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Stable 1,2,5-Trimethylpyrrole Metal Complexes*

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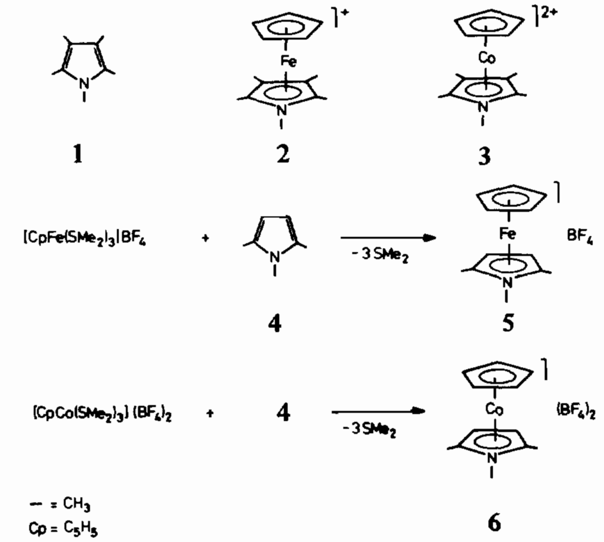
Recently, we have demonstrated the ability of pentamethylpyrrole (**1**) to form the stable complexes 2 and 3 on π-coordination [1]. Similarly, 2,3,4,5-tetramethylpyrrole forms a stable cyclopentadienyliron complex [2] while the analogous *N*-methylpyrrole complex could not be characterised formerly [3] due to its poor stability though a sufficiently stable $Cr(CO)_3$ complex is mentioned [4]. We have therefore been interested in the coordination ability of 1,2,5-trimethylpyrrole (**4**).

Experimental

Reactions were routinely carried out in an argon atmosphere in purified solvents. $[C_5H_5Fe(SMe_2)_3]BF_4$ [5] and $[C_5H_5Co(SMe_2)_3](BF_4)_2$ [6] were prepared according to published procedures. For NMR data see Table I.

[$C_5H_5Fe(C_4H_2Me_2NMe)]BF_4$ (5)

0.79 g (2 mmol) $[C_5H_5Fe(SMe_2)_3]BF_4$ is added to a solution of 0.41 ml (3 mmol) 1,2,5-trimethylpyrrole in 30 ml CH_2Cl_2 at −30 °C. After stirring for 1 h at room temperature the solution is filtered into 30 ml of ether. The resulting precipitate gives 0.41 g of yellow–orange crystals from CH_2Cl_2/ether, 65% yield. *Anal.* Found (calc.): C, 44.4 (44.91); H, 4.8 (5.04); Fe, 17.5 (17.40)%.



[$C_5H_5Co(C_4H_2Me_2NMe)](BF_4)_2$ (6)

0.42 g (0.87 mmol) $[C_5H_5Co(SMe_2)_3](BF_4)_2$ and 0.096 g (0.88 mmol) 1,2,5-trimethylpyrrole are refluxed in 10 ml of $ClCH_2CH_2Cl$ for 5 h. The resulting precipitate gives 0.32 g of yellow crystals from CH_3NO_2/ether, 91% yield. *Anal.* Found (calc.): C, 34.3 (35.43); H, 3.6 (3.90); Co, 14.5 (14.49)%.

Results

The coordination of 1,2,5-trimethylpyrrole (**4**) at the C_5H_5Fe fragment proceeds, as observed for

TABLE I. NMR Data of the Compounds 1–6 (δ ppm)

Compound	^1H NMR	^{13}C NMR
C_4Me_4NMe (1)	^{a}3,4-Me 1.80, 2,5-Me 2.03, NMe 3.25	^{b}CMe 9.81, 9.93, NMe 29.55, C-3,4 112.57, C-2,5 121.93
$[CpFe(C_4Me_4NMe)]BF_4$ (2)^f	^{c}3,4-Me 2.15, 2,5-Me 2.53, NMe 3.41, Cp 4.50	^{d}3,4-Me 9.91, 2,5-Me 10.55, NMe 35.73, Cp 76.01, C-3,4 87.53, C-2,5 95.21
$[CpCo(C_4Me_4NMe)](BF_4)_2$ (3)^f	^{c}3,4-Me 2.40, 2,5-Me 2.82, NMe 3.87, Cp 6.23	^{c}3,4-Me 10.04, 2,5-Me 10.91, NMe 38.21, Cp 93.27, C-3,4 105.06, C-2,5 114.67
$C_4H_2Me_2NMe$ (4)	^{e}2,5-Me 2.13, NMe 3.30, 3,4-H 5.60	^{e}2,5-Me 12.49, NMe 30.83, C-3,4 105.77, C-2,5 128.87
$[CpFe(C_4H_2Me_2NMe)]BF_4$ (5)	^{e}2,5-Me 2.54, NMe 3.43, Cp 4.63, 3,4-H 6.28	^{e}2,5-Me 12.64, NMe 35.70, C-3,4 72.32, Cp 74.69, C-2,5 97.88
$[CpCo(C_4H_2Me_2NMe)](BF_4)_2$ (6)	^{c}2,5-Me 2.88, NMe 3.93, Cp 6.44, 3,4-H 6.62	^{e}2,5-Me 12.60, NMe 38.08, C-3,4 87.25 Cp 93.05, C-2,5 120.01

$^a CCl_4$. $^b C_6D_6$. $^c CD_3NO_2$. ^{d}Acetone-d_6. $^e CD_2Cl_2$. ^{f}From ref. 1.

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*Heterocycles as coordinating ligands, Part II; for Part I see ref. 1.

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pentamethylpyrrole [1], on reaction with $[C_5H_5Fe(SMe_2)_3]BF_4$. The resulting compound $[C_5H_5Fe(C_4H_2Me_2NMe)]BF_4$ (**5**) forms an air stable orange–yellow salt with properties very similar to those of the pentamethylpyrrole complex **2**. Analogously, reaction of the pyrrole **4** with $[C_5H_5Co(SMe_2)_3](BF_4)_2$ gives the dicationic complex $[C_5H_5Co(C_4H_2Me_2NMe)](BF_4)_2$ (**6**) which parallels the properties of the pentamethylpyrrole complex **3**.

Looking at the NMR data (Table I) we see that there is no significant difference in the shift of the C_5H_5 ligand changing the pyrrole ligand both in the Fe and Co series. In ^{13}C NMR, the upfield coordination shift of the ring membered carbon atoms of the pyrrole ligands is about 25 to 35 ppm for the iron and 7 to 13 ppm for the cobalt complexes, and the C-2 and C-3 carbon atoms in the trimethylpyrrole complexes are very similar in this point. We therefore suppose that the bonding properties in these complexes do not change markedly on methylation of the carbon ring atoms, but this point needs further investigation.

We have not been able to isolate the *N*-methylpyrrole complex $[C_5H_5Fe(C_4H_4NMe)]BF_4$ mentioned previously [3] according to the method described above. Therefore, it may be concluded that blocking of the 2,5-position by methyl substituents prevents the η^5-η^1-rearrangement of the pyrrole ligand which initiates decomposition reactions.

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