Butadiene 'Sandwich Compounds': Synthesis of Bis(η-1,4-di-*tert*-butylbuta-1,3-diene) Complexes of Titanium and Vanadium

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The vapours of titanium or vanadium react with 1,4-di-*tert*-butylbuta-1,3-diene to afford the novel, homoleptic diene complexes [M(η-1,4-$Bu^t_2C_4H_4)_2$], M = Ti, V.

Although alkene and diene complexes of transition metals are extremely common, simple neutral homoleptic butadiene complexes are limited to the tris complexes of molybdenum and tungsten, [M(η-$C_4H_6)_3$], M = Mo, W, prepared by cocondensation of the metal atoms with butadiene.[1] The reaction of vapours of the remaining transition metals with butadiene leads predominantly to butadiene oligomerisation products,[2] although niobium and tantalum atoms give modest yields of the bis(diene)methallyl complexes [M(η-$C_4H_6)_2$(η-MeC_3H_4)], M = Nb, Ta,[3]

Recently we have exploited the sterically demanding nature of the bulky 1,3,5-tri-*tert*-butylbenzene ligand to synthesise electronically unsaturated bis(η-arene) complexes [M(η-$Bu^t_3C_6H_3)_2$], M = *e.g.* Zr, Hf, Y, Gd.[4,5] We were therefore interested to explore the reactions of metal atoms with bulky, substituted dienes, in which we anticipated that the bulky substituents might inhibit ligand oligomerisation and afford novel, stable organometallic products. 2,2,7,7-Tetramethylocta-3,5-diene (1,4-di-*tert*-butylbuta-1,3-diene) is reasonably accessible,[6] and in this paper we describe the reactions of the latter with titanium and vanadium atoms.

Cocondensation of electron-beam vaporised titanium with an excess of 1,4-di-*tert*-butylbuta-1,3-diene at 77 K gave a red-brown matrix. After warming to room temperature, the product was extracted from the reactor with hexane and the excess ligand removed by sublimation (20 °C/10^{-4} mbar). Extraction of the residue with pentane, filtration, removal of solvent and finally sublimation at 60 °C/10^{-4} mbar afforded [Ti(η-1,4-$Bu^t_2C_4H_4)_2$], **1**, as dark-red crystals in 5–10% yield. Similarly, vanadium vapour reacted with 1,4-di-*tert*-butylbuta-1,3-diene to give deep purple, crystalline [V(η-1,4-$Bu^t_2C_4H_4)_2$],† **2**, in slightly higher yield (10–15%) after work-up (see Scheme 1).

Compounds **1** and **2** are extraordinarily soluble in hydrocarbon solvents and extremely sensitive to minute traces of oxygen or water. They are somewhat thermally sensitive in

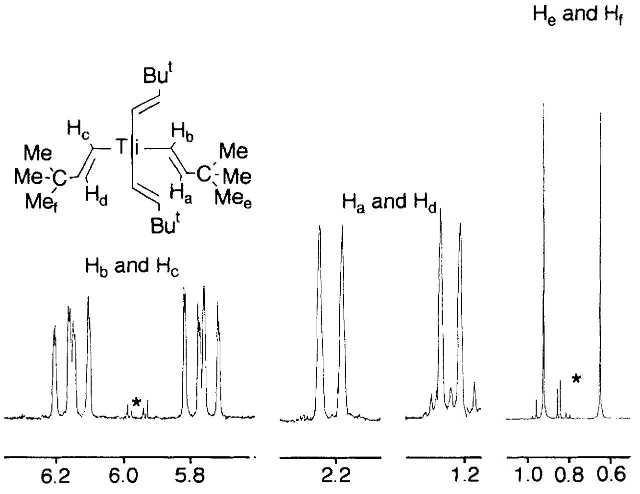

Fig. 1 ^1H NMR spectrum of **1** in [$^2H_8$]toluene at 298 K. Peaks marked with an * are due to traces of free ligand.

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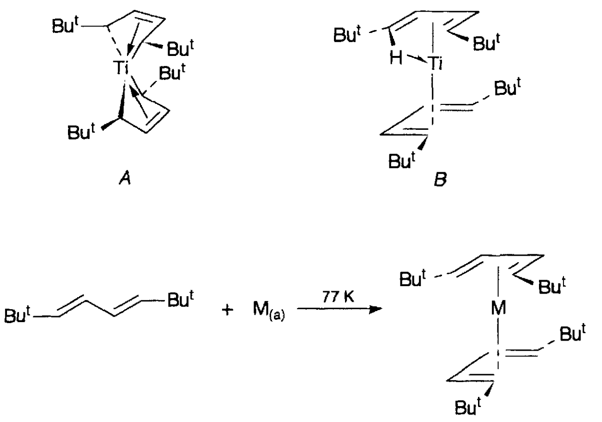
† Satisfactory microanalysis has been obtained.



M = Ti, 1
M = V, 2

Scheme 1

solution, decomposing over a few days to metal and free ligand.

The titanium complex **1** shows a weak molecular ion peak at m/z 380 (^{48}Ti) in the FAB mass spectrum (Nujol matrix); no evidence for the coordination of three or more ligands was found. The ^{1}H NMR spectrum‡ (Fig. 1) clearly illustrates the pseudo-tetrahedral arrangement of C=C double bonds about the titanium centre. Upon coordination of two molecules of the diene to Ti, the symmetry of the ligand is lowered and, while both diene ligands remain equivalent, the ends of each diene ligand are now distinguishable. Consequently, the characteristic $AA'XX'$ pattern seen for free 1,4-di-*tert*-butylbutadiene is replaced by four simple multiplets, one for each alkenic proton in **1**. Connectivity between the alkenic protons was demonstrated by selective decoupling experiments. The ^{1}H NMR spectrum showed negligible change through the temperature range 343 to 193 K, indicating the barrier to rotation of the diene ligands in this 'open sandwich' compound to be appreciable.

^{13}C NMR spectra‡ are consistent with the ^{1}H NMR spectrum. Assignments were made on the basis of ^{13}C{^{1}H}, INEPT and heteronuclear ^{13}C–^{1}H COSY spectra. Four signals assignable to the butadiene skeleton, C_{a-d}, were observed between δ 110–120, representing a small upfield shift from those of the free ligand (δ 143.3, J_{CH} 150 Hz and δ 126.3, J_{CH} 149 Hz). Strikingly, whilst J_{C_bH}/J_{C_cH} remain at *ca.* 155 Hz on complexation, J_{C_aH}/J_{C_dH} shrink to *ca.* 120 Hz. The latter value is more typical of a saturated sp^3 carbon than for an alkenic sp^2 carbon, and the reduced size of the coupling constants may indicate that the metallocyclopentene structure A[7] is a more accurate representation of **1**. The dynamic agostic structure B[8] would be an alternative possibility, although the temperature independence of the NMR spectra might seem to mitigate against the latter representation. However, without structural data, further speculation on the bonding in these complexes would be speculative.

The vanadium analogue **2** shows a molecular ion peak at m/z 383 (^{51}V) in the FAB mass spectrum (Nujol matrix). The ESR spectrum of a dilute solution of **2** in toluene at room temperature reveals a well-resolved isotropic octet, indicating coupling to a single ^{51}V nucleus ($I = \frac{7}{2}$, 100%), with $A(\mathrm{V})_{iso}$ = 76.1 G and g_{iso} = 1.957. No proton hyperfine coupling was observed.

Compounds **1** and **2** represent the first homoleptic diene complexes of titanium and vanadium, and also the first examples of what might be termed butadiene 'sandwich' compounds. The stability of these unusual, highly electron deficient 12- and 13-electron complexes is remarkable, and we are currently studying the chemistry of these compounds, as well as trying to prepare other transition metal and f-element analogues.

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‡ *NMR data* for **1** (Bruker ACP250, 298 K, [$^2H_8$]toluene), see Fig. 1 for labelling scheme; ^{1}H, δ 6.22 (ddd, 1H, J_{HH} 1.3, 11.0, 14.6 Hz, H_b or H_c), 5.83 (ddd, 1H, J_{HH} 1.2, 10.9, 14.5 Hz, H_c or H_b), 2.28 (br d, 1H, J_{HH} 1H, J_{HH} 14.3 Hz, H_a or H_d), 1.31 (br d, 1H, J_{HH} 14.3 Hz, H_d or H_a), 0.99 (s, 9H, H_e or H_f), 0.91 (s, 9H, H_f or H_e); ^{13}C{gated decoupled}: δ 118.5 (d, J_{CH} 156 Hz, C_b or C_c), 118.2 (d, J_{CH} 120 Hz, C_a or C_d), 116.4 (d, J_{CH} 155 Hz, C_c or C_b), 112.2 (d, J_{CH} 120 Hz, C_d or C_a), 35.8 (s, C-Me_3), 35.0 (C-Me_3), 33.6 (q, J_{CH} 118 Hz, C_e or C_f), 32.7 (q, J_{CH} 118 Hz, C_f or C_e).