Alkoxycarbonyl, Acyl, and Alkyl Complexes of Nickel(II) and Palladium(II)

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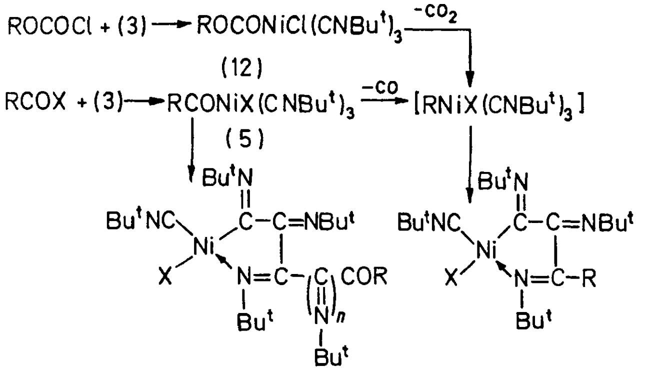
Summary Oxidative addition of haloformates and acyl halides to Pd $\mathrm{(CNBu^t)_2}$, Pd $\mathrm{(PPh_3)_4}$, Ni $\mathrm{(CNBu^t)_4}$, and Ni $\mathrm{(PPh_3)_4}$ gave ROCO-, RCO-, and R-Pd$^{\mathrm{II}}$ or Ni$^{\mathrm{II}}$ complexes and some Pd$^{\mathrm{I}}$ and Ni$^{\mathrm{I}}$ complexes.

We describe here the preparation of some alkoxycarbonyl and acyl complexes of nickel and palladium from oxidative addition of organic halides, and their elimination reactions.[1-3] Many acyl halides and haloformates add smoothly in benzene or toluene to $\mathrm{Pd(CNBu^t)_2}$ (**1**) and $\mathrm{Pd(PPh_3)_4}$ (**2**) affording the corresponding *trans*-acyl and -alkoxycarbonyl compounds.[4] In contrast, the oxidative addition of $\mathrm{ClCO_2Ph}$ to (**1**) at room temperature in benzene leads to the chloride bridged palladium(I) dimer, $\mathrm{Pd_2Cl_2(CNBu^t)_4}$[5] and diphenyl carbonate with evolution of CO. The ready decarbonylation suggests instability of the PhO–C(=O) bond in a hypothetical adduct $\mathrm{PdCl(CO_2Ph)(CNBu^t)_2}$ compared to the RO–C(=O) bond in $\mathrm{PdCl(CO_2Me)(CNBu^t)_2}$.

Some oxidative addition to $\mathrm{NiL_4}$ (**3**; $\mathrm{L{=}CNBu^t}$, **4**; $\mathrm{L{=}PPh_3}$) are shown in the Scheme.[3,4] The formation of (**8a**) presumably involves the intermediacy of an alkyl compound (**6**) since an analogous compound (**8b**) has been obtained by the oxidative addition of MeI to (**3**).[3] Apparently the acyl–nickel bond in (**5**) is more susceptible to cleavage than is the aroyl–nickel bond.

The formation of (**10c**) from $\mathrm{NiI(R^1)(PR^2{}_3)_2}$ ($\mathrm{R^2}$ = cyclohexyl, isopropyl) and $\mathrm{PPh_3}$ has recently been reported.[5] These results indicate instability of the R–Ni bond in (**9**) compared to that of $\mathrm{NiX(R)[P(alkyl)_3]_2}$. The initial adduct $\mathrm{NiCl(COR)(PPh_3)_2}$ is not isolable. However, an



(7a) X=Cl, R=Ph, *n*=2 (8a) X=Cl, R=Me
(7b) X=Cl, R=Me, *n*=1 (8b) X=I, R=Me
(8c) X=Cl, R=PhCH$_2$

Scheme 1

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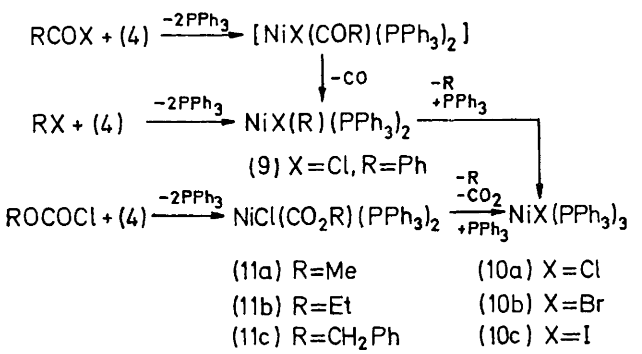
† Satisfactory elemental analyses were obtained.

analogous acyl complex NiCl(COPh)[(—)-tribornylphosphite]$_2$ has been isolated.[6] We propose Scheme 2 for the formation of (**9**) and (**10**). In the reaction of acetyl iodide with (**4**) we failed to isolate NiI(COR)(PPh$_3$)$_2$ or NiI(R)(PPh$_3$)$_2$, the only isolable compound being NiI$_2$(PPh$_3$)$_2$.



Scheme 2

A possible preparative route to Ni^I complexes is suggested in Scheme 2.[7]

Again the formation of (**10a**) may involve an unstable alkyl nickel intermediate. The formation of (**8a**) or (**8c**) [from the reaction of (**4**) with chloroformate] is accounted for by oxidative addition of the chloroformate followed by a fast decarboxylation of the alkoxycarbonyl intermediate (**12**) (Scheme 1). The reaction with ClCO$_2$Et fails to give an appreciable amount of a complex of type (**8**), instead it produces a brown paramagnetic polymeric complex of formula "NiCl(CNBu^t)$_2$," ν_{max} 2200, 2180 (N≡C), 1740 (C=N), and 1600 cm^{-1}. The reaction of (**3**) with ClCO$_2$Ph produces CO, (PhO)$_2$CO, and a very small amount of Ni(CO)(CNBu^t)$_3$, the majority of the nickel-containing products not being identifiable.

Decarbonylation is a general reaction with ClCO$_2$Ph but decarboxylation predominates in the reaction with alkyl haloformates. Thus the elimination is not only governed by the metal (including the auxiliary ligands) but also by the organic group of the alkoxycarbonyl group attached to the metal.

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