Reductions of Schiff Base–Metal Complexes and Preparation of Organometallic Derivatives of Iron(III)

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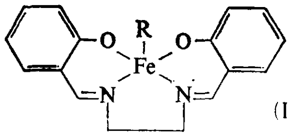
PREVIOUSLY[1,2] we have reported on the reduction of *NN'*-ethylenebis(salicylideneiminato)cobalt(II) (CoSaEn) and on the preparation of organometallic compounds derived from it. The chemical reduction of CoSaEn has been confirmed later.[3] We now report that the sodium reduction of Schiff's base–metal complexes is a general phenomenon. Sodium reductions were successfully carried out with the nickel and with iron complexes of *NN'*-ethylenebis(salicylideneimine). These metal chelates were treated with the stoicheiometric (1 : 1) amounts of sodium in tetrahydrofuran. The reduced species give green to blue solutions, which are extremely sensitive to air. By using an excess of sodium, a second electron may be introduced into the metal ligand system: this was shown to be the case for CoSaEn.[2] In the case of the analogous compound of copper, CuSaEn, only reduction to the bright red dianion was observed.

Treatment of reduced FeSaEn with benzyl chloride or treatment of the iodo-derivative [FeSaEn]I with phenyl magnesium bromide,† followed by hydrolysis, led to the formation of organometallic derivatives of FeSaEn of formula [FeSaEn]R (R = $PhCH_2$, Ph). The yields of crude products are substantially quantitative.

$$\mathrm{Na[FeSaEn]} + \mathrm{PhCH_2Cl} \rightarrow \mathrm{NaCl} + \mathrm{[FeSaEn]CH_2Ph} \tag{1}$$

$$\mathrm{[FeSaEn]I} + \mathrm{PhMgBr} \rightarrow \mathrm{MgBrI} + \mathrm{[FeSaEn]Ph} \tag{2}$$

Compounds (I) were characterised by complete (oxygen excluded) elemental analysis, thermal



(I)

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† FeSaEn was prepared under nitrogen from anhydrous iron(II) acetate and the Schiff base in dimethylformamide and [FeSaEn]I by iodine oxidation of the former.

degradation, and infrared spectra. These are brown solids rapidly decomposed by air either in solution or in the solid state, slightly soluble in tetrahydrofuran and acetone, practically insoluble in hydrocarbons. The attachment of the alkyl group to the metal was demonstrated by thermal decomposition (60—80°) *in vacuo* which resulted in the formation of the hydrocarbon originated from the coupling of the R groups. The compounds are paramagnetic. Magnetic measurements are now in progress and will be reported in a forthcoming publication.

Organometallic derivatives of iron in a formal oxidation state 3+ are very rare. The only organometallic compounds of iron(III) reported so far contain the four-nitrogen chelate system of Aetioporphyrin I.[4] Moreover, the isolation of the compounds reported enlarges considerably the domain of donor atoms which were traditionally regarded until now as having stabilising properties on iron-to-carbon σ-bonds.

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[3] G. Costa and G. Maestroni, *Tetrahedron Letters*, 1967, 1783.
[4] D. A. Clarke, R. Grigg, and A. W. Johnson, *Chem. Comm.*, 1966, 208.