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Preliminary communication

TRIMETHYLTANTALUM(V) CHELATE COMPLEXES

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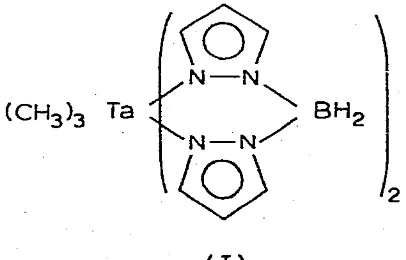
Summary

Interaction of trimethyldichlorotantalum with potassium bis(pyrazolyl)borate, $K^+[pz_2BH_2]^-$, gives the chloride-free complex $Me_3Ta(pz_2BH_2)_2$; other examples of similar reactions are reported.

Niobium(V) and tantalum(V) methyl chlorides $MeMCl_4$, Me_2MCl_3, Me_3MCl_2 (M = Nb, Ta) are known to form adducts with various donor ligands [1, 2], with chloride ion [2] to give $[EtN][Me_3MCl_3]$, and to give complexes by insertion of neutral molecules such as MeSCN [3] and NO [4] into the M—CH_3 bond. Reactions involving removal of chloride do not appear to have been reported, although recently Schrock [5] has synthesised pentamethyl-tantalum and -niobium. The use of an anion with an additional donor function should also lead to an increase in the coordination number and hence probably, the thermal stability by blocking sites required for decomposition.

The reaction of Me_3TaCl_2 in diethyl ether with two equivalents of potassium bis(pyrazolyl)borate, $K^+[pz_2BH_2]^-$, gives trimethylbis[bis(pyrazolyl)-borate]tantalum(V) (I). Similar trimethylplatinum compounds have been recently reported [6].



(I)

Analogous reactions with sodium, thallium and silver salts of various anions are currently being investigated and we are extending the work to other alkyl halides such as CH_3TiCl_3, CH_3WCl_5 etc. NMR data for several of the tantalum products are listed in Table 1.

$Me_3Ta(pz_2BH_2)_2$ is a yellow crystalline compound which does not sublime (10^{-4} mm Hg) at temperatures below its decomposition point (120°). It is characterised by infrared, NMR and mass spectra and by analysis. IR (nujol): ν(Ta—C) 481, 504 cm^{-1}; ν(B—H) 2390 cm^{-1} and strong bands associated with pyrazolyl group. NMR (CH_2Cl_2) τ 2.35 d, 2.85 d, 3.80 t (C_3H_3N); τ 8.20 s ($TaCH_3$ ratio 4/4/4/9. Mass spectrum: highest peak observed *m/e* 543 (M^+ —30). (Found: C, 35.1; H, 4.8; N, 21.5. $C_{15}H_{25}B_2N_8Ta$ calcd.: C, 34.7; H, 4.6; N, 19.2%).

TABLE 1

NMR SPECTRA (CH_2Cl_2 solution at 60 MHz, 35°C)

Compound	Ta—CH_3 (τ)	Other resonances (τ)
$Me_3Ta(pz_2BH_2)_2$	8.20 s	2.35 d, 2.85 d, 3.80 t
$Me_3Ta(CH_3COCHCOCH_3)_2$	8.80 (br)	8.05, 4.80
$Me_3Ta(CF_3COCHCOCH_3)_2$	8.65 (br)	7.75 (complex), 4.70
$Me_3Ta(O_2CCH_3)_2$	7.75	8.45
$Me_3Ta(C_4H_2O_4)$ [a]	8.65 s	7.35

[a] $C_4H_2O_4$ = squarate.

The NMR spectrum, as expected for a non-rigid 7-coordinate complex, shows broadening of the Ta—CH_3 peak on cooling below 0°, although this does not split into two singlets even on cooling to —90° [cf. other 7-coordinate species [2] e.g., Me_3TaCl_2 (2,2'-bipy)]. The pyrazolyl resonances also broaden and one, τ 2.85, splits into two peaks (coalescence temperature —75°) showing non-equivalence of the coordinated pyrazolyl groups in the 7-coordinate structure.

References

1 G.W.A. Fowles, D.A. Rice and T.D. Wilkins, J. Chem. Soc. Dalton, (1973) 961; C. Santini-Scampucci and J.G. Riess, J. Chem. Soc. Dalton, (1973) 2436, and ref. therein.

2 G.W.A. Fowles, D.A. Rice and J.D. Wilkins, J. Chem. Soc. Dalton, (1974) 1080.

3 J.D. Wilkins, J. Organometal. Chem., 65 (1974) 383.

4 J.D. Wilkins and M.G.B. Drew, J. Organometal. Chem., 69 (1974) 111.

5 R.R. Schrock, Central Research Department, E.I. Dupont and Co. Wilmington, personal communication and presentation at Leeds-Sheffield Symposium, March 1974.

6 R.B. King and A. Bond, J. Amer. Chem. Soc., 96 (1974) 1338.