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Reactivity of Nitrile–Metal Complexes with β-Dicarbonyls.
Part 1. Addition of Acetylacetone to *trans*-[Ni(PPh$_2$-Me)$_2$(C$_6$Cl$_5$) (N≡C–CH$_3$)]$^+$BF$_4^-$

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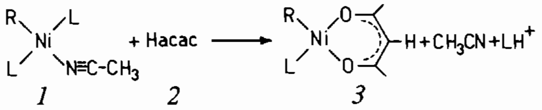
The 'end on' coordination of nitriles to metal centres is known to strongly enhance the electrophilic character of this important class of organic compounds [1a]. Thus, addition of alcohols, water, ammonia and amines to metal-coordinated nitriles easily affords the corresponding C-functionalized imino-complexes, this feature being crucial in the metal catalyzed electrophilic reactivity of nitriles [2].

In the frame of our interest in the activation of nitriles towards nucleophiles such as β-dicarbonyls, we took into account the potential reactivity of the stable acetonitrile complex *trans*-[Ni(PPh$_2$-Me)$_2$(C$_6$Cl$_5$)(CH$_3$CN)]$^+$BF$_4^-$ (*1*) with acetylacetone (*2*). Rather surprisingly [1], complex *1* was found to react with *2* according to eqn. (1) to give compound *3*. The expected reaction was, in fact, the nucleophilic addition of *2* to the coordinated electrophile to react with *2* according to eqn. (1) to give compound change in the [NiL$_2$(C$_6$Cl$_5$)] remainder of the molecule.



L=PPh$_2$Me; R=C$_6$Cl$_5$ (1)

Actually, a very complex reaction took place involving i) displacement of CH$_3$CN, ii) coordination of *2* to Ni^{II}, iii) protonation of the phosphine and release of the phosphonium ion, iv) formation of the Ni^{II}–acac ring.

The reaction proceeds under mild conditions and is quantitative. A 5 × 10^{-2} *M* solution of *1* in 1,2-dichloroethane reacts with *2* (0.8 *M*), in several hours at room temperature, to give complex *3*. This was isolated as yellow-orange crystals and characterized by elemental analysis, i.r. and ^{1}H NMR [4]. The ^{1}H NMR spectrum of *3* shows the methyl protons of the acac$^-$ ligand as two well separated resonances (τ 8.37 and 8.15) in agreement with the different nature of the two ligands in *trans* to the coordinated acac$^-$ moiety.

If the reaction is carried out in the presence of Et$_3$N (to enhance the nucleophilicity of *2* upon deprotonation) again no addition of *2* to metal-coordinated CH$_3$CN takes place and Et$_3$N undergoes metal coordination to give a complex of approximate composition [Ni(PPh$_2$Me)(C$_6$Cl$_5$)(Et$_3$N)(acac)] [5], *4*. Remarkably, the addition of the base dramatically increases the reaction rate, as shown by the i.r. spectrum of a 1,2-dichloroethane solution of *1* (3 × 10^{-2} *M*) containing Hacac (0.8 *M*) and Et$_3$N (0.2 *M*), in which solution the immediate disappearance of the coordinated nitrile stretching absorption band (2290 cm^{-1}) can be observed.

Metal complexes containing both phosphine and oxygen-bonded β-carbonylenolato ligands are uncommon [6, 7] and complexes of composition NiR′-(PR$_3$)(β-carbonylenolato) have recently been prepared by reaction of β-carbonylenolate sodium salts with [NiX(C$_6$H$_5$)(PR$_3$)$_2$] [8] and by treatment of Ni(acac)$_2$ with AlR$_2$OEt and PEtPh$_2$ [9].

Reaction 1 is likely to be an easy way of access to a variety of phosphino-β-carbonylenolato complexes from easily accessible metal species containing at least one basic ligand (*vide infra*) and conveniently labile leaving groups such as *e.g.* nitriles. As to the original aim of this research, the data here reported strongly suggest the necessity of employing 'metallic' electrophiles as reagents with free β-dicarbonyls not containing phosphines or other ligands susceptible of easier metal-mediated protonation.

References

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3 Complex *1* was prepared following the procedure described for the preparation of [Ni(PPh$_2$Me)$_2$(C$_6$Cl$_5$)(CH$_3$-CN)]$^+$ClO$_4^-$ (M. Wada and T. Shimohigashi, *Inorg. Chem., 15,* 954 (1976).

4 Calcd. for NiC$_{24}$H$_{20}$Cl$_5$O$_2$P: C, 47.46; H, 3.31. Found: C, 47.22; H, 3.39. ^{1}H NMR (in CDCl$_3$, τ scale): 8.38 doublet, J(PH) 10.6 Hz, 3H), 8.37 (singlet, 3H), 8.15

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(singlet, 3H), 4.60 (singlet, H), 2.30–2.85 (complex multiplet, 10 H). I.r. (nujol mull): ν_{CO} at 1515 and 1565 cm^{-1} (vs).

5 Calcd. for $NiC_{30}H_{35}Cl_5O_2PN$: C, 50.8; H, 4.94; N, 1.97. Found: C, 47.14; H, 4.93; N, 1.58. I.r. (nujol mull): ν_{CO} at 1515 and 1565 cm^{-1} (vs). The ^{1}H NMR spectrum ($CDCl_3$) shows the resonances attributable to complex *3* and to Et_3N (in *ca.* 1:1 molar ratio) and to other not attributed weak absorptions. Attempts to purify compound *4* by recrystallization from CH_2Cl_2/CH_3OH led to complete loss of Et_3N with generation of *3*.

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