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Preliminary communication

1,2- AND 1,2,5-SUBSTITUTED PYRROLES FROM AN (η^5-pyrrolyl)-TRANSITION METAL COMPLEX

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Summary

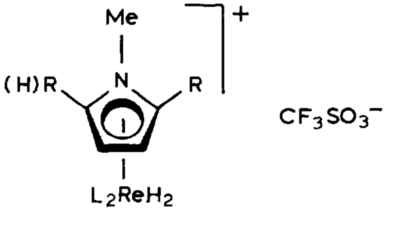
Reaction of (L)$(Ph_3P)_2ReH_2$ (L = η^5-pyrrolyl) with acyl chlorides leads directly to *N*-acylpyrroles in high yields; with methyl triflate cations (L′)$(Ph_3P)_2ReH_2^+$ (L = η^5-*N*-methylpyrrole) are formed, which release *N*-methylpyrroles by heating in DMSO.

We recently described [1] the highly regioselective C-alkylation and arylation of the η^5-pyrrolyl ligand in (η^5-C_4H_4N)$(Ph_3P)_2ReH_2$ (I), giving, after decomplexation 2-, or 2,5-substituted pyrroles (IV or VI).

Here we report that complexes I–III react with acyl chlorides to give directly the corresponding *N*-acylpyrroles in high yield. *N*-methylpyrroles were also obtained by treatment of I–III with methyl triflate and subsequent heating in DMSO.

Reaction of I–III with acetyl or benzoyl chloride (1.2 molar equiv.) takes place immediately in CD_2Cl_2 solution at 20 °C to give quantitatively the corresponding *N*-acylpyrroles which were identified by ^1H NMR spectroscopy. In the case of the reaction of III (R = Ph) and benzoyl chloride, 1-benzoyl-2,5-diphenylpyrrole (VII, R = Ph, R′ = PhCO) was isolated in 91% yield and identified by comparison with an authentic sample [2].

Under the same conditions I–III react with methyl triflate (1.2 molar equiv.) to form quantitatively cationic complexes VIII, which were converted into the corresponding *N*-methylpyrroles (identified by ^1H NMR spectroscopy) by heating in DMSO-d_6 (80 °C, 10–15 min).



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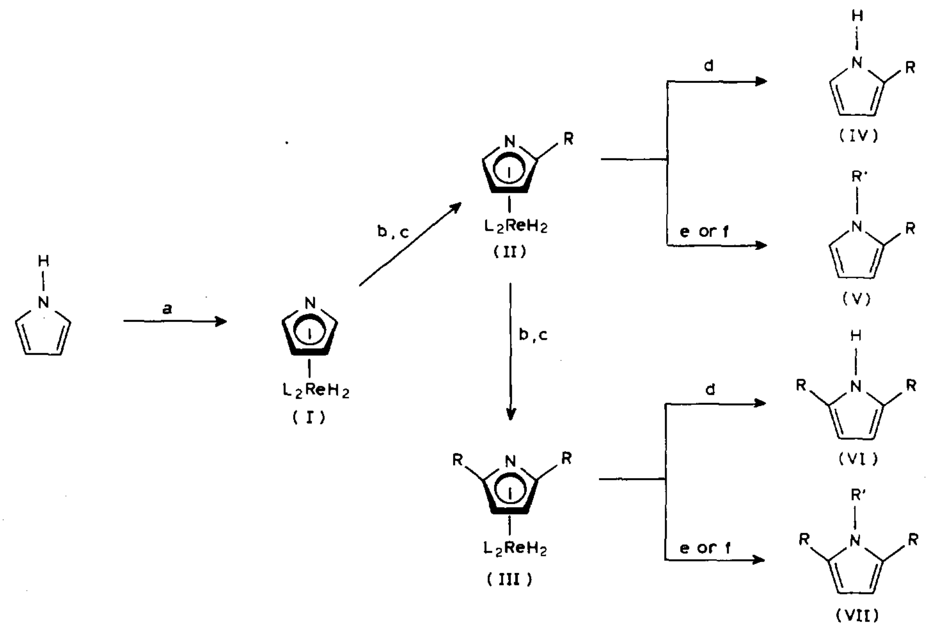

SCHEME 1. L = PPh_3; R = Me, n-Bu, Ph; R′ = Me, MeCO, PhCO; Reagents: (a) L_2ReH_7-3-3,dimethylbutene; (b) I_2-K_2CO_3; (c) RLi; (d) DMSO- $HBF_4 \cdot Et_2O$; (e) R′COCl; (f) MeOTf-DMSO.

In some cases the product was isolated and identified by comparison with an authentic sample. Thus, II (R = Ph) gave 1-methyl-2-phenylpyrrole (V, R = Ph, R′ = Me) [3], and III (R = Ph) gave 1-methyl-2,5-diphenylpyrrole (VII, R = Ph, R′ = Me) [4] in 92 and 86% yields, respectively.

There are a few examples in the literature of electrophilic attack [5,6] on the η^5-pyrrolyl nitrogen, but in only one case has such a reaction led to the formation of a *N*-substituted pyrrole i.e./(η^5-C_4H_4N)$Mn(CO)_3$ when treated with diphenylketene gave 1-(diphenylacetyl)pyrrole, together with a three-nuclear complex containing two η^1,η^5-bonded pyrrolyl ligands [6].

The reported work, although preliminary at this stage, provides further evidence that the η^5-pyrrolyl ligand in transition-metal complexes can undergo a variety of highly selective transformations, affording considerable synthetic potential.

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