*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

## Preliminary communication

# Neopentyl and related alkyls of chromium(IV) and other transition metals

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(Received March 22nd, 1972)

We have discussed means whereby transition metal alkyls can be stabilized by prevention of hydride transfer and alkene elimination and we have isolated a number of compounds containing trimethylsilylmethyl, $(CH_3)_3SiCH_2$ [1,2]. Studies[3] of relative stabilities indicate that for a similar reason benzyl and neopentyl compounds are more stable than other alkyls; indeed benzyls of titanium, zirconium and vanadium[4] are known and neopentyls of molybdenum and tungsten and other metals have been mentioned[5].

It is of particular interest that the unusual oxidation state of chromium(IV) can be obtained so readily with carbon as a ligand in these alkyls; and it now appears that carbon takes its place as a first row element along with fluorine (in $CrF_4$), oxygen[7] (in $Cr(OR)_4$) and nitrogen[8] (in $Cr(NR_2)_4$), in forming tetrahedral chromium(IV) species; presumably similar boron compounds $Cr(BR_2)_4$ will be prepared in due course. The size of the coordinating atom may be an important factor in the formation of such species by oxidation or disproportionation, though the size of the ligand evidently has some bearing as the diisopropyl amide gives the monomeric chromium(III) compound $Cr(N\text{-}i\text{-}Pr_2)_3$ as well as that of chromium(IV).

The monomeric chromium compounds obtained using lithium or Grignard reagents derived from $(CH_3)_3CCH_2Cl$, $(C_6H_5)_3CCH_2Cl$, and $(C_6H_5)(CH_3)_2CCH_2Cl$ are all intensely colored crystalline solids, readily soluble in petr. ether and other organic solvents. The magnetic moments (ca. 2.7 B.M.) are all consistent with values expected for a $d^2$ system (*cf.* ref. 2) and the electron spin resonance spectra of frozen solutions are characteristic of the triplet state ($S = 1$) with axial symmetry consistent with tetrahedral chromium(IV). The electronic absorption spectra essentially a strong band at ca. 20 000 $cm^{-1}$ ($\epsilon$ = ca. 1000) assigned as $^3A_2 \rightarrow {}^3T_1$, also accord with this formulation.

ESR evidence has also been obtained for a chromium(IV) benzyl although like the vanadium benzyl[4] it could not be isolated. The molybdenum and tungsten benzyls[5] of formula $M_2(CH_2Ph)_6$ are isolable.

In view of the stability of the chromium(IV) alkyls it is no great surprise that

TABLE 1

| *Compound* | *Form* | *M.p. (°C)* |
|---|---|---|
| $Ti(CH_2CMe_3)_4$ | yellow prisms | 99 |
| $Zr(CH_2CMe_3)_4$ | off-white prisms | 103 |
| $Ta(CH_2CMe_3)_3Cl_2$ | pale yellow needles | 115 |
| $Cr(CH_2CMe_3)_4$ | maroon needles | 110 |
| $Cr(CH_2CMe_2Ph)_4$ | purple needles | ca. 120 (dec) |
| $Cr(CH_2CPh_3)_4$ | purple prisms | ca. 130 (dec) |

neopentyls of titanium, zirconium and tantalum (Table 1) can be isolated and further obvious extensions of the chemistry of alkyls stabilized against elimination[1] can be anticipated,

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