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## Preliminary communication

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### DIRECT HETEROARYLATION OF FERRICINIUM SALTS

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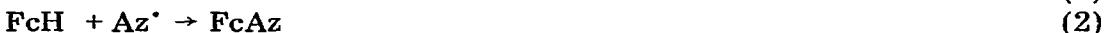
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#### Summary

The reaction of sodium azolides (pyrazolide, dimethylpyrazolide, imidazolide, benzotriazolide) with a ferricinium salt yields azolylferrocenes.

The interaction of azole anions ( $Az^-$ ) with ferricinium salts ( $FcH^+$ ) leads to the reduction of the latter to ferrocene ( $FcH$ ) and to the formation of short-lived radicals, which can be identified using spin traps [1]. The reaction, however, proceeds further: hydrogen in the ferricinium cation or ferrocene is substituted by a heterocyclic radical, the reaction takes place by a free-radical mechanism:



We are unable, at present, to distinguish between pathways 2 and 3, but expect to communicate this result in our future publications. It is apparent, however, that neutral azolylferrocenes and ferrocene are formed by the reaction. While investigating the interaction of ferricinium hexafluorophosphate with sodium salts of pyrazole, 3,5-dimethylpyrazole, imidazole and benzotriazole in tetrahydrofuran, we discovered the formation of azolylferrocenes.

Mass spectra of these compounds (Table 1) demonstrate the highest intensity for the molecular ions ( $M$ ). The fragmentation behaviour of these molecular ions is characteristic for N-substituted azoles the mass-spectra of which are described elsewhere [2—6].

TABLE 1

## MASS SPECTRA OF N-SUBSTITUTED AZOLYLFERROCENES

Pyrazolylferrocene	252 ( <i>M</i> ), 225 ( <i>M</i> — HCN), 199 ( <i>M</i> — HCN — CN)
Imidazolylferrocene	252 ( <i>M</i> ), 225 ( <i>M</i> — HCN), 198 ( <i>M</i> — 2HCN)
3,5-Dimethylpyrazolylferrocene	280 ( <i>M</i> ), 254 ( <i>M</i> — C <sub>2</sub> H <sub>2</sub> ), 239 ( <i>M</i> — CH <sub>3</sub> CN)
Benzotriazolylferrocene	303 ( <i>M</i> ), 275 ( <i>M</i> — N <sub>2</sub> ), 274 ( <i>M</i> — N <sub>2</sub> H)

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