

Unusual alkylidene ligands: synthesis and structure of the cyclopentadienylydene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$

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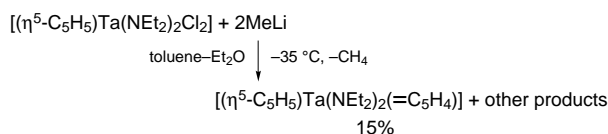
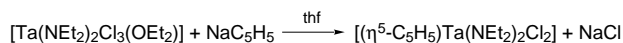
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The unique alkylidene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$ **2 is prepared in low yield from the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2\text{Cl}_2]$ **1** with 2 equiv. of MeLi and is fully characterised including an X-ray structural determination.**

Transition-metal cyclopentadienyl complexes are situated at the heart of modern organometallic chemistry.¹ Of the known bonding modes of C_5H_5 and its analogues, the $\eta^5:\eta^1\text{-C}_5\text{H}_4$ structure that bridges two metal centres is well established and has played a role in the development of transition-metal metallocene chemistry.² We wish to report a new bonding mode of the C_5H_4 ligand that is ostensibly formed upon decomplexing the η^5 portion of a bridging $\eta^5:\eta^1\text{-C}_5\text{H}_4$ moiety, *viz.* the $\eta^1\text{-C}_5\text{H}_4$ alkylidene, or cyclopentadienylydene, ligand in the mononuclear complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$.

Upon reacting a thf solution of $[\text{Ta}(\text{NEt}_2)_2\text{Cl}_3(\text{OEt}_2)]^3$ with 1 equiv. of NaC_5H_5 , a red solution is obtained from which yellow–orange crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2\text{Cl}_2]$ **1** can be isolated in high yield (Scheme 1).[†] When $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2\text{Cl}_2]$ **1** is reacted with 2 equiv. of MeLi (-35°C , toluene– Et_2O), the reaction quickly develops an orange colour and is accompanied by the evolution of a gas that is shown to be CH_4 by GCMS analysis (Scheme 1). After work-up of the oil obtained from this reaction, orange crystals of compound **2** may be obtained in low yield. In addition to resonances assigned to the C_5H_5 and NEt_2 ligands, the ^1H NMR data for **2** $\{[\text{H}_8]\text{thf}\}$ reveal two multiplets at δ 6.68 (CH^α) and 5.49 (CH^β) that integrate to two protons each and its ^{13}C NMR spectrum (C_6D_6) reveals three ^{13}C resonances at δ 235.7, 124.5 and 113.6. On the basis of these NMR data, including HETCOR and NOE spectra, and an X-ray crystallographic study (*vide infra*), **2** is formulated as the terminal alkylidene, or cyclopentadienylydene, complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$ (Scheme 1).

Although the orange–brown oil obtained from the $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2\text{Cl}_2] + 2\text{MeLi}$ reaction contains multiple products (including paramagnetic species), $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$ **2** is the only product that we could isolate from the reaction mixture and then in only *ca.* 15% yield based on C_5H_5 (7.5% based upon tantalum). This low yield is not improved by changes in the reaction time, temperature, solvent, or the work-up procedure, nor can $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$ **2** be prepared in greater yield by other synthetic methods.



Scheme 1

The molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$ **2** was determined by X-ray crystallography and is presented in Fig. 1.† The overall geometry can be described as a three-legged piano stool containing a terminal alkylidene ligand, as indicated by the short Ta–C(1) distance of 2.037(4) Å, which is well within the range expected for d^0 Ta=C double bonds.⁴ The C_5H_4 ligand is planar and is clearly π localised as the diene, as indicated by the alternating C–C bond lengths around the ring. The plane of the C_5H_4 alkylidene ligand is slightly tilted from perpendicular with respect to the $\eta^5\text{-C}_5\text{H}_5$ plane (dihedral angle 74.8°) and the NEt_2 ligands are considerably tilted such that the Ta–N(3)–C(31)–C(33) plane is 54.9° and Ta–N(4)–C(41)–C(43) is 142.2° from the $\eta^5\text{-C}_5\text{H}_5$ plane. Such an arrangement places the two TaNC₂ planes nearly perpendicular (92.9°) to each other. Finally, the short Ta–N bonds of *ca.* 1.97 Å indicate significant N(p_π)–Ta(d_π) electron donation from the amido ligand.⁵

Related structures containing C_5H_4 ligands have been described, for example the $\eta^5:\eta^1\text{-C}_5\text{H}_4$ ligand is well established in complexes such as $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5:\eta^1\text{-C}_5\text{H}_4)\text{NbH}]_2$,⁶ $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5:\eta^1\text{-C}_5\text{H}_4)\text{WH}]_2$,⁷ $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5:\eta^1\text{-C}_5\text{H}_4)\text{-Mo}]_2$ ⁸ and $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5:\eta^1\text{-C}_5\text{H}_4)\text{Ti}(\text{PMe}_3)]_2$.⁹ If the *ipso* carbon (only) of the η^5 portion of an $\eta^5:\eta^1\text{-C}_5\text{H}_4$ ligand is decomplexed, an $\eta^4:\eta^1\text{-C}_5\text{H}_4$ ligand is generated, an example of which is seen in $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4:\eta^1\text{-C}_5\text{H}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)]$,¹⁰ and if the *ipso* carbon of an $\eta^1\text{-C}_5\text{H}_4$ ligand bridges two metals, a $\mu(\eta^1)\text{-C}_5\text{H}_4$ complex results as in Wilkinson's $[\{\text{Re}(\text{=NBu}^i)_2(\eta^1\text{-C}_5\text{H}_5)\}_2\{\mu(\eta^1)\text{-C}_5\text{H}_4\}(\mu\text{-O})]$.¹¹ Finally, we note that Herrmann and coworkers have generated transient $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(=\text{C}_5\text{H}_5)]$ from the reaction of

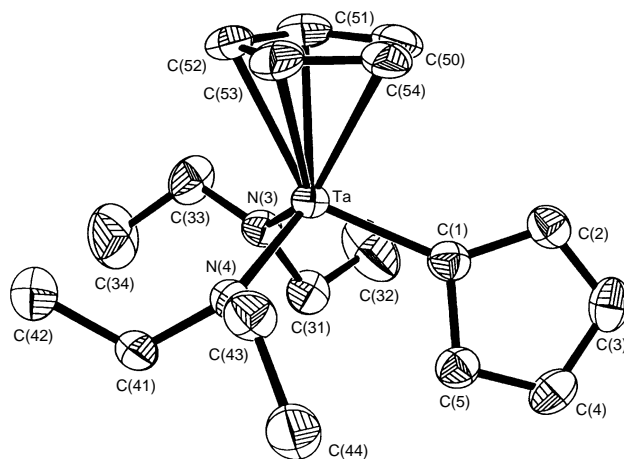


Fig. 1 Molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$ **2** with atoms drawn as 50% ellipsoids. Selected bond distances (Å) and angles ($^\circ$): Ta–C(1) 2.037(4), Ta–N(3) 1.969(3), Ta–N(4) 1.966(3), C(1)–C(5) 1.455(5), C(1)–C(2) 1.451(5), C(2)–C(3) 1.367(5), C(3)–C(4) 1.426(6), C(4)–C(5) 1.369(5); N(3)–Ta–N(4) 100.59(12), N(3)–Ta–C(1) 105.47(13), N(4)–Ta–C(1) 101.30(13), Ta–C(1)–C(2) 136.1(3), Ta–C(1)–C(5) 118.4(3), C(1)–C(2)–C(3) 109.4(3), C(2)–C(3)–C(4) 108.8(3), C(3)–C(4)–C(5) 108.1(3), C(4)–C(5)–C(1) 109.5(3).

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{thf})]$ with $\text{N}_2\text{C}_5\text{H}_4$,¹² but this complex rapidly dimerises by a [2 + 2] cycloaddition of the cyclopentadienyliene ligands to afford $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{-Mn}(=\text{C}_5\text{H}_4\text{C}_5\text{H}_4=)\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$.

The formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2(=\text{C}_5\text{H}_4)]$ **2** appears to involve both an intermolecular cyclopentadienyl transfer reaction and a C–H activation process of some type. Initial experiments have shown that $[(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(\text{NEt}_2)_2\text{Cl}_2]$ **1** reacts with 2 equiv. of CD_3Li to afford CD_3H gas, but no CH_4 . Further mechanistic experiments are in progress.

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Footnotes

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† New compounds gave analytical and ^1H and ^{13}C NMR spectroscopic data in accord with their formulation.

‡ Crystal parameters for $\text{C}_{18}\text{H}_{29}\text{N}_2\text{Ta}$ **2**: space group *Pbca* (no. 61), $a = 15.1346(9)$, $b = 15.5030(9)$, $c = 15.6133(9)$ Å. Refinement: $R = 0.0231$ and $R_w = 0.0495$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request

to the CCDC for this material should quote the full literature citation and the reference number 182/404.

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