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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 ($\text{X} = \text{Br}$ or Cl) with $\text{Mg}(\text{C}_5\text{H}_5)_2$ or $\text{Sn}(\text{CH}_3)_3(\text{C}_5\text{H}_5)$ produces the complexes $[\text{M}(\text{C}_5\text{H}_5)_4\text{X}]$ ($\text{X} = \text{Cl}$, $\text{M} = \text{Nb}$ or Ta ; $\text{X} = \text{Br}$, $\text{M} = \text{Ta}$) and $[\text{Nb}(\text{C}_5\text{H}_5)\text{Br}_3]$.

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 available¹. However, we now find that the complexes $[\text{M}(\text{C}_5\text{H}_5)_n\text{X}]$ ($\text{M} = \text{Nb}$ or Ta ; $\text{X} = \text{Cl}$ 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 $\text{Mg}(\text{C}_5\text{H}_5)_2$ ² or $\text{Sn}(\text{CH}_3)_3(\text{C}_5\text{H}_5)$ ³. In contrast the reaction of $[\text{VCl}_3(\text{thf})_3]$ ($\text{thf} = \text{tetrahydrofuran}$) with $\text{Mg}(\text{C}_5\text{H}_5)_2$ or $\text{Sn}(\text{CH}_3)_3(\text{C}_5\text{H}_5)$ generally produces $[\text{V}(\text{C}_5\text{H}_5)_2\text{Cl}]$ regardless of the molar proportions used. A typical preparation is as follows.

Reaction of TaX_5 with $\text{Mg}(\text{C}_5\text{H}_5)_2$

The tantalum halide (ca 6g) was mixed with 0.5mol of $\text{Mg}(\text{C}_5\text{H}_5)_2$ 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 ₅ H ₅)Br ₄] ^b	Red-orange crystals 226°, 0.5 mmHg	872 vs, 1018 m, 1125 w, 1432 s.	TaBr ₄ 497-505	TaBr ₃ 418-428
[Ta(C ₅ H ₅)Cl ₄] ^c	Yellow crystals 230°, 0.05 mmHg	878 vs, 1018 m, 1128 w, 1432 s.	TaCl ₄ 321-327	TaCl ₃ 286-290
[Nb(C ₅ H ₅)Br ₃] ^d	Black platelets 300°, 0.04 mmHg	850 s, 865 s, 1020 m, 1130 w, 1435 s.	Nb(C ₅ H ₄)Br ₂ 315-319	Nb(C ₅ H ₄)Br 236-238
[Nb(C ₅ H ₅)Cl ₄] ^e	Red crystals	800 w, 870 vs, 900 w, 1020 m, 1075 w, 1130 w, 1260 w, 1420 s.	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 $[\text{Ta}(\text{C}_5\text{H}_5)\text{X}_4]$ 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-cyclopentadienyl⁴ 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 $[\text{Nb}(\text{C}_5\text{H}_5)\text{Br}_3]$.

The reactions of $\text{Mg}(\text{C}_5\text{H}_5)_2$, and $\text{Sn}(\text{CH}_3)_3(\text{C}_5\text{H}_5)$ with MX_5 represent the first reliable and reproducible method of synthesising $[\text{M}(\text{C}_5\text{H}_5)\text{X}_n]$ type compounds where M = Ta or Nb. We have since learned that other workers have synthesised $[\text{Nb}(\text{C}_5\text{H}_5)\text{Cl}_4]$ from NbCl_5 and $\text{Sn}(\text{Bu}^n)_3(\text{C}_5\text{H}_5)$ ⁵. Cyclopentadienyls which are stronger reducing agents, e.g. NaC_5H_5 produce intractable partially reduced mixtures.

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REFERENCES

- 1 See, for example, K.N. Anisimov, N.E. Kolobova and A.A. Pasynskii, *Izvestia Akad. Nauk S.S.S.R., Ser. Khim.*, (1969) 2238.
- 2 W.A. Barber, *Inorg. Syntheses*, Vol. 6, p.11.
- 3 H.P. Fritz and C.G. Kreiter, *J. Organometal. Chem.*, 1, (1964), 323.
- 4 H.P. Fritz, *Adv. Organometal. Chem.*, 1, (1964), 240.
- 5 M.L.H. Green, personal communication*.

* 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.