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PRELIMINARY NOTE

Niobium Organometallic Chemistry. Part II * : Unexpected Synthesis of a Complex containing Niobium - Fluorine Bonds. Crystal Structure of a fluorinated Niobiacyclopentadiene Compound.

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A wide variety of bis(cyclopentadienyl)niobium complexes with substitued acetylenes has recently been synthesised. The preparation of the stable complexes $Cp_2NbX(R_1\text{-}C{\equiv}C\text{-}R_2)$ (I) (Cp = η^5-C_5H_5; X = H; R_1 = R_2 = Me, nPr; R_1 = Me, R_2 = iPr, nPr) from Cp_2NbH_3 has been reported [2]. CH_3I converted the compounds (I) to the iodo-analogs (X = I) while CO caused smooth conversion to carbonyl (alkylenyl)complexes $Cp_2Nb(CO)(R_1C{=}CR_2H)$ [2]. The chloro-analogs of (I) $Cp_2NbCl(R_1\text{-}C{\equiv}C\text{-}R_2)$ (X = Cl; $R_1{=}R_2{=}CF_3$; $R_1{=}CH_3$, R_2=H) have been prepared by the reaction of substitued acetylenes with Cp_2NbCl_2 in the presence of sodium amalgam [3].

We now find that the reaction of a highly electron withdrawing acetylene (hexafluorobutyne hfb; $R_1{=}R_2{=}CF_3$) with Cp_2NbH_3 is much more complex than thought and results in the reduction of niobium and in the formation of new niobium (IV) complexes. Irradiation of a toluene solution of Cp_2NbH_3 [2] in the presence of hexafluorobutyne affords after further work-up four new compounds (1) (yield ca 30%), (2) (ca 20%), (3) (ca 10%) and (4) (very low yield).

* See reference [1]

Complex (1) is a brown air-sensitive compound, very sparingly soluble in organic solvents. (1) was identified as the new difluoro derivative Cp_2NbF_2 from analytical data and the following properties :

- infrared data : the spectrum shows no bands characteristic of CF_3 groups in the 1000-1200 cm^{-1} range but exhibits the usual η^5-C_5H_5 peaks and two extra bands at 520 and 480 cm^{-1} assignable to ν(Nb-F) [4];

- ESR spectrum (CH_2Cl_2 solution at room temperature) : ten lines arise from ^{93}Nb coupling, each of these being split into three lines due to hyperfine coupling with two equivalent fluorine atoms ($\langle a_{Nb} \rangle$ = 115 G; $\langle a_F \rangle$ = 22 G).

On the basis of these results and high-resolution mass spectroscopy (parent peak at m/e 260.9820; calculated for $NbC_{10}H_{10}F_2$ m/e 260.9814), we propose that Cp_2NbF_2 has the usual structure of $(\eta^5\text{-}C_5H_5)_2MX_2$ complexes [5]. (1) is the first bis(cyclopentadienyl)niobium derivative containing Nb-F bonds. Its formation from $CF_3\text{-}C{\equiv}C\text{-}CF_3$ was unexpected although the cleavage of C-F in hexafluorobutyne has been seen in other reactions of this molecule with nucleophiles [6].

Analytical results for the green compound (2) show the hbf/Nb ratio is equal to 2. The ^1H and ^{19}F N.M.R. spectra show no signals despite a high solubility in almost all organic solvents. However, (2) exhibits a beautiful E.S.R. spectrum (in T.H.F. solution at room temperature) of ten lines due to coupling of the unpaired electron with ^{93}Nb (g = 2.0010, $\langle a_{Nb} \rangle$ = 64 G). The above results and the high-resolution mass spectrum (parent peak at m/e 546.9654, calculated for $NbC_{18}F_{12}H_{10}$ m/e 546.9655) suggest that (2) is a niobiacyclopentadiene complex or a coordinated butadiene complex rather than a bis(σ-alkylenyl)complex.

In view of this uncertainty, a single-crystal X-ray crystallographic investigation was undertaken [7]. It confirms that (2) is a niobiacyclopentadiene derivative. The NbC_4 ring is located on a crystallographic mirror plane and the π-electron framework is largely localized between C_2-C_3 and C_6-C_7 (C_2-C_3=1.30 Å; C_6-C_7=1.29 Å; C_2-C_6=1.50 Å; Nb-C_3=2.24 Å; Nb-C_7=2.22 Å)(see carbon atom numbering on the figure). These features are similar to those reported by MAGUE [8] for the RhC_4 ring in $RhCl(H_2O)[As(CH_3)_3](hfb)_2$. No structural data was given for the niobia- and vanadia-cyclopentadiene compounds recently prepared from Cp_2MCl_2 (M=Nb,V) and 1,4-dilithio-tetraphenylbutadiene [9].

Compounds (3) and (4) were respectively identified as the new complexes $Cp_2NbF[C(CF_3){=}CH(CF_3)]$ and $Cp_2NbH[C(CF_3){\equiv}C(CF_3)]$.

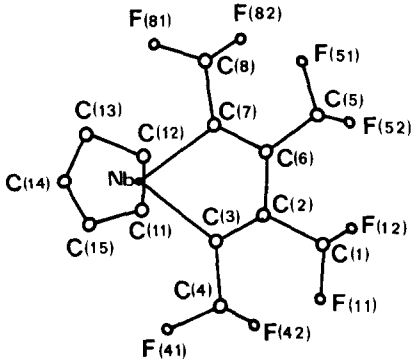

Figure : Projection of the structure of the metallocyclic compound (2) on the crystallographic mirror plane which contains the following atoms : Nb,C_1,C_2...,C_8,F_{11},F_{41},F_{51} and F_{81}.

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