Å, β = 115.73(1)°, U = 2776.4 Å^3, Z = 4, D_c = 1.341 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 3.98 mm^{-1}, $F(000)$ = 1144, T = 295 K. The structure was determined by Patterson methods and refined[9] to a minimum of $\Sigma w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 79 + 4G - 7G^2 - 195H + 123H^2 - GH$, $G = F_o/F_{max.}$, $H = \sin\theta/\sin\theta_{max.}$][10] from 2644 reflections with $2\theta < 45°$ and $F > 4\sigma_c(F)$ (σ_c from counting statistics only), measured with a Stoe–Siemens diffractometer and on-line profile fitting.[11] Anisotropic thermal parameters were refined for all non-H atoms, H atoms were not included. Final $R = 0.038$, $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2} = 0.041$, for 254 parameters. Two-fold disorder was resolved and refined for one carbon atom. 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.