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Preliminary communication

THE PREPARATION OF MONO(η^5-CYCLOPENTADIENYL) COMPLEXES OF NIOBIUM AND TANTALUM

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SUMMARY

Treatment of NbX_5 or TaX_5 (X = Br or Cl) with $Mg(C_5H_5)_2$ or $Sn(CH_3)_3(C_5H_5)$ produces the complexes $[M(C_5H_5)X_4]$ (X = Cl, M = Nb or Ta; X = Br, M = Ta) and $[Nb(C_5H_5)Br_3]$.

In our attempts to open up the chemistry of niobium and tantalum in mononuclear complexes of low oxidation state, we required compounds containing a single η^5-cyclopentadienyl ligand. These were, in contrast to the bis(η^5-cyclopentadienyl) complexes of niobium and tantalum, not easily available[1]. However, we now find that the complexes $[M(C_5H_5)X_n]$ (M = Nb or Ta; X = Cl or Br; n = 4 in most cases, otherwise 3) are readily prepared by the reaction of MX_5 with one equivalent of cyclopentadienyl derivatives such as $Mg(C_5H_5)_2$[2] or $Sn(CH_3)_3(C_5H_5)$[3]. In contrast the reaction of $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) with $Mg(C_5H_5)_2$ or $Sn(CH_3)_3(C_5H_5)$ generally produces $[V(C_5H_5)_2Cl]$ regardless of the molar proportions used. A typical preparation is as follows.

Reaction of TaX_5 with $Mg(C_5H_5)_2$

The tantalum halide (ca 6g) was mixed with 0.5mol of $Mg(C_5H_5)_2$ in toluene (100cm^3). After 12h. at 25° the toluene was removed under reduced pressure (10^{-3}mmHg) and the residue

Table - Mono(cyclopentadienyl) complexes

	Form and sublimation temp. (°C)	Characteristic i.r. peaks[a] cm^{-1}	Principal ions in mass spectra m/e		
$[Ta(C_5H_5)Br_4]$[b]	Red-orange crystals 226°, 0.5 mmHg	872 vs, 1018 m, 1125 w, 1432 s.	$Ta(C_5H_5)Br_3$ 483-489	$TaBr_4$ 497-505	$TaBr_3$ 418-428
$[Ta(C_5H_5)Cl_4]$[c]	Yellow crystals 230°, 0.05 mmHg	878 vs, 1018 m, 1128 w, 1432 s.	$Ta(C_5H_5)Cl_3$ 351-355	$TaCl_4$ 321-327	$TaCl_3$ 286-290
$[Nb(C_5H_5)Br_3]$[d]	Black platelets 300°, 0.04 mmHg	850 s, 865 s, 1020 m, 1130 w, 1435 s.	$Nb(C_5H_4)Br_3$ 394-400	$Nb(C_5H_4)Br_2$ 315-319	$Nb(C_5H_4)Br$ 236-238
$[Nb(C_5H_5)Cl_4]$[e]	Red crystals	800 w, 870 vs, 900 w, 1020 m, 1075 w, 1130 w, 1260 w, 1420 s.	$Nb(C_5H_5)Cl_3$ 263-267	$NbCl_4$ 232-235 vw	$NbCl_3$ 198-204 vw

a Nujol mulls.

Analyses: found (required) percent.

b C 11.0(10.6); H 0.96(0.84); Ta 33.5(32.0); Br 55.5(56.5).

c C 15.7(15.5); H 1.40(1.30); Ta 47.1(46.7); Cl 36.0(36.6).

d C 14.8(15.1); H 1.40(1.27); Br 60.4(60.3).

e C 20.5(20.0); H 2.01(1.68); Nb 30.8(31.0); Cl 45.9(47.3).

(yellow, X = Cl; or orange, X = Br) extracted with dichloromethane to give a crystalline product. Pure $[Ta(C_5H_5)X_4]$ was obtained by sublimation (230°, 0.05mmHg) or recrystallisation from dichloromethane. Characterisation was by i.r. spectroscopy (which showed a band pattern characteristic of mono- rather than bis-cyclopentadienyl[4] complexes), mass spectrometry (which confirmed the presence of four, or in one case, three, halogen atoms per metal atom) and elemental analysis (see Table). When M = Nb and X = Br some reduction occurs and the product is $[Nb(C_5H_5)Br_3]$.

The reactions of $Mg(C_5H_5)_2$ and $Sn(CH_3)_3(C_5H_5)$ with MX_5 represent the first reliable and reproducible method of synthesising $[M(C_5H_5)X_n]$ type compounds where M = Ta or Nb. We have since learned that other workers have synthesised $[Nb(C_5H_5)Cl_4]$ from $NbCl_5$ and $Sn(Bu^n)_3(C_5H_5)$[5]. Cyclopentadienyls which are stronger reducing agents, e.g. NaC_5H_5 produce intractible partially reduced mixtures.

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5 M.L.H. Green, personal communication*.

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* since submission of this communication a referee has drawn our attention to the publication, which has just appeared, by M.J. Bunker, A. De Cian and M.L.H. Green, J.C.S. Chem. Comm., (1977), 59, who have explored the alkyl(cyclopentadienyl)tin route in greater depth.