

Synthesis of Anionic Sandwich Compounds: $[\text{Ti}(\eta\text{-C}_6\text{H}_5\text{R})_2]^-$ and the Crystal Structure of $[\text{K}(18\text{-crown-6})(\mu\text{-H})\text{Mo}(\eta\text{-C}_5\text{H}_5)_2]$

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Treatment of $\text{Mo}(\mu\text{-C}_5\text{H}_5)_2\text{H}_2$ with potassium hydride and 18-crown-6 gives the compound $[\text{K}(18\text{-crown-6})(\mu\text{-H})\text{Mo}(\eta\text{-C}_5\text{H}_5)_2]$ whose crystal structure has been determined; the compounds $\text{Ti}(\eta\text{-C}_6\text{H}_5\text{R})_2$, $\text{R} = \text{H}$ or Me undergo reduction with potassium metal to give the salts $\text{K}^+[\text{Ti}(\eta\text{-C}_6\text{H}_5\text{R})_2]^-$, $\text{R} = \text{H}$ or Me .

The first ionisation energies of the compounds $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2$, (1) and $\text{Ti}(\eta\text{-C}_6\text{H}_5\text{R})_2$, $\text{R} = \text{H}$ (2) and Me (3), are very low and occur at 6.4, 5.5–6.0, and 5.4 eV^{1,2} respectively. These low values reflect the strong electron releasing properties of the $\eta\text{-C}_5\text{H}_5$ and $\eta\text{-C}_6\text{H}_5\text{R}$ ligands. Indeed, we have previously likened the $\text{Mo}(\eta\text{-C}_5\text{H}_5)\text{H}$ radical to the Me group since both form stable covalent bonds to metals such as lithium and magnesium, for example, in the compounds $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\mu\text{-Li})]_4$ and $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2[\text{MgBr}(\text{thf})_2]\text{H}$,^{3,4} thf = tetrahydrofuran.

The low ionisation energies of bis-arene and bis-cyclopentadienyl sandwich compounds accounts for the absence of simple anionic derivatives, in contrast, for example, to the well-known $\eta\text{-cyclopentadienylcarbonyl}$ anions of the transition metals, $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_n]^-$, in which the CO groups act as electron acceptors.

We were interested to examine whether a covalent molybdenum-potassium bond could be formed using the $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2$ system and studied the reaction between potassium

hydride and (1) in thf in the presence of 18-crown-6. After several days standing at room temperature excellent orange crystals (4) appeared amongst the potassium hydride powder. The ¹H n.m.r. spectrum of (4) shows a high field band assignable to a Mo–H bond [¹H n.m.r. spectrum, 300 MHz in C₄D₈O: δ , 3.63 (s, 24H, C₁₂H₂₄O₆), 3.56 (s, 10H, 2 $\eta\text{-C}_5\text{H}_5$), –7.74 (s, 1H, Mo–H)]. The crystal structure has been determined.

Crystal data for (4): C₂₂H₃₅KMoO₆, $M = 530.56$, monoclinic, space group $I2/c$, [equivalent positions: $\pm(x, y, z; x, -y, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}-y, z)$], $a = 16.777(3)$, $b = 11.910(2)$, $c = 24.917(4)$ Å, $\beta = 101.85(1)^\circ$, $U = 4872.8$ Å³, $D_c = 1.447$ Mg m⁻³, $Z = 8$, $\mu = 7.3$ cm⁻¹, $F(000) = 2208$, $R = 3.85\%$, $R_w = 4.98\%$ for 3760 observed reflections $I > 3\sigma(I)$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å. Data were collected using an Enraf-Nonius CAD4 diffractometer out to $2\theta = 54^\circ$. The structure was solved by Patterson and Fourier methods and

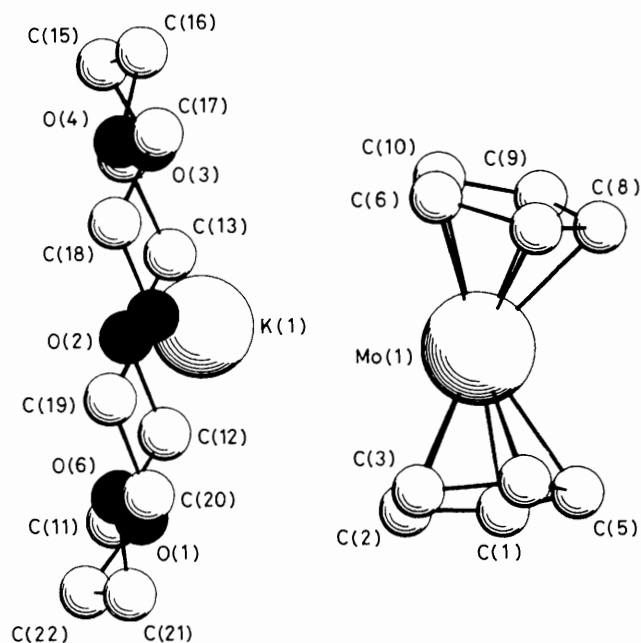


Figure 1. Molecular structure of $[\text{K}(\text{C}_{12}\text{H}_{24}\text{O}_6)(\mu\text{-H})\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2]$, (4). The oxygen atoms are shaded for clarity. Important interatomic distances (Å): Mo(1)–K(1) 3.614(1), Mo(1)–C₅H₅ plane [C(1)–C(5)] 1.937, Mo(1)–C₅H₅ plane [C(6)–C(10)] 1.921, K(1)–O(1) 2.853(4), K(1)–O(2) 2.935(4), K(1)–O(3) 2.844(4), K(1)–O(6) 2.883(4).

refined by full-matrix least squares with anisotropic vibration parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions which were modified between cycles of refinement.† Crystallographic calculations were carried out using the Oxford CRYSTALS package⁵ on the VAX 11/750 in the Chemical Crystallography Laboratory, Oxford University.

The crystal structure, shown in Figure 1⁶ confirms the stoichiometry of (4) as $[\text{K}(18\text{-crown-6})(\mu\text{-H})\text{MO}(\eta\text{-C}_5\text{H}_5)_2]$. The final difference map contains a peak which may be attributed to the bridging hydride. The Mo(1)–peak distance is 1.664 Å, comparable with that [1.685(3) Å] found for Mo–H in (1) by neutron diffraction,⁷ and K(1)–peak = 2.801 Å. The disposition of the cyclopentadienyl ligands [interplanar angle = 153.26°, cf. 145.8° in (1)], and the position of the peak in the plane formed by the centroids of the cyclopentadienyl rings and Mo(1) also support the assignment of the bridging hydride. The Mo(1)–K(1) distance is 3.614(1) Å and assuming that the hydride is as found there must be Mo–H–K contacts which may be discussed in terms of a two-electron, three-centre covalent bond.

The crystal structure shows that the potassium is pulled out of the 18-crown-6 ring (by 0.866 Å from the plane defined by the six oxygen atoms), by the anion, as found for $(18\text{-crown-6})_2\text{K}_2\text{MoO}_4 \cdot 5\text{H}_2\text{O}$ ⁸ and in contrast with $(18\text{-crown-6})\text{KNCS}$ ⁹ where the potassium sits in the cavity of the 18-crown-6. Co-ordination of the cyclic ether has caused it to adopt approximate D_{3d} symmetry when it is found to have only 1 symmetry in the free molecule.¹⁰

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

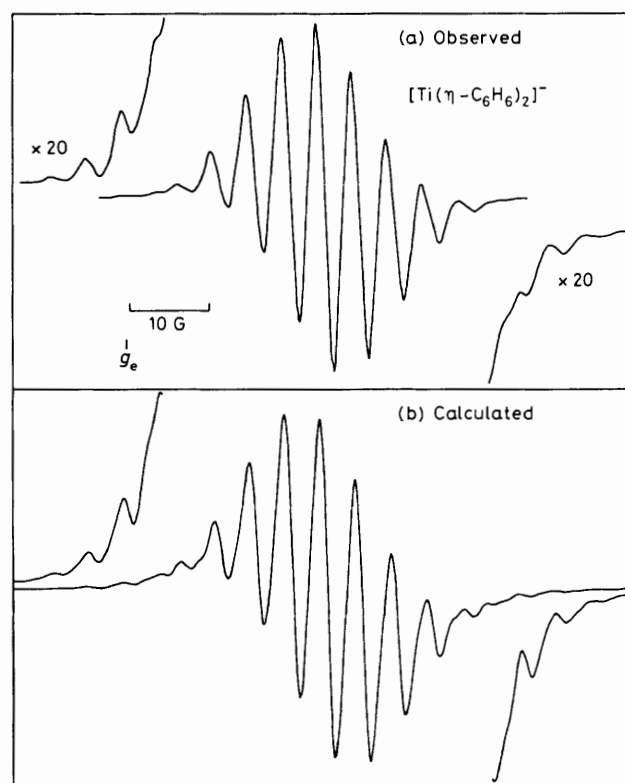
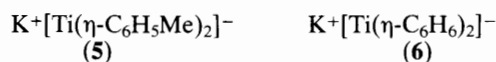
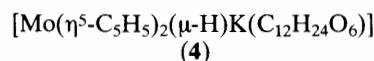
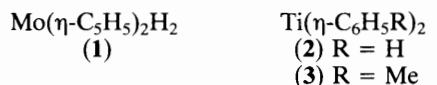


Figure 2. (a) The e.s.r. spectrum of $\text{K}[\text{Ti}(\eta\text{-C}_6\text{H}_6)_2]^\bullet$, (6), in thf at 300 K; operating frequency 9.506 GHz, power 15 mW, modulation amplitude 1.25 G. (b) Simulated spectrum with $A_{\text{H}} = 4.52$ G, $A_{\text{Ti}} = 4.7$ G, and peak to peak line-widths of 2.3 G (proton hyperfine) and 2.0 G (Ti hyperfine). The wings of the spectrum are shown expanded 20 times.



Treatment of (4) with carbon monoxide (1 atm) gives a yellow crystalline compound which upon hydrolysis forms the previously described⁴ cyclopentenyl derivative, $\text{Mo}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_7)(\text{CO})_2$ [yield from (4) ca. 60%].

We also studied the reduction of the bis-η-arene compounds $\text{Ti}(\eta\text{-C}_6\text{H}_5\text{R})_2$, R = H or Me, (2) and (3) with potassium film and with potassium hydride in thf. Each compound gave deep green solutions from which dark blue crystals of excellent appearance could be separated.

The analytical data for the toluene compound are entirely consistent with the formulation $\text{K}^+[\text{Ti}(\eta\text{-C}_6\text{H}_5\text{Me})_2]^-$ (5). The e.s.r. spectrum of (5) consists of a single resonance $g_{\text{av.}} = 1.985$ with hyperfine structure showing an envelope of nine lines ($A_{\text{H}} = 4.5$ G). The intensities and g value are consistent with an unpaired electron interacting with ten equivalent hydrogens in an ion with an ${}^2A_{1g}$ ground state.

The solution e.s.r. spectrum of the blue crystalline benzene derivative $\text{K}^+[\text{Ti}(\eta\text{-C}_6\text{H}_6)_2]^-$, (6), shows satellites due to coupling to titanium in addition to proton hyperfine structure, Figure 2(a). The spectra are interpreted by analogy with those of $\text{V}(\eta\text{-C}_6\text{H}_6)_2$ and $\text{Nb}(\eta\text{-C}_6\text{H}_6)_2$ ¹¹ and by using a simulated spectra, e.g. Figure 2(b). The latter incorporated the effect of

the ^{47}Ti (7.3%, $I = 5/2$) and ^{49}Ti (5.5%, $I = 7/2$) isotopes and the best fit was obtained with $g = 1.986$, $A_{\text{H}} = 4.52$ G, $A_{\text{Ti}} = 4.7$ G.

The values of A_{H} for the isoelectronic series $[\text{Ti}(\eta\text{-C}_6\text{H}_6)_2]^-$, $\text{V}(\eta\text{-C}_6\text{H}_6)_2$,¹² and $[\text{Cr}(\eta\text{-C}_6\text{H}_6)_2]^{+13}$ are $A_{\text{H}} = 4.5$, 4.1, and 3.4 G respectively. The decrease may be understood in terms of the contraction of the metal d_{z^2} orbital, which contains most of the electron density, with increasing nuclear charge, and a consequent reduction in overlap with the hydrogen atoms of the arene.^{11,13}

Previously Timms had observed a blue solution from the reaction between potassium and titanium tetrachloride in benzene which he correctly suspected to contain the anion $[\text{Ti}(\eta\text{-C}_6\text{H}_6)_2]^-$.¹⁴ Related anionic compounds are $\text{K}[\eta\text{-C}_5\text{H}_5)_2\text{V}]^-$,¹⁵ and $\text{Na}[(\text{Me}_5\text{C}_5)_2\text{Mn}]$.¹⁶

The compounds (5), (6) are the first isolated and characterised examples of a -1 oxidation state for titanium. The stability to isolation of the compounds (4)—(6) demonstrates that the $\eta\text{-C}_5\text{H}_5$ and $\eta\text{-C}_6\text{H}_6$ ligands are able to remain bound to the metal under quite extreme circumstances of electron density on the metal centre.

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