Synthesis and reactivity of the first stable chromium(VI) alkylidene complexes

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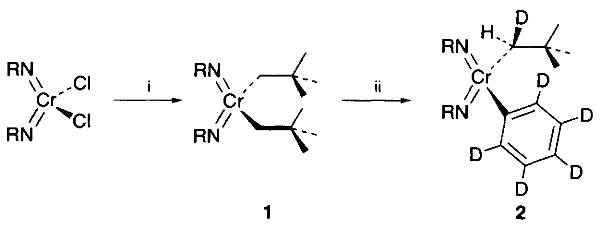
The chromium(VI) dialkyl complex $[Cr(NC_6H_3Pr^i_2\text{-}2,6)_2(CH_2CMe_3)_2]$ readily eliminates CMe_4 in room-temperature hydrocarbon and ether solutions to generate the hexavalent alkylidene species $[Cr(NC_6H_3Pr^i_2\text{-}2,6)_2({=}CMe_3)]$ which can be trapped in the presence of strong donor molecules to give the first stable hexavalent chromium alkylidene complexes $[Cr(NC_6H_3Pr^i_2\text{-}2,6)_2({=}CHCMe_3)(L)]$ (L = thf, PMe_3); in aromatic hydrocarbon solutions, the products obtained are those arising from C–H activation across the chromium–carbon double bond.

High-valent alkylidene complexes are relatively common for the heavier Group 6 metals molybdenum and tungsten and find important applications in alkene metathesis and polymer synthesis *via* ring-opening metathesis polymerisation (ROMP).[1–3] Chromium alkylidene (or carbene) chemistry on the other hand tends to be dominated by low-valent derivatives which find significant applications in organic synthesis.[4] In view of the highly oxidising nature of hexavalent chromium species, it is not surprising that examples of simple hexavalent chromium alkylidene complexes have proved elusive. It is therefore of considerable significance that we are now able to report the synthesis and characterisation of the first stable chromium(VI) alkylidene complexes,† obtained upon thermolysis of the Cr^{VI} dialkyl complex $[Cr(NC_6H_3Pr^i_2\text{-}2,6)_2(CH_2CMe_3)_2]$ **1**.

1 is readily prepared from $[Cr(NC_6H_3Pr^i_2\text{-}2,6)_2Cl_2]$[6] by treatment with 2 equiv. of Me_3CCH_2MgCl according to Scheme 1. In contrast to its *tert*-butylimido analogue[7] **1** is highly crystalline‡ and crystals suitable for an X-ray structure determination were readily grown from a saturated pentane solution at −30 °C. The molecular structure is shown in Fig. 1.§ The molecule is pseudo-tetrahedral with an N–Cr–N angle of 111.71(8)°, slightly smaller than the corresponding angles found in $[Cr(NBu^t)_2(CH_2Ph)(\eta^2\text{-}CH_2Ph)]$[8] [116.09(8)°] and $[Cr(NBu^t)_2(C_6H_2Me_3\text{-}2,4,6)_2]$ [114.5(3)°].[9] The C–Cr–C angle is 119.07(9)°. The Cr–N distances of 1.642(2) and 1.646(2) Å lie at the long end of the range found for other bis(imido)chromium(VI) species (typically 1.54–1.64 Å);[10–12] the Cr–C bond lengths of 2.030(2) and 2.042(2) Å are unexceptional. Two hydrogens, one attached to each of the α-methylene carbons, were located close to the metal centre [Cr···H(25B) = Cr···H(30B) 2.33(3) Å compared with Cr···H(25A) 2.51(3) Å and Cr···H(30A) 2.52(3) Å] which, along with Cr–C–H$_\alpha$ angles of 97.3(16)° and 97.1(16)° for H(25B) and H(30B) respectively, may be indicative of weak α-agostic interactions.



Scheme 1 *Reagents and conditions*: i, Me_3CCH_2MgCl (2 equiv.), Et_2O, room temp., 15 h; ii, C_6D_6, 40 °C, 24 h; R = $C_6H_3Pr^i_2\text{-}2,6$

Upon standing at room temperature in C_6D_6 **1** loses CMe_4 to give a single new species (**2**) in which the deuteriobenzene solvent has been incorporated (Scheme 1). ^1H and ^{13}C NMR spectroscopies show the presence of $CHDCMe_3$ and C_6D_5 ligands; in particular a 1 : 1 : 1 triplet resonance at δ 2.85 is attributable to the α-methylene proton coupled to the geminal deuterium. The metal-bound carbon of the C_6D_5 ligand is also clearly apparent at δ 192.2 along with one of the other phenyl ring carbons which occurs as a 1 : 1 : 1 triplet at δ 135.7 ($^1J_{CD}$ 26.9 Hz).

A study of the conversion of **1** to **2** in deuteriobenzene revealed clean first-order kinetics consistent with rate-determining loss of neopentane to give the transient three-coordinate chromium(VI) alkylidene species **3** (Scheme 2), which is then presumed to react rapidly with a C–D bond of C_6D_6 to give **2** as the sole product. The rate of the reaction is independent of solvent, giving virtually identical rate constants in C_6D_6 (15.2 ± 0.6 × 10^5 s^{-1}), $[^2H_8]$thf (14.7 ± 0.4 × 10^5 s^{-1}) and $[^2H_{10}]$*p*-xylene (15.8 ± 0.7 × 10^5 s^{-1}) implying that the solvent plays no role in the rate-determining α-hydrogen abstraction process (for some dialkyl complexes, base is known to assist alkane elimination[13]). The final products, however, are highly solvent dependent; in thf, for example, the base adduct $[Cr(NC_6H_3Pr^i_2\text{-}2,6)_2({=}CHCMe_3)(thf)]$ **4** is generated cleanly. The thf ligand is readily displaced by a strong donor such as PMe_3 to give the tertiary phosphine adduct **5**. Both **4** and **5** display high frequency resonances in ^1H NMR (δ 14.62, **4**; 14.79, **5**) and ^{13}C NMR (δ 328.0, **4**; 339.9, **5**) spectra characteristic of the metal–alkylidene moiety. These adducts do not themselves activate C–H bonds under thermal conditions.

Monitoring the reaction in C_6D_6 over the range 303–318 K affords the activation parameters $\Delta H^\ddagger$ = 93.7 (±2.6) kJ mol^{-1}

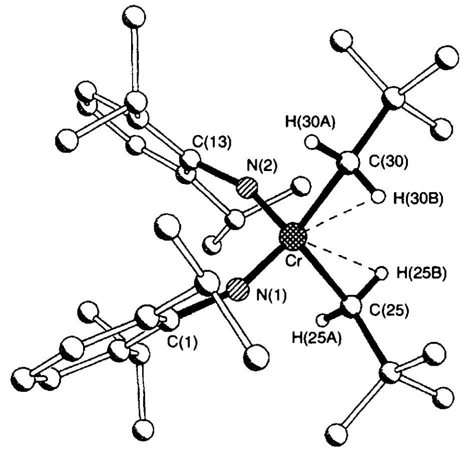
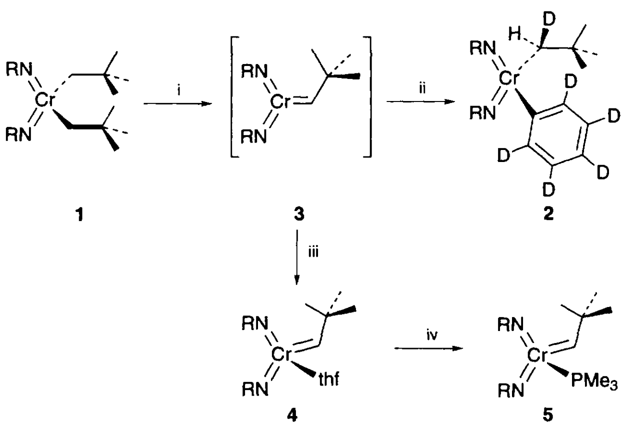


Fig. 1 Molecular structure of **1** with atom labels. Only H atoms attached to C(25) and C(30) are shown. Selected dimensions (Å and °): Cr–N(1) 1.646(2), Cr–N(2) 1.642(2), Cr–C(25) 2.030(2), Cr–C(30) 2.042(2), Cr–H(25B) 2.33(3), Cr–H(30B) 2.33(3), N(1)–C(1) 1.392(3), N(2)–C(13) 1.394(3); N(1)–Cr–N(2) 11.71(8), C(25)–Cr–C(30) 119.07(9), Cr–N(1)–C(1) 156.2(2), Cr–N(2)–C(13) 158.3(2).



Scheme 2 *Reagents and conditions*: i, room temp.; ii, C_6D_6, room temp.; iii, thf, room temp.; iv, PMe_3 (1 equiv.), room temp., 30 min

and $\Delta S^\ddagger = -20\ (\pm 6)\ \mathrm{J\ K^{-1}\ mol^{-1}}$. The small negative entropy change is consistent with solvent playing no role in the α-hydrogen abstraction process and may be rationalised as a result of some ordering during the hydrogen transfer between the methylene carbon atoms. It is possible that the weak α-agostic hydrogen interactions evident in **1** may help to facilitate the hydrogen-transfer reaction.

The reactivity of these high-valent alkylidene species towards C–H(D) bonds is unusual and sets them apart from relatively common high-valent molybdenum and tungsten alkylidene complexes which show no propensity to activate C–H bonds. We were further surprised to find that neither the thf adduct **4**, nor **3** generated directly from the dialkyl precursor complex **1**, is reactive towards simple alkenes such as ethene or norbornene. Sealed NMR samples of the chromium species in C_6D_6 in the presence of several molar equivalents of the alkenes afforded the C–D activation product **2** exclusively leaving the alkenes unreacted. Such selectivity is quite remarkable and contrasts with the well established reactivity of Mo and W alkylidene complexes towards alkenes. Studies are continuing to gain further insight into the factors influencing the reactivity of these high-valent chromium alkylidene species.

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Footnotes

† Sundermeyer *et al.*[5] have reported an unusual phosphine-substituted alkylidene species which is best represented as a zwitterion; its reactivity is quite different to the simple alkylidene complexes described here.

‡ *Selected spectroscopic data*: for **1**: ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ 6.90 (m, 6 H, C_6H_3), 3.80 (spt, $^3J_{HH}$ 6.8 Hz, 4 H, C*H*Me$_2$), 2.52 (s, 4 H, C*H*$_2$Me$_3$), 1.33 (s, 18 H, CH$_2$C*Me*$_3$) 1.12 (d, $^3J_{HH}$ 6.8 Hz, 24 H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K) δ 157.9 (*ipso*-C), 145.2 (*o*-C), 127.3 (*p*-C), 123.1 (*m*-C), 94.9 (*C*H$_2$CMe$_3$), 35.0 (CH$_2$*C*Me$_3$), 33.4 (CH$_2$C*Me*$_3$), 28.5 (*C*HMe$_2$), 23.9 (CH*Me*$_2$). For **2**: ^{1}H NMR (C_6D_6, 400 MHz, 298 K), δ 6.93 (m, 6 H, C_6H_3), 3.94 (spt, $^3J_{HH}$ 6.8 Hz, 4 H, C*H*Me$_2$), 2.85 (s, 0.3 H, C*H*DCMe$_3$), 1.29 (s, 9 H, CMe$_3$), 1.12 (d, $^3J_{HH}$ 6.8 Hz, 12 H, CH*Me*$_2$), 1.09 (d, $^3J_{HH}$ 7.20 Hz, 12 H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K), δ 192.2 (*ipso-C*, C_6D_5), 157.9 (*ipso*-C, C_6H_3), 145.8 (*o*-C, C_6H_3), 136.0 (*p*-C, C_6H_3), 135.7 (C_6D_5), 123.1 (*m*-C, C_6H_3), 98.0 (*C*HDCMe$_3$), 35.8 (*C*Me$_3$), 33.1 (C*Me*$_3$), 28.6 (*C*HMe$_2$), 24.1 (CH*Me*$_2$). For **4**: ^{1}H NMR ([^{2}H$_8$]thf, 400 MHz, 298 K), δ 14.62 (s, 1 H, =C*H*CMe$_3$), 6.77–7.00 (m, 6 H, C_6H_3), 4.07 (spt, $^3J_{HH}$ 6.7 Hz, 2 H, C*H*Me$_2$), 3.54 (spt, $^3J_{HH}$ 6.4 Hz, 2 H, C*H*Me$_2$), 1.31 (s, 9 H, =CHC*Me*$_3$), 1.24 (d, $^3J_{HH}$ 7.0 Hz, 6 H, CH*Me*$_2$), 1.21 (d, $^3J_{HH}$ 6.8 Hz, 6 H, CH*Me*$_2$), 1.05 (d, $^3J_{HH}$ 6.8 Hz, 6 H, CH*Me*$_2$), 0.88 (d, $^3J_{HH}$ 6.8 Hz, 6 H, CH*Me*$_2$). ^{13}C{^{1}H} NMR ([^{2}H$_8$]thf, 100.6 MHz, 298 K), δ 328.0 (=*C*HCMe$_3$), 160.9 (*ipso*-C), 158.8 (*ipso*-C), 142.8 (*o*-C), 142.2 (*o*-C), 124.5 (*p*-C), 123.6 (*p*-C), 122.6 (*m*-C), 122.3 (*m*-C), 49.3 (*C*Me$_3$), 31.8 (C*Me*$_3$), 29.1 (*C*HMe$_2$), 28.4 (*C*HMe$_2$), 24.2, 24.1, 23.57* (CH*Me*$_2$) (* two coincident resonances). For **5**: ^{1}H NMR ([^{2}H$_8$]thf, 400 MHz, 298 K), δ 14.79 (s, $^3J_{PH}$ 6.4 Hz, 1 H, =C*H*CMe$_3$), 7.08 (m, C_6H_3), 4.31 (spt, $^3J_{HH}$ 6.8 Hz, 2 H, CH*Me*$_2$), 4.01 (spt, $^3J_{HH}$ 6.8 Hz, 2 H, C*H*Me$_2$), 1.55 (d, $^2J_{PH}$ 9.6 Hz, 9 H, PMe$_3$), 1.29 (s, 9 H, =CHC*Me*$_3$), 1.22 (d, $^3J_{HH}$ 7.2 Hz, 6 H, CH*Me*$_2$), 1.17 (d, $^3J_{HH}$ 6.8 Hz, 6 H, CH*Me*$_2$), 1.13 (d, $^3J_{HH}$ 6.8 Hz, 6 H, CH*Me*$_2$), 1.11 (d, $^3J_{HH}$ 6.8 Hz, 6 H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K), δ 339.9 (d, $^2J_{PC}$ 26 Hz, =CHCMe$_3$), 157.0 (*ipso*-C), 153.2 (*ipso*-C), 144.7 (*o*-C), 141.3 (*o*-C), 122.5 (*p*-C), 123.0 (*p*-C), 122.5 (*m*-C), 122.4 (*m*-C), 49.0 (*C*Me$_3$), 31.8 (C*Me*$_3$), 28.6 (*C*HMe$_2$), 28.0 (*C*HME$_2$), 23.8 (PMe$_3$), 19.5, 19.2 (CH*Me*$_2$). ^{31}P{^{1}H} NMR ([^{2}H$_8$]thf, 162 MHz, 298 K), δ 21.6 (s, PMe$_3$).

§ *Crystal data* for **1**: $C_{34}H_{56}CrN_2$, $M = 544.81$, monoclinic, space group $P2_1/n$, $a = 10.6808(10)$, $b = 17.081(2)$, $c = 18.494(2)$ Å, $\beta = 101.869(2)°$, $U = 3301.9(6)$ Å^3, $Z = 4$, $D_c = 1.096$ g cm^{-3}, $F(000) = 1192$, $\mu = 0.37$ mm^{-1}, $T = 160$ K. 10938 reflections were measured on a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for absorption by a semiempirical method from redundant and symmetry-equivalent reflections.[14] Structure solution was by direct methods,[14] refinement by full-matrix least-squares analysis on F^2 for all 5426 independent reflections ($R_{int} = 0.0410$).[14] $R_w = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1146$ for all data, conventional R [on F values of 4952 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0408, goodness of fit $S = 1.058$ on F^2 for 361 refined parameters. All non-H atoms were refined with anisotropic displacement parameters, H-atoms were constrained, except for hydrogens attached to C(25) and C(30) whose coordinates were freely refined [C–H refined distances are in the range 0.89(3)–0.98(3) Å with H–C–H angles 106(2) and 107(2)°] and whose isotropic displacement parameters were set to be 120% of those of the carrier carbon atoms. 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 182/160.

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