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Reduction of Transition-metal Salts by *N*-Propyl-1,4-dihydronicotinamide

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Synopsis. It was found that *N*-propyl-1,4-dihydronicotinamide reduces bis(benzonitrile)dichloropalladium, palladium(II) acetate, and chlorides of rhodium(III), platinum(IV), and ruthenium(III) smoothly in organic solvents affording a facile method for the preparation of low valent catalysts *in situ*.

Many reagents are known to reduce high valent transition-metal salts to metals or metal complexes of lower oxidation state, typical ones being metal hydrides, alkylmetals, ethanolic potassium hydroxide, metals, and hydrazine.[1] They are used for the preparation of low valent transition-metal catalyst. Mild reducing agents not attacking other organic molecules in the system are desirable in the preparation of a catalyst *in situ*. Zinc powder is a mild reductant but its heterogeneity often gives irreproducible results. We would like to report that a well-known 1,4-dihydropyridine derivative, mild and soluble in organic solvents, behaves as an effective organic reductant of some transition-metal salts.

Palladium(II) acetate and bis(benzonitrile)dichloropalladium were reduced to palladium metal by *N*-propyl-1,4-dihydronicotinamide (PNAH), but not phosphine complexes of palladium(II) such as dichlorobis(triphenylphosphine)palladium(II) or dichloro-1,2-bis(diphenylphosphino)ethanepalladium(II). This might suggest that the dissociation of a ligand(s) is essential for the reaction. Platinum(IV) chloride and ruthenium(III) chloride were reduced to platinum(II) and ruthenium(II), respectively. No reduction was observed for copper(I) chloride, nickel(II) acetate, or iron(II) nitrate.[2] For iron(II) chloride and cobalt(II) nitrate, change takes place in the spectrum in methanol in contrast to the case in water.[3] Attempt to identify the product was unsuccessful. A complex (or salt) of $PtCl_4(PNA^+)_2$ was isolated (65% yield) by the reduction of platinum(IV) chloride hydrate.

In the presence of triphenylphosphine, which stabilizes the low oxidation state of transition metals, reduction by PNAH gives low valent complexes such as chlorotris(triphenylphosphine)rhodium(I) (87%) and tetrakis(triphenylphosphine)palladium(0) (63%).

$$RhCl_3\cdot 3H_2O + PNAH \xrightarrow[PC_{18}H_{15}]{\text{Lutidine}} RhCl(PC_{18}H_{15})_3 + PNA^+$$

This procedure affords a facile method for the preparation of catalytically active low valent transition-metal complexes *in situ* because the reagent is insensitive to air and moisture, not attacking organic compounds except activated carbonyl compounds and cationic compounds.[4] Since the standard reduction potential for PNAH is -0.387 V,[5] reduction of metal ions or complexes with higher electrode potentials than the value could be achieved by this reagent. The resulting low valent complexes or metals were stable under the reaction conditions. PNAH did not attack chlorotris(triphenylphosphine)rhodium(I) even under reflux in ethanol.

Experimental

Changes of the spectra in the reactions were monitored with a Union Giken SM 401 spectrophotometer in organic solvents such as benzene, acetonitrile, ethanol, and methanol, which were purified by the usual manner. Products were identified by elemental analyses, NMR and IR.

Reduction of Bis(benzonitrile)dichloropalladium(II) or Palladium(II) Acetate. PNAH was added to a solution of the palladium species in order to precipitate black palladium powder quantitatively.

Preparation of Tetrakis(triphenylphosphine)palladium(0). Palladium(II) acetate, 0.89 mmol, triphenylphosphine, 4.96 mmol, and PNAH, 1.80 mmol were placed in a flask and deaerated. Benzene (30 cm^3) and 2,6-lutidine (0.1 cm^3) were injected into the flask and the solution was stirred overnight. The resulting precipitate was filtered off, the filtrate being concentrated and then treated with ethanol. Brown precipitate was washed with ether to give tetrakis(triphenylphosphine)palladium(0), 648 mg (0.56 mmol, 63%), which showed a spectrum identical with that of the authentic sample (Found: C, 73.61; H, 5.28%).

Preparation of Chlorotris(triphenylphosphine)rhodium(I). A solution of rhodium(III) chloride hydrate, 0.38 mmol, triphenylphosphine, 1.53 mmol, PNAH, 0.42 mmol, and 2,6-lutidine, 0.38 mmol in ether was stirred under nitrogen at room temperature for 2.5 h. The precipitate was collected and washed with 5 cm^3 of ethanol, and with three portions of 5 cm^3 of ether. After being dried under nitrogen, 305 mg (0.33 mmol, 87%) of the complex was obtained, which showed a spectrum identical with that of the authentic sample (Found: C, 69.42; H, 4.79%).

Reduction of Platinum(IV) Chloride. Platinum(IV) chloride hydrate (0.12 mmol) was dissolved in 5 cm^3 of methanol, and a solution of PNAH (0.60 mmol) in 3.5 cm^3 of methanol was added to the solution. After being stirred for 3 h under nitrogen, the white precipitate was collected and washed with methanol to give 52 mg of $PtCl_4(PNA)_2$ (0.08 mmol, 65%). Found: C, 31.85; H, 3.94; N, 8.12%. Calcd for $C_{18}H_{26}N_4Cl_4O_2Pt$: C, 32.29; H, 3.92; N, 8.04%. IR(KBr) 3390 (amide), 3195 (amide), 3060 (=C–H), 2940 (C–H), 1688 (C=O), and 1618 (C=C) cm^{-1}.

Reduction of Other Salts. Experimental conditions were the same as in the case of $PtCl_4$. Ruthenium(II) chloride hydrate was reduced to blue Ru(II) which turned yellow ($Ru^{II}(NH_3)_4$) in the presence of aqueous ammonia. No further attempt was made to isolate the product. Pink solution of cobalt(II) nitrate turned orange on addition of PNAH solution. The solution obtained was air sensitive but gave

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no characteristic color of $Co^{I}(bipy)_3$ by the addition of 2,2′-bipyridine.[6]

References

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