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Preliminary communication

Organo-iron and -cobalt phthalocyanines in alkylation and arylation of olefins

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It has been shown recently that organic derivatives of cobalt(III) complexes with dimethylglyoxime, corrin and bis(salicylidene)ethylenediamine will bring about the alkylation and arylation of olefins in the presence of palladium(II) salts[1,2]. To appreciate the influence of the oxidation state of the metal on the reactivity of its chelate in such a reaction we studied methylation and phenylation of styrene with the corresponding derivatives of di- and tervalent cobalt and iron phthalocyanines[3,4] in the presence of lithium chloropalladate.

All the compounds tested were shown to transfer an organic ligand to the olefin:

$$\mathrm{RMPc}^{n-} + \mathrm{PhCH{=}CH_2} \xrightarrow{\mathrm{Pd}^{2+}} \mathrm{PhCH{=}CHR},$$

$R = \mathrm{Me, Ph}$; $M = \mathrm{Fe, Co}$; $n = 0, 1, 2$; Pc = phthalocyanine.

Yields of the substituted styrenes varied from very low to good (Table 1). Thus a high yield of propenylbenzene was obtained with methyliron(II) phthalocyanine while methyl transfer from the corresponding complex of iron(III) proceeded much less readily. Similarly in the cobaloxime series[2] the corresponding phenyl derivatives transfer organic groups very slowly. For example, when phenyl derivatives of $\mathrm{Co^{III}}$, $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ were treated with styrene and $\mathrm{Li_2PdCl_4}$, only small amounts of *trans*-stilbene were obtained, the yield being worst in the case of the tervalent iron complex: in contrast, diphenylcobalt(II) phthalocyanine appeared to be the most powerful phenylating agent of the complexes examined by us up to now. Probably both the valence state of the metal and the *trans* effect of the second phenyl ligand are responsible for the high reactivity of this compound. DMF was the solvent used in this case because the solubility of diphenylcobalt(II) phthalocyanine in this solvent is better than in THF. (Our previous experience with organocobaloximes[2] has shown that yields of substituted olefins in DMF and THF do not differ significantly.) The amount of *trans*-stilbene formed corresponded to the transfer of one phenyl group from the complex. The reaction was fast and was complete within 30 min.

TABLE 1[a]

Organometallic complex[b] [R–M]	*Solvent*	*Olefin produced*	*Yield (%)*
$Li(CH_3Fe^{II}Pc)\cdot 6$ THF	Tetrahydrofuran	Propenylbenzene	70
$(CH_3Fe^{III}Pc)\cdot$THF	Tetrahydrofuran	Propenylbenzene	13.4
$Li(CH_3Fe^{II}Pc)\cdot 6$ THF	Acetonitrile	Propenylbenzene	7
$(CH_3Fe^{III}Pc)\cdot$THF	Acetonitrile	Propenylbenzene	1.3
$Li(C_6H_5Fe^{II}Pc)\cdot 4$ THF	Tetrahydrofuran	*trans*-Stilbene	2.4
$(C_6H_5Fe^{III}Pc)\cdot 2$ THF	Tetrahydrofuran	*trans*-Stilbene	0.1
$Li_2[(C_6H_5)_2Co^{II}Pc]\cdot 8$ THF	Dimethylformamide	*trans*-Stilbene	45
$(C_6H_5Co^{III}Pc)\cdot 1.5$ THF	Tetrahydrofuran	*trans*-Stilbene	0.24
$(CH_3CO^{III}Pc)\cdot 2$ THF	Tetrahydrofuran	Propenylbenzene	3
$(CH_3Co^{III}Pc)\cdot 2$ THF	Methanol	Propenylbenzene	11
$CH_3Co^{III}(Dmg)\cdot 2$ Py	Methanol	Propenylbenzene	76[c]

[a] Reactions were carried out at room temperature under nitrogen with a molar ratio of reagents: [R–M] /Li_2PdCl_4 / styrene = 1 / 3 / 4. Reaction time was 24 h.

[b] $(CH_3Fe^{III}Pc)\cdot$THF was obtained by oxidation of $Li(CH_3Fe^{II}Pc)\cdot 6$ THF with Ph_3CCl while iodine was used as oxidating agent to prepare $(C_6H_5Fe^{II}Pc)\cdot 2$ THF and $(C_6H_5Co^{III}Pc)\cdot 1.5$ THF from $Li(C_6H_5Fe^{II}Pc)\cdot 4$ THF and $Li_2[(C_6H_5)_2Co^{II}Pc]\cdot 8$ THF respectively.

[c] See ref. 2.

Thus it appears that for the σ-organometallic complexes considered, the ability to transfer the organic moiety to an olefin is dependent upon the electron density on the metal. This suggestion may be proved by comparing the reactivities of the isoelectronic complexes $[RFe^{III}Pc]^-$ and $[RCo^{III}Pc]$. Further, it is noteworthy that the yield of propenylbenzene from methylcobalt(III) complexes is considerably lower here than in the cobaloxime series. This seems also to be due to electronic charge effects since the electron density on the metal decreases on changing bis(dioximates) for phthalocyanine complexes which have closed conjugated systems in the chelated macrocycles.

As has been shown by Schrauzer[5] and Costa *et al.*[6], the reactivity of alkylcobalt chelates in the exchange of organic ligands with metal ions is profoundly influenced by the effective charge on the cobalt atom. A comparison of these results with our data enables us to suggest that the reaction under consideration involves an electrophilic attack of Pd^{II} on the carbon atom bonded to the transition metal. This stage well may consist of either a complete or a partial transfer of an organic group from cobalt to palladium (*cf.* refs. 6 and 7).

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