Tetrahedron Letters No. 5, pp 463 - 466, 1974. Pergamon Press. Printed in Great Britain.

PATHWAYS OF THERMAL ARYL TRANSFER FROM COORDINATED TRIARYLPHOSPHINES TO NICKEL

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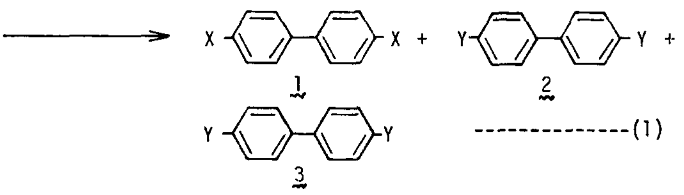
(Received in Japan 12 November 1973; received in UK for publication 28 December 1973)

Thermal decomposition (in toluene, 80°) of <u>trans</u>-$PhNiBr(PPh_3)_2$ in the presence of excess PPh_3, gave diphenyl in quantitative yield together with a univalent nickel complex $NiBr(PPh_3)_3$.[1] Unexpectedly, m- or p-substituted σ-aryl nickel complexes, m- or p-$XC_6H_4NiCl(PPh_3)_2$, gave three different diaryls, Ph_2, m- or p-XC_6H_4-Ph, and (m- or p-$XC_6H_4)_2$(X=CH_3, Cl) in varying ratios (reaction (1), (2) and Table 1).[2] The corresponding tri-p-tolylphosphine complex, σ-$PhNiCl[(p\text{-}CH_3C_6H_4)_3P]_2$, also gave the three diaryls (Y=CH_3) confirming the aryl transfer from the phosphine to nickel followed by the coupling.

p-$XC_6H_4NiCl[(p\text{-}YC_6H_4)_3P]_2$
X=CH_3 or Cl, Y=H;
X=H, Y=CH_3



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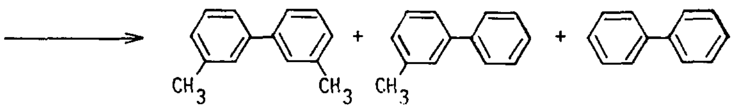
m-$CH_3C_6H_4NiCl(PPh_3)_2$



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Similar aryl transfer has been known for some reactions of palladium complexes[3] and of carbonyl(phosphine)osmium complexes.[4] Migration of a phenyl group to platinum is also observed in some reactions of $(Ph_3M)PtCl(PEt_3)_2$(M=Ge, Sn).[5] More closely related reactions are diphenyl formation in the catalytic oxygenation of PPh_3 with an unstable oxygen complex, $Ni(O_2)(PPh_3)_2$[6] and in the reaction of CH_3MgBr with $NiCl_2(PPh_3)_2$.[7] The mechanistic details, however, are unknown.

For incorporation of an aryl group of phosphine ligands into the diaryl products, our results rules out a mechanism involving the widely observed ortho-metalation path.[8] Transient formation of hydridobenzyne nickel complex by β-elimination is also rejected as evident from the product distribution. The observed diaryl formation is not due to coupling of aryl free radicals derivable from thermal reaction of (σ-Aryl)NiCl(PAr'$_3$)$_2$ since no abstraction of hydrogen from the solvent is observed for σ-α-naphthylnickel complex, (σ-Naph)NiBr(PPh$_3$)$_2$,[1] and no radical polymerization occurs during the thermal reaction[1] in the presence of acrylonitrile or methyl acrylate.

Table 1. Diaryl product distribution ratios from p-XC$_6$H$_4$NiCl[(p-YC$_6$H$_4$)$_3$P]$_2$[a]

diaryl products	X=CH$_3$ Y=H	X=Cl Y=H	X=H Y=CH$_3$
1	6	20	0.72
2	4	10	1.3
3	1	1	1

a) In toluene at 90° for 1 hr (quant. decompn.)

Apparently the diaryl formation involves a sequence of reactions of arylnickel species, and the lability of nickel complexes in d$^{8-10}$ configuration suggests formation of various solution species. Although it is impossible to describe all the elemental reactions involved in this complex thermal reaction, several key steps (3-6) may reasonably be deduced from the available data. The thermal reaction of an equimolar mixture of PhNiCl(PPh$_3$)$_2$ and p-CH$_3$C$_6$H$_4$NiCl(PPh$_3$)$_2$ at 80° produced a mixture of (C$_6$H$_5$)$_2$, p-CH$_3$C$_6$H$_4$·C$_6$H$_5$, and (p-CH$_3$C$_6$H$_4$)$_2$ in a mole ratio of 1.0 : 1.1 : 0.4. In view of the well-known thermal instability of Ph$_2$Ni(PPh$_3$)$_2$ at 20°, the diaryl is presumably derived from unstable bis(aryl)nickel species.[9] The formation of a mixed diaryl (Ar-Ar') provides evidence for a ligand exchange reaction (eq. 3). Such an exchange reaction could occur through a bimetallic intermediate. This view receives support from the fact that the addition of an excess of PPh$_3$ strongly retards the rate of the diaryl formation

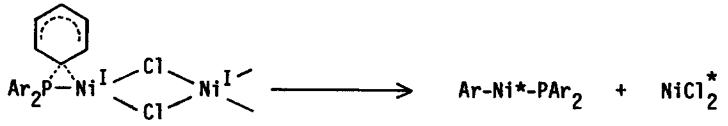
$$\mathrm{ArNi^{II}XL_2} + \mathrm{Ar'Ni^{II}XL_2} \rightleftharpoons \mathrm{ArAr'Ni^{II}L_2} + \mathrm{Ni^{II}X_2L_2} \qquad \text{----------(3)}$$

X=Cl, Br; L=PAr$'_3$; Ar=Ar' or Ar≠Ar'

$$\mathrm{ArAr'Ni^{II}L_n} \longrightarrow \mathrm{Ar\text{-}Ar'} + \mathrm{Ni^{0}L_n} \qquad \text{----------(4)}$$

$$\mathrm{Ni^{0}L_n} + \mathrm{Ni^{II}X_2L_n} \rightleftharpoons \mathrm{2Ni^{I}XL_n} \qquad \text{----------(5)}$$

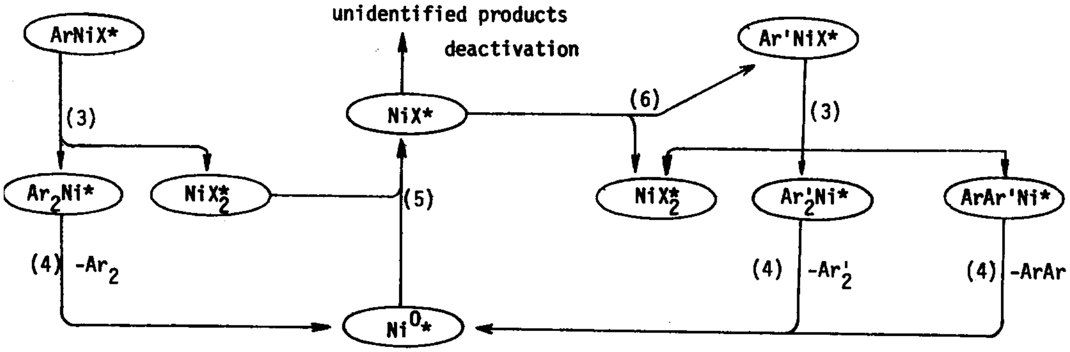
from ArNiCl$(PPh_3)_2$. The irreversible diaryl formation (4) shifts equil (3) and (5) in favor of Ni(I) species. Consistently, the abundance of di-p-tolyl in the initial decomposition stage (e.g., **1**:**2**:**3**=8:5:1 mol ratio) of $(p\text{-}CH_3C_6H_4)NiCl(PPh_3)_2$ implies incipient elimination of the p-tolyl groups σ-bonded to the metal. The elimination is then followed by several steps including equil. (5) and the aryl transfer. The effect of an electron-donating group introduced at the para-position of the triarylphosphine on the product distribution (Table 1) suggests an electrophilic attack of the metal at the aryl carbon attached to the phosphorous atom. This attack is an intramolecular process since the use of a coordinating solvent, e.g. THF, or an addition of an excess of PPh_3 does not change the product distribution. No biaryl being detected in the thermal reaction of $Ni^{II}X_2(PAr_3)_2$ or $Ni^0(PAr_3)_{3-4}$ under comparable conditions, it is likely that a species containing Ni(I) ion plays an important role in the aryl transfer. Considering the propensity of d^9 species to form a binuclear species,[10] we postulate that the aryl transfer is induced in a binuclear chloro-bridged-nickel(I) species(eq. 6). The aryl nickel species thus formed reacts with another aryl nickel species to give diaryls as the final product as schematically shown below (Scheme). The nearly statistical product distribution of substituted diaryls



----------(6)

*Other ligands are not shown.

Scheme



X=Cl, PAr$'_2$;* PAr$'_3$ ligands are abbreviated for clarity.

is thus explicable. The formation of diphenyl in the thermal decomposition of preformed $NiCl(PPh_3)_3$ (in toluene, 80°) also provides a piece of support for the Scheme. The observed variation in incorporation of the aryl group of the phosphines into the diaryl (Table 1) indicates that the aryl transfer reaction of the nickel(I) species is not quantitative even after complete thermal reaction. Unidentified deactivation paths of the intermediate halonickel(I) species exist requiring further investigations.

The authors acknowledge experimental assistance of Mr. M. Terada.

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