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Preliminary communication

NIOBIUM ORGANOMETALLIC CHEMISTRY

I. REACTIONS OF DI-η^5-CYCLOPENTADIENYL COMPOUNDS WITH SULFUR AND SOME SULFUR-CONTAINING COMPOUNDS

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Summary

The 17-electron species $(\eta\text{-}C_5H_5)_2NbMe_2$ reacts with cyclooctasulfur and with carbon disulfide to give, the 18-electron species $(\eta\text{-}C_5H_5)_2NbS_2Me$ (III) and $(\eta\text{-}C_5H_5)_2Nb(CS_2)Me$ (IV), respectively. Addition of methyl iodide to IV gives $[(\eta\text{-}C_5H_5)_2Nb\{C(S)SMe\}MeI]$. With sodium diethyldithiocarbamate and M'X (NH_4PF_6, $NaBF_4$), $(\eta\text{-}C_5H_5)_2NbCl_2$ yields the compounds $[(\eta\text{-}C_5H_5)_2Nb(S_2CNEt_2)]^+X^-$.

As part of our programme of developing unequivocal selective routes to σ-alkylated derivatives of di-η^5-cyclopentadienyl-transition metal complexes and of assessing what reactions can be carried out with them without breaking the metal—carbon σ bond, we now report the reactions of the di-η^5-cyclopentadienyldimethylniobium $(\eta\text{-}C_5H_5)_2NbMe_2$ (II) with cyclooctasulfur and carbon disulphide, along with the synthesis of some related complexes.

Although II has been described and studied by electron spin resonance [1], no reactions involving removal of one or two methyl groups have been reported. However, Lemenovskii et al. [2] showed that the treatment of $(\eta\text{-}C_5H_5)_2NbCl_2$ with butyllithium in ether followed by air oxidation gave $(\eta\text{-}C_5H_5)_2Nb(O)Bu$ [2a] and $[(\eta\text{-}C_5H_5)_2NbBu]_2O$ [2b].

Thermal or photochemical treatment of II with cyclooctasulfur in benzene results in a smooth reaction and the disulfur compound $(\eta\text{-}C_5H_5)_2NbS_2Me$ (III) can be readily isolated by chromatography on an alumina column in ca 60% yield**. III is an air-stable, orange complex, very soluble in the common or-

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[**] All experiments were performed under vacuum or nitrogen atmosphere. All new complexes (III—VI) gave satisfactory analyses and their infrared spectra showed absorptions characteristic of η-bonded cyclopentadienyl groups.

ganic solvents except alkanes. It is monomeric, the parent peak in the mass spectrum appearing at 302. The infrared spectrum (and more specially a strong and sharp band at 540 cm^{-1} attributed to ν(S—S)), the ^1H NMR spectrum (4.42, C_5H_5, s,10; 8.92, CH_3, s,3)* and the ^{13}C NMR spectrum (105.8, C_5H_5, s; 7,7, CH_3, s)** are consistent with the proposed structure.

The formation of III, the first disulfurdi-η^5-cyclopentadienylniobium complex with a metal—carbon σ bond, corresponds to an oxidation of the 17-electron-species II by sulfur. In contrast, the disulfur—niobium complexes previously known $[(\eta\text{-}C_5H_5)_2NbS_2X]$ (X = Cl, Br, SCN etc) [3a] were obtained by the reaction of $(\eta\text{-}C_5H_5)_2NbCl_2(OH)$ with H_2S in methanol in the presence of an ionic halide or pseudo-halide. X-ray studies of the chloro and cyano disulfur compounds have shown that the S_2 entity is bonded in a side-on fashion [3b].

The formation of compound III confirms that cyclooctasulfur can react with organometallic derivatives to give species containing MS_x metallocycles with various values of x. For instance, $(\eta\text{-}C_5H_5)_2Ti(CH_3)_2$ leads to $(\eta\text{-}C_5H_5)_2TiS_5$ [4] while $(\eta\text{-}C_5H_5)_2MH_2$ (M = Mo, W) gives $(\eta\text{-}C_5H_5)_2MS_4$ [5].

Complex III reacts with HCl in tetrahydrofuran at room temperature to give $(\eta\text{-}C_5H_5)_2NbCl_2$ in good yield, along with small amounts of an unidentified white compound; no detectable amount of $(\eta\text{-}C_5H_5)_2NbS_2Cl$ was formed.

Irradiation of benzene solutions of II in presence of an excess of carbon disulfide gives the η^2-CS_2 complex IV (yield 56%; parent peak at 314; ν(C—S) at 1130 cm^{-1}; ^1H NMR 4.60, C_5H_5, s, 10; 8.92, CH_3, s, 3).

Reactions 2 and 4 (see Scheme) clearly indicate that two of the most prominent features of the chemical behavior of II are (i) the easy transformation into 18-electron complexes by substitution of one of the two methyl groups with a two-electron ligand and (ii) the stability of the metal—carbon σ bond.

The reaction between IV and methyl iodide was performed at room temperature in toluene. A pale yellow compound (V) precipitated (η 60%). This complex, which is not very air sensitive, is only sparingly soluble in usual organic solvents, and this precluded ^1H NMR measurements. The proposed structure (see Scheme 1) is suggested by comparison with the results obtained by Fowles et al. for the correspondingly allyl complex [6].

Attempts to transform complex IV into a thiocarbonyl compound by action of triphenylphosphine failed, and gave only intractable material.

Addition of a water solution of sodium diethyldithiocarbamate to a water suspension of $[(\eta\text{-}C_5H_5)_2NbCl_2]$, followed by addition of a M'X solution (M'X = NH_4PF_6, $NaBF_4$) gives the dithiocarbamate complexes VI. In contrast to the hexafluorophosphate compound, the tetrafluoroborate is rather soluble in water; both are only sparingly soluble in usual organic solvents. Their infrared spectra, which exhibit the usual absorptions of the dithiocarbamate ligand and those of the anions, are very similar to the spectra of the vanadium derivatives prepared from $(\eta\text{-}C_5H_5)_2VCl_2$ by Casey and Thackeray [7]. Structure VI with a bidentate dithiocarbamate group seems more likely than a structure with a monodentate dithiocarbamate ligand and a coordinated water molecule. With

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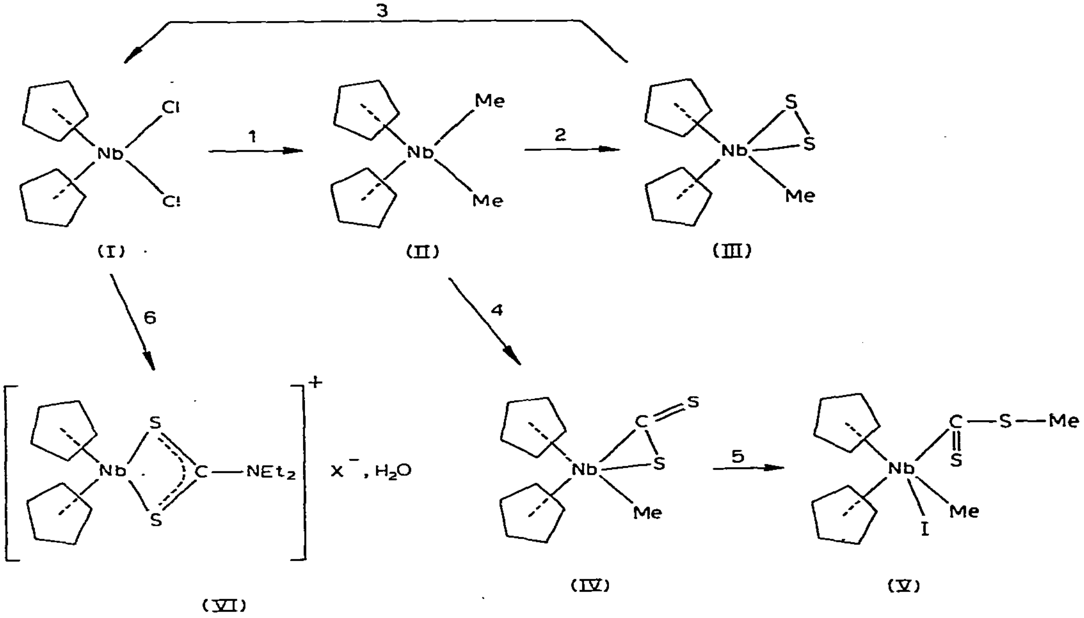
* ^1H NMR data: (relative to TMS, assignment, s: singlet, relative intensity).

** ^{13}C NMR data: (δ relative to TMS, assignment, s: singlet).



Scheme 1. Reactions of some di-η^5-cyclopentadienylniobium compounds with sulfur and some sulfur-containing compounds. (1) $LiCH_3$ in ether; (2) S_8 in benzene; (3) HCl in tetrahydrofuran; (4) CS_2 in benzene; (5) CH_3I in toluene; (6) $Na[S_2CNEt_2]$ in H_2O and $M'X$ ($M'X = NH_4PF_6, NaBF_4$).

the same ligand, the zirconium compound $(\eta\text{-}C_5H_5)_2ZrCl_2$ affords the mono-η-cyclopentadienyl complex $(\eta\text{-}C_5H_5)Zr(S_2CNEt_2)_3$ [8].

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