Synthesis and *X*-Ray Crystal Structure of an Arylchromium(VI) Derivative $(\mathrm{Bu^tN})_2\mathrm{Cr}(2,4,6\text{-}\mathrm{Me_3C_6H_2})_2$

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The mesityl compound $(\mathrm{Bu^tN})_2\mathrm{Cr}(2,4,6\text{-}\mathrm{Me_3C_6H_2})_2$ was prepared by action of the Grignard reagent on $(\mathrm{Bu^tN})_2\mathrm{Cr(OSiMe_3)_2}$ and the structure determined by *X*-ray crystallography.

Among the chromium group transition metals relatively few σ-organo derivatives are known for $\mathrm{Mo^{VI}}$ and $\mathrm{W^{VI}}$ including $\mathrm{WMe_6}$,[1] $\overline{\mathrm{W(CH_2C_6H_4C}}\mathrm{H_2}\text{-}o)_3$,[2] and compounds also having imido or oxo groups present, notably $\mathrm{MoO_2mes_2}$ (mes = mesityl),[3] $\mathrm{WO(CH_2CMe_3)_4}$,[4] and $[(\mathrm{Bu^tN})_2\mathrm{MMe_2}]_2$, M = Mo,[5] or W.[6] There appears to be only one organochromium(VI) complex, namely $[(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Cr_2(NPh)_4}]$,[7] but no σ-organo derivatives.

We now report the synthesis from $(\mathrm{Bu^tN})_2\mathrm{Cr(OSiMe_3)_2}$[8] of the first examples of σ-organochromium(VI) compounds to be isolated, namely the imido arylchromium(VI) derivatives $(\mathrm{Bu^tN})_2\mathrm{Crmes_2}$, m.p. 146 °C, (**1**) and $(\mathrm{Bu^tN})_2\mathrm{Cr}(2,6\text{-}\mathrm{Me_2C_6H_3})_2$, m.p. 106 °C, (**2**), by reaction (1).

The deep red air stable compounds are formed in >60% yield. They are very soluble and stable in hydrocarbons or ethers but slowly decompose in halogenated solvents. *X*-Ray quality crystals of (**1**) were obtained from hexane solutions and crystalline (**2**) from hexamethyldisiloxane solutions at −21 °C. The presence of the *o*-methyl groups on the phenyl rings undoubtedly contributes to the air and thermal stability and it is noteworthy that no analogous compound could be isolated when $(\mathrm{Bu^tN})_2\mathrm{Cr(OSiMe_3)_2}$ was treated with *o*-tolyl- or phenyl-magnesium bromide or as previously reported[6] when diphenylzinc was used. In the latter case reductive elimination of both biphenyl and t-butylphenylamine was observed.

$$(\mathrm{Bu^tN})_2\mathrm{Cr(OSiMe_3)_2} + 2\mathrm{RMgBr} \xrightarrow[\text{Room temp.}]{\text{Hexane}} (\mathrm{Bu^tN})_2\mathrm{CrR_2} + \text{`}2\mathrm{Mg(OSiMe_3)Br}\text{'} \qquad (1)$$

(**1**) R = mes
(**2**) R = 2,6-xylyl

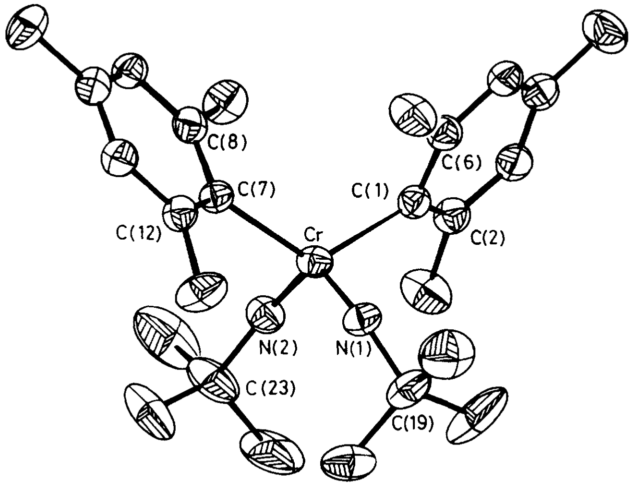

Figure 1. The molecular structure of $(Bu^tN)_2Crmes_2$ (**1**). Selected bond lengths (Å) and angles (°) are: Cr–N(1) 1.623(5), Cr–N(2) 1.622(5), Cr–C(1) 2.019(6), Cr–C(7) 2.029(6), N(1)–C(19) 1.453(6), N(2)–C(23) 1.445(6); N(1)–Cr–N(2) 114.7(3), C(1)–Cr–C(7) 121.3(2), N–Cr–C 100.9(3)—110.0(2), Cr–N(1)–C(19) 159.8(3), Cr–N(2)–C(23) 159.4(3), Cr–C(1)–C(2) 127.9(4), Cr–C(1)–C(6) 115.1(4), Cr–C(7)–C(8) 115.9(4), Cr–C(7)–C(12) 127.2(4).

X-Ray diffraction study showed (**1**) to be monomeric with distorted tetrahedral geometry at the chromium atom (Figure 1).† The nature of this distortion is interesting in that the angle between the two Cr=N–Bu^t bonds is smaller than that between the two Cr–C bonds. However, both are greater than the tetrahedral angle. The bonding of the mesityl groups is also unsymmetrical, with Cr–C–C angles at the bonded carbon of *ca.* 127° and 115°. These distortions contrast strongly with those found in the related molecules O_2Mmes_2, M = Re,Os,[9] in which the O=M=O angles are greater than the C–M–C angles. The difference is most probably due to steric effects introduced by the Bu^t groups on nitrogen in the present complex, but in the Re and Os species, interesting electronic effects are also present.

Analogous aryl derivatives of Mo^{VI}, $(Bu^tN)_2Momes_2$, $(Bu^tN)_2Mo(2,6\text{-}Me_2C_6H_3)_2$, $(Bu^tN)_2Mo(o\text{-tolyl})_2$, and of W^{VI}, $(Bu^tN)_2Wmes_2$ have also been prepared, and the chemistry of this novel group of complexes is being studied.

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† *Crystal data* for (**1**): $C_{26}H_{40}N_2Cr$, $M = 432.61$, monoclinic, $a = 9.145(2)$, $b = 18.893(3)$, $c = 15.226(4)$ Å, $\beta = 91.49(2)°$, $U = 2629.8$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.09$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu = 4.36$ cm^{-1}. Data recorded using a CAD4 diffractometer in $\omega/2\theta$ scan mode; corrected for absorption empirically 5189 data measured, 4620 unique, 2841 observed $[I > 1.5\sigma(I)]$. Structure solved *via* heavy atom method, refined by least squares with hydrogens isotropic, non-hydrogens anisotropic, to R, $R_w = 0.053$, 0.044 respectively for 422 parameters. 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, 1986.