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# σ-CARBON-BONDED COMPLEXES OF PYRIDINES WITH NICKEL(II)

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Oxidative substitution of tetrakis(triphenylphosphine)nickel(0) with a chloro- or bromo-pyridine takes place in toluene at room temperature to afford a dimeric complex, $[NiX(\sigma\text{-pyridyl})(PPh_3)]_2$. The σ-pyridyl nickel(II) complex is very stable and has a strong preference for the dimeric structure, the bridging ligand being readily replaced by other halide and pseudo halide ions. $[NiCl(2\sigma\text{-}C_5H_4N)(PPh_3)]_2$ acts as a very powerful catalyst for completely selective cross coupling between 2-chloropyridine and methylmagnesium bromide.

Alkyl and aryl nickel(II) complexes of the type $NiX(R)(PR'_3)_2$ have been extensively investigated,[1)] since they are involved as an intermediate in cross coupling of Grignard reagents with organic halides catalyzed by nickel(II) phosphine complexes.[2)] Recently the synthetic method was extended to Grignard coupling with halopyridines,[3)] but the σ-pyridyl nickel(II) intermediate has not yet been isolated. The present communication describes preparation of very stable σ-pyridyl nickel(II) complexes, and demonstrates the effective catalysis by one of them in completely selective coupling between 2-chloropyridine and methylmagnesium bromide.

Preparation and Properties of σ-Pyridyl Complexes. All the operations were carried out in an atmosphere of purified nitrogen. To a 2 x $10^{-3}$ M solution of tetrakis(triphenylphosphine)nickel(0) in toluene (100 ml) was added dropwise a little more than equimolar amount of a chloro- or bromo-substituted pyridine to produce a brownish yellow precipitate, which was recrystallized from dichloromethane-methanol. The corresponding iodo complex was prepared by metathesis of the chloro complex with sodium iodide in a mixture of dichloromethane and methanol (1:1 by volume). Some properties of the compounds thus prepared are summarized in Table 1.

Table 1. Some σ-Pyridyl Nickel(II) Complexes

| | Complex | Yield | Mol wt[a] | $\nu$(Ni-X) | Dec temp |
|---|---|---|---|---|---|
| | | % | Found (Calcd) | $cm^{-1}$ | °C |
| 1 | $[NiCl(2\sigma\text{-}C_5H_4N)(PPh_3)]_2$ | 60 | 829 (869) | 289, 248 | 187 |
| 2 | $[NiBr(2\sigma\text{-}C_5H_4N)(PPh_3)]_2$ | 55 | 790 (958) | 191, 170 | 170 |
| 3 | $[NiI(2\sigma\text{-}C_5H_4N)(PPh_3)]_2$ | 80[b] | 840(1052) | 152, 134 | 160 |
| 4 | $[NiCl(3\sigma\text{-}C_5H_4N)(PPh_3)]_2$ | 40 | | | 124 |
| 5 | $[NiCl(2\sigma\text{-}6\text{-}Cl\text{-}C_5H_3N)(PPh_3)]_2$ | 90 | 947 (940) | | 194 |

a Determined in dichloromethane (0.011 $mol\cdot l^{-1}$) at 35°C by means of a vapor pressure osmometer manufactured by Knauer, Germany.

b Yield of metathesis reaction of 1.

They are all air-stable and gave satisfactory analysis.

The observed molecular weight of each compound is near the value calculated for a dimer. The IR spectra in Nujol of these dimeric complexes exhibit two bands assignable to the Ni-X(bridging) stretching vibration. The higher frequency band may be related to the Ni-X bond trans to the phosphine and the lower one to the Ni-X bond trans to the pyridyl ligand. Although chloro(phenyl)bis(triphenylphosphine)nickel(II) is air-sensitive and decomposes at 122-3 °C,[4)] the decomposition temperature of the 2σ-pyridyl complexes is much higher in the order of Cl $>$ Br $>$ I.

Compound 5 shows the highest solubility, giving a well-resolved $^1H$ NMR spectrum in $CD_2Cl_2$. A multiplet at 8.03 ppm is assigned to the ortho protons and that at 7.31 ppm to the meta and para protons in phenyl rings of triphenylphosphine. The seven-line signal in the 6.0-7.0 ppm region is tentatively assigned to the pyridyl protons in the first-order fashion: $H^3$ 6.45 doublet, $H^4$ 6.21 triplet, and $H^5$ 6.65 ppm doublet ($J_{34} = J_{45} = 7.8Hz$, $J_{35} = 0$). Each proton in the σ-carbon-bonded pyridyl ligand resonates at much higher field than that in α-chloropyridine,[5)] indicating that the metal atom is an electron donor when viewed as a substituent on the pyridine ring.

Reactions of the σ-Pyridyl Complexes. Contrary to the aryl complexes, the σ-pyridyl nickel(II) complexes have a strong preference for the dimeric structure. Thus the reactions of excess triphenylphosphine with 1 and 2 to split the halogen bridge were unsuccessful, and refluxing of these complexes in pyridine gave $NiCl_2(py)_2$ in ca. 40% yields. Reactions of 1 with sodium bromide, iodide, azide, cyanate, thiocyanate, and selenocyanate in $CH_2Cl_2$-MeOH resulted in almost quantitative metathesis affording the corresponding dimeric complexes $[NiX(2\sigma\text{-}C_5H_4N)(PPh_3)]_2$. Molecular weight data certify the dimeric nature of these compounds and the IR spectra are also in conformity with the bridged structure of the halide and pseudo halide ions. $[NiSCN(2\sigma\text{-}6\text{-}MeO\text{-}C_5H_3N)(PPh_3)]_2$, which was prepared in a similar fashion, exhibits a single methyl resonance at 4.0 ppm from TMS in $CD_2Cl_2$, suggesting the existence of only one geometrical isomer such as exemplified by 6. When complex 5 was allowed to react with a little more than twice moles of sodium acetylacetonate in $CH_2Cl_2$-MeOH at room temperature for 1 hr, a yellow orange product 7 was obtained in a 60% yield. IR and NMR spectra (two methyl signals at 1.9 and 2.0 ppm and one methine singlet at 5.6 ppm) are consistent with the suggested structure.

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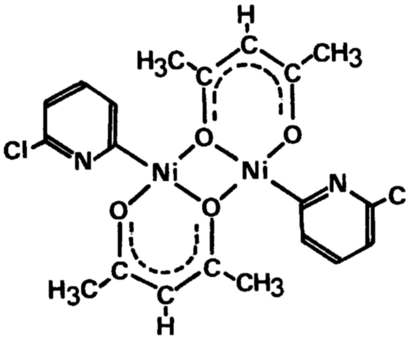

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The reaction of 7 with triphenyl phosphite in refluxing methanol induced decomposition of the complex and gave the coupled product 6,6'-dichloro-2,2'-bipyridine in a 70% yield, leaving tetrakis(triphenyl phosphite)nickel(0). The reactions of 1 with methyllithium and methylmagnesium bromide were examined, but the diorgano nickel(II) compound was not obtained. Fortunately, however, compound 1 was found to catalyze the cross coupling between 2-chloropyridine and methylmagnesium bromide. Thus to a tetrahydrofuran solution (100 ml) containing 2-chloropyridine ($4.8 \times 10^{-2}$ mol) and complex 1 ($8.6 \times 10^{-4}$ mol) was added dropwise a THF solution (60 ml) of the Grignard reagent ($6.0 \times 10^{-2}$ mol) and the mixture was stirred for a while at room temperature. Color of the solution turned from yellowish brown to deep green and magnesium bromide chloride precipitated. 2-Methylpyridine in the distillate from the reaction mixture was identified by GLC. The yield was 100% and no trace of residual 2-chloropyridine or other coupling products was found.

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