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Preliminary communication

Syntheses of organonickel compounds by decarboxylation reactions

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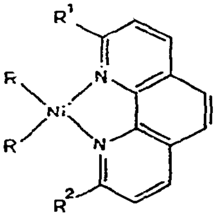
Decarboxylation reactions have been extensively used in the preparation of organometallics of main group elements[1,2], and recently the method has been extended to some transition metal organometallics[3-6], *e.g.*, $C_6F_5Cu(quinoline)$[3], in which the metals have closed *d* shell configurations. We have now prepared the organonickel compounds, R_2NiL ($R = C_6F_5$, *p*-$MeOC_6F_4$, or *p*-$EtOC_6F_4$; L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)), from the corresponding carboxylate complexes by decarboxylation reactions, thereby establishing that the method can be used for metals with unfilled *d* shells.

$$(RCO_2)_2NiL \longrightarrow R_2NiL + 2CO_2$$

A further novel feature is the formation of the α-substituted phenanthroline complexes I-III during the preparation of $R_2Ni(phen)$ (R = *p*-$MeOC_6F_4$ or *p*-$EtOC_6F_4$).



(I : $R = R^1 = p\text{-}MeOC_6F_4$, $R^2 = H$;
II : $R = R^1 = R^2 = p\text{-}MeOC_6F_4$;
III : $R = R^1 = p\text{-}EtOC_6F_4$, $R^2 = H$)

The carboxylates, $(RCO_2)_2Ni(bipy)\cdot 2H_2O$ and $(RCO_2)_2Ni(phen)\cdot H_2O$ ($R = C_6F_5$, *p*-$MeOC_6F_4$, or *p*-$EtOC_6F_4$)*, were decomposed in boiling toluene for 1.5-2 h except for $(C_6F_5CO_2)_2Ni(phen)\cdot H_2O$, which was heated for 4 h in boiling benzene in the presence of benzoyl peroxide. (Without the peroxide negligible yields of organometallic product were obtained.) After column chromatography (neutral Florisil; acetone) of the crude products, the compounds, $R_2Ni(bipy)$ (R = *p*-$MeOC_6F_4$ or *p*-$EtOC_6F_4$), were isolated pure (yields, 60-75%)**, but $(C_6F_5)_2Ni(bipy)$ (previously prepared via pentafluorophenyllithium[7]) and $R_2Ni(phen)$ ($R = C_6F_5$, *p*-$MeOC_6F_4$, or *p*-$EtOC_6F_4$) required further purification (preparative TLC; silica gel; benzene or benzene/acetone) and were obtained

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*Obtained analytically pure (C,H,N), ν asym.(CO_2) 1640-1600 and ν sym.$(CO)_2$ 1380-1360 cm^{-1}, from reactions of the stoichiometric amounts of nickel carbonate, the appropriate carboxylic acids, and 2,2′-bipyridine or 1,10-phenanthroline in aqueous ethanol.

**Satisfactory analyses (C, H, F, N) were obtained.

in lower yields (8–22%)★. The identities of these compounds were confirmed by NMR spectroscopy in acetone-d_6. The proton spectra showed absorptions due to aromatic protons at 7.3–9.0 ppm downfield from internal tetramethylsilane ($\delta = 0$) with additional features at ca. 3.9 ppm (OMe) for the *p*-methoxytetrafluorophenyl derivatives and at ca. 4.2 (OCH_2) and 1.3 (Me) ppm for the *p*-ethoxy derivatives, while the fluorine spectra showed resonances centred at ca. 166 (*m*-F), 163(*p*-F), and 116(*o*-F) ppm upfield from external trichlorofluoromethane for the pentafluorophenyl derivatives, and at ca. 160(*m*-F) and 118(*o*-F) ppm for the tetrafluorophenyl derivatives. The assignments are based on those for related organometallics[8].

The polyfluoroaryl-substituted phenanthroline complexes, I–III, were separated from the corresponding $R_2Ni(phen)$ complexes by preparative TLC as described above (yields, I (11%), II (1%), III (7%)), and the compostions were indicated by analytical data (*e.g.* I: Found: C, 51.1; H, 2.3; F, 29.4; N, 3.6; mol. wt. (by osmometry in acetone), 791 (1.36% w/v). $C_{33}H_{16}F_{12}N_2NiO_3$ calcd.: C, 51.1; H, 2.1; F, 29.4; N, 3.6%; mol. wt., 775.) The identities of I–III and in particular the positions of the polyfluoroaryl substituents were established by comparison of their NMR spectra with those of the corresponding $R_2Ni(phen)$ (R = *p*-$MeOC_6F_4$ or *p*-$EtOC_6F_4$) complexes and *p*-alkoxytetrafluorobenzoic acids. For example, the relevant data for I and II are given in Table 1.

TABLE 1

SPECTRA OF SOME *p*-METHOXYTETRAFLUOROPHENYLNICKEL COMPOUNDS IN ACETONE-d_6 [a]

Compound	Proton				Fluorine			
	phen[b]		$MeOC_6F_4X$[c]		*ortho*-F[d]		*meta*-F[d]	
	α-H[e]	other H[f]	X = Ni	X = C	Ni–C_6F_4	C–C_6F_4	Ni–C_6F_4	C–C_6F_4
(*p*-$MeOC_6F_4)_2Ni(phen)$	8.78(2)	7.6–8.4(6)	3.93(6)		118(4)		160(4)	
I	8.88(1)	7.7–8.5(6)	3.95(6)	4.25(3)	118(4)	143(2)	160(4)	158(2)
II		7.8–8.6(6)	3.97(6)	4.25(6)		[g]		
p-$MeOC_6F_4CO_2H$				4.20		142(2)		159(2)

[a] Proton chemical shifts in ppm downfield from internal tetramethylsilane; fluorine chemical shifts in ppm upfield from external trichlorofluoromethane. Numbers of atoms obtained from integration are in parentheses. [b] Assignments based on those for 1,10-phenanthroline[12]. [c] Triplets, $J \leqslant 3$Hz. [d] Multiplets. [e] Doublet of doublets. [f] Complex multiplets. [g] Insufficiently soluble for a satisfactory fluorine spectrum. The solutions of the other organonickel compounds were near saturated.

Formulations I–III were further supported by the observation that each compound gives two intense absorptions attributable[9] to carbon–fluorine stretching at 1000–940 cm^{-1} (one due to C_6F_4Ni at 965–940 cm^{-1}; one due to C_6F_4C at 1000–985 cm^{-1}), whereas $R_2Ni(phen)$ complexes give one at 955–945 cm^{-1} and $(RCO_2)_2Ni(phen)\cdot H_2O$ complexes one at 995–985 cm^{-1}. Since free radical substitution of pyridine occurs preferentially in the α-position[10], the formation of I–III is consistent with attack by polyfluoroaryl free radicals on 1,10-phenanthroline.

★Satisfactory analyses (C, H, F, N) were obtained.

The absence of significant broadening or shifts of the NMR absorptions of the organonickel compounds is indicative of diamagnetism (solid $(C_6F_5)_2Ni(bipy)$ is known to be diamagnetic[7]), and the visible spectra of the compounds in methanol show one broad asymmetric, or two absorption bands at 380–465 nm, consistent[11] with approximately planar four coordination for nickel.

Pentafluorobenzoic, *p*-methoxytetrafluorobenzoic, and *p*-ethoxytetrafluorobenzoic acids do not decarboxylate in boiling toluene under the conditions used for the decomposition of the nickel carboxylates, clearly indicating that decarboxylation is facilitated by the formation of nickel complexes.

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