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Cyclopentadienylnickel Trimethylarsine Complexes*

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Numerous cyclopentadienylnickel complexes containing a wide variety of phosphorus donor ligands are well known [1], but apart from some cations containing chelating arsenic ligands [2] only triphenylarsine complexes $C_5H_5Ni(AsR_3)X$ and $[C_5H_5Ni(AsR_3)_2]BF_4$ (R = C_6H_5, X = Br, I, CH_3) [3] have been described in the literature. Some difficulties with the synthesis of $C_5H_5Ni(AsMe_3)X$ (Me = CH_3) were mentioned by Manning [4] without details. This prompted us to investigate the coordination ability of $AsMe_3$ in cyclopentadienylnickel complexes.

Experimental

$[C_5H_5Ni(AsMe_3)_2]BF_4$ (1)

0.63 ml (5.86 mmol) $AsMe_3$ were added to 0.81 g (2.93 mmol) $[C_5H_5Ni(C_5H_6)]BF_4$ dissolved in 7 ml nitromethane. After stirring for 10 min at room temperature 30 ml ether were added. The precipitate was washed with ether and dried *in vacuo* to give 1.10 g (84%) **1**. Green solid, λ (10^{-3} M in CH_2Cl_2 at 25 °C) 43.4 cm^2 ohm^{-1} mol^{-1}. ^1H NMR (acetone-d_6) δCH_3 1.63, δC_5H_5 5.67 ppm.

$C_5H_5Ni(AsMe_3)CN$ (2a)

0.15 g (3.1 mmol) NaCN were added to 0.45 g (1 mmol) **1** in 15 ml acetone. After stirring for one hour the solvent was removed *in vacuo* and the remaining solid was extracted with 10 ml of benzene. Evaporation of the filtrate gave 0.17 g (63%) **2a**. Dark green solid, m.p. 123 °C. IR ν(CN) at 2100 cm^{-1}. ^1H NMR (benzene-d_6) δCH_3 0.88, δC_5H_5 4.97 ppm.

$C_5H_5Ni(AsMe_3)I$ (2b)

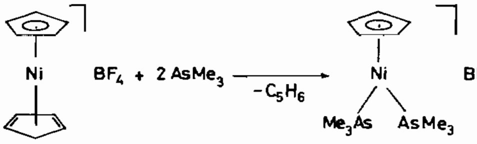
0.45 g (3.4 mmol) LiI (anhydrous) were added to a suspension of 0.5 g (1.1 mmol) **1** in 15 ml ether and 5 ml acetone. After stirring for one hour at room temperature the solvent was evaporated *in vacuo* and the residue was extracted with 15 ml of benzene. The compound was purified by chromatography (Florisil Merck, benzene) to give 0.13 g (32%) **2b**. Purple solid, m.p. 134 °C. λ (10^{-3} M in CH_2Cl_2 at 25 °C) < 6 cm^2 ohm^{-1} mol^{-1}. ^1H NMR (benzene-d_6) δCH_3 0.97, δC_5H_5 4.97 ppm.

$C_5H_5Ni(AsMe_3)Me$ (2c)

1.1 mmol LiMe in ether were added to 0.5 g (1.1 mmol) **1** in 15 ml ether at −78 °C. After stirring for one hour the solvent was removed *in vacuo*. Chromatography (Florisil Merck, benzene) gave 0.1 g (35%) 2c. Brown solid. ^1H NMR (benzene-d_6) $\delta NiCH_3$ −0.50, $\delta AsCH_3$ 0.83, δC_5H_5 5.23 ppm.

Results

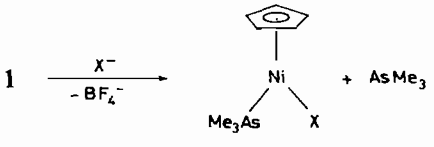
Various methods exist to prepare $C_5H_5Ni(PR_3)X$ complexes starting from nickelocene, the phosphane ligand and CX_4 [5], NiX_2 [6], HX [7] or LiX [8], but none of these reactions gives stable trimethylarsine complexes. In all these cases rapid decomposition occurs even under mild conditions to yield nickel salts containing no cyclopentadienyl group. Thus we tried to prepare the cation $[C_5H_5Ni(AsMe_3)_2]^+$ **1** at first. It has been shown to be necessary to start from the highly reactive diene complex $[C_5H_5Ni(C_5H_6)]^+$ [9], in which the weakly coordinated diene ligand could be substituted by the arsine groups (1).



(1)

1

1 is fairly stable in the solid state under argon but is rapidly decomposed by donor solvents. Anionic groups substitute one arsine ligand in **1** (2), but apparently strong donor properties are needed to stabilize the complex type **2** equalizing thus the poor donor properties of $AsMe_3$. In fact, in cyclo-



(2)

2

X = CN (a), I (b), CH_3 (c)

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*Synthesis and reactivity of dienyl metal compounds, Part XXV, for Part XXIV see ref. 13.

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pentadienylnickel complexes the properties of $AsMe_3$ are more similar to those of the $SbMe_3$ [10] or EMe_2 (E = S, Se, Te) [11] groups than to PMe_3 [12]. Thus, strong donor ligands L like PMe_3 [12] or RNC [13] substitute the iodide ligand in C_5H_5-Ni(L)I to give the cations $[C_5H_5Ni(L)_2]^+$ while no cationic cyclopentadienyl complex could be obtained on treatment of **2b** with $AsMe_3$.

The reason for the low stability of cyclopentadienylnickel arsine complexes is not completely understood but it seems that both donor and acceptor properties of the donor atom are necessary to stabilize the cyclopentadienyl nickel bond. The lack of one causes rapid decomposition, demonstrated by the carbonyl group as an example for weak donor properties as well as by the NR_3 group [14] as an example for the complete absence of acceptor properties, $AsMe_3$ apparently being weak in both.

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