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Novel Reduction of Various Organic Compounds with Water in the Presence of Precipitated Metals[1)]

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It was found that various organic compounds were reduced in good yields by refluxing them with precipitated metals in water. Water was proved to be indispensable as a hydrogen donor. The reduction of compounds which are insoluble in water was facilitated by using a mixture of dioxane and water. It is of interest that the reduction of nitriles with this catalyst afforded the hydrochlorides of the corresponding primary amines. The results imply the participation of the chloride ion on the ppt-metal catalyst. A selective reduction of C=C was observed in some α,β-unsaturated ketones, such as mesityl oxide and 1,3-diferrocenyl-2-buten-1-one. The relative activity of the various precipitated metals depends not only upon the kinds of the metals but also upon their combination. It is assumed that the surface of the ppt-Ni is acidic as a result of the coexisting chloride ion, which might participate in the catalytic reaction.

In 1952, Urushibara and Chuman discovered a new nickel catalyst[2)] and named it Urushibara nickel (abbreviated as U-Ni). It is prepared by the acid- or base-treatment of precipitated nickel (ppt-Ni in abbreviation), which is itself obtained by an ion-exchange reaction between a nickel chloride solution and zinc dust. This new nickel catalyst was proved to be useful for the catalytic hydrogenation of various organic compounds[3)] and also for other organic catalytic reactions[4)]; it has also been found that the catalytic activity of U-Ni is comparable to that of Raney-Ni. However, the nature of ppt-Ni as a precursor of the U-Ni had not yet been well studied. In a previous communication,[1)] it was reported that some organic compounds, such as olefins, ketones and nitro compounds, were catalytically reduced by refluxing them with water in the presence of ppt-Ni. It is noticeable that this reduction is performed by a simple procedure without any hydrogen gas, and that the ppt-Ni is generally useful for the reduction of various organic compounds. The present paper will deal with an extended investigation of reduction with water in the presence of ppt-Ni, and will discuss the function of ppt-Ni as a catalyst.

Results

The Reduction of Organic Compounds in the Presence of Ppt-Ni. The ppt-Ni is easily prepared by adding a hot aqueous solution of nickel chloride to zinc dust. After it has been dried under reduced pressure, it is so stable that it can be preserved in the air for a long time. Various organic compounds involving C=C, NO_2, C≡N, and C=O groups were reduced in satisfactory yields when refluxed with water in the presence of ppt-Ni; the results are summarized in Table 1.

In these reactions, it is noteworthy that water plays a dual role, serving both as a solvent and as a hydrogen donor. Indeed, while water was proved to be effective enough as a hydrogen donor,*1 methanol and ethanol are

1) Preliminary report: K. Sakai and K. Watanabe, This Bulletin, **40**, 1548 (1967).

2) Y. Urushibara, *ibid.*, **25**, 280 (1952); Y. Urushibara and S. Nishimura, *ibid.*, **28**, 446 (1955).

3) K. Hata and S. Taira, *Yuki Gosei Kagaku Kyokai Shi (J. Soc. Org. Syn. Chem. Japan)*, **16**, 596 (1958).

4) K. Watanabe, This Bulletin, **32**, 1281 (1959); K. Watanabe and K. Sakai, *ibid.*, **39**, 8 (1966); K. Sakai, T. Ito and K. Watanabe, *ibid.*, **40**, 1660 (1967).

*1 According to a private communication from Y. Urushibara and H. Tomoda, an effective reaction occurs without refluxing when an aqueous solution of acids or bases, such as HCl or NaOH, is added, drop by drop and in admixture with the sample to be reduced, into a stirred mixture of ppt-Ni and water.

TABLE 1. THE REACTION BETWEEN VARIOUS ORGANIC COMPOUNDS AND WATER IN THE PRESENCE OF PRECIPITATED NICKEL

Each run was carried out by refluxing for 12 hr.

Exp. No.	Compound		Nickel content of catalyst	Solvent		Reduction Product[a]		Recovered material
		g	g		ml		%	%
1	Styrene[b]	10	4	Water	100	Ethylbenzene	81.4	19.6
2	Nitrobenzene[b]	10	4	Water	100	Aniline	98	—
3	*p*-Nitrobiphenyl	1	2	Water Dioxane	30 10	*p*-Aminobiphenyl	80	20
4	*o*-Nitrobiphenyl	1	2	Water Dioxane	30 10	*o*-Aminobiphenyl	70	30
5	Benzonitrile[c]	10	4	Water	100	Benzylamine-HCl[d] Benzamide	90 Trace	+
6	2-Cyanopyridine	0.5	1	Water	20	Nickel chelate[e] of 2-pyridylmethylamine	>80	—
7	3-Cyanopyridine	0.5	1	Water Dioxane	40 20	3-Pyridylmethylamine[d]	>80	—
8	4-Cyanopyridine	0.5	1	Water Dioxane	40 20	4-Pyridylmethylamine[d]	>80	—
9	Benzaldehyde[b]	10	4	Water	100	Benzyl alcohol	>90	—
10	*m*-Nitrobenzaldehyde	1	2	Water Dioxane	30 10	*m*-Aminotoluene	>90	+
11	Ethyl methyl ketone[b]	10	4	Water	100	2-Butanol	87	13
12	Cyclohexanone[b]	10	4	Water	100	Cyclohexanol	90	+
13	2-Methylcyclohexanone	1	0.4	Water	10	2-Methylcyclohexanol	42	58
14	Menthone	5	2	Water Dioxane	40 20	*exo*-Menthol *endo*-Methol	3 1	>95
15	Camphor	5	2	Water Dioxane	40 10	*exo*-Borneol *endo*-Borneol	2 0.4	>97
16	Ethyl cyclopentanone-2-carboxylate	1	0.4	Water	10	Ethyl cyclopentanol-2-carboxylate	71	29
17	Acetophenone[g]	8	2	Water	70	1-Phenylethanol Ethylbenzene	25 26	49
18	Benzophenone[g]	8	2	Water Dioxane	40 30	Benzhydrol Diphenylmethane	31 40	29
19	Formylferrocene	0.5	1	Water Dioxane	20 10	Methylferrocene 1-Methyl-2-(ferrocenyl-methyl)ferrocene	80 10	—
20	Acetylferrocene	0.5	1	Water Dioxane	20 10	Ethylferrocene	30	60
21	Benzoylferrocene	1	2	Water Dioxane	20 10	Benzylferrocene	<80	—
22	Diacetylferrocene	0.5	1	Water Dioxane	20 10	Diethylferrocene 1-Ethyl-1′-acetyl-ferrocene 1-Acetyl-1′-(1-hydroxy-ethyl)ferrocene	10 40 Trace	>40
23	Mesityl oxide[b]	10	4	Water	100	Isobutyl methyl ketone	95[f]	—
24	1,3-Diferrocenyl-2-buten-1-one	0.5	1	Water Dioxane	20 10	1,3-Diferrocenyl-1-butanone	>90	—
25	Dypnone	1	2	Water Dioxane	30 10	1,3-Diphenylbutane	>90	—
26	Benzylideneacetone[g]	1	2	Water Dioxane	30 10	*n*-Butylbenzene 4-Phenyl-2-butanone 4-Phenyl-2-butanol	6 26 68	—

a) The yields were calculated from the results of gas chromatographic analysis, except for Exp. No. 5. b) The reaction time was 16 hr. c) The reaction time was 20 hr. d) The amine was obtained as hydrochloride from the reaction mixture by evaporation. e) The composition of the nickel chelate was found to be $[Ni_2(2\text{-pyridylmethylamine})_5(2\text{-pyridinecarboxylic acid})(H_2O)_3Cl]$. f) More than 90% even when refluxed for 5 hr. g) Each product was identified by infrared spectra after the isolation by gas chromatography.

unsatisfactory. Whereas compounds insoluble in water were reduced only in poor yields, the use of a mixture of dioxane and water facilitated the reaction.

As may be seen in Table 1, ethylenic double bonds were easily hydrogenated in high yields; for example, ethylbenzene was obtained in an 81.4% yield from styrene, and isobutyl methyl ketone, in a 95% yield from mesityl oxide. In the reduction of unsaturated ketones, such as mesityl oxide and 1,3-diferrocenyl-2-buten-1-one,[5] the ethylenic double bonds were preferentially hydrogenated, while the carbonyl groups were unaffected.

Ketones were generally reduced to the corresponding secondary alcohols. In some cases a reduction of the carbonyl group to the methylene group was observed, as in the Clemmensen reduction.[6] Thus, dypnone, acetylferrocene, and benzoylferrocene[7] were mainly converted to 1,3-diphenylbutane, ethylferrocene, and benzylferrocene respectively. The reduction of acetophenone yielded a mixture containing 1-phenylethanol and ethylbenzene, while benzophenone similarly gave benzhydrol and diphenylmethane. Benzylideneacetone gave a more complicated product consisting of 4-phenyl-2-butanol, 4-phenyl-2-butanone, and *n*-butylbenzene. Menthone and camphor were respectively 96% and 97% recovered unchanged, while only a small amount of the corresponding alcohols were obtained.

Nitriles were predominantly converted to primary amines without the formation of secondary amines, which are often produced as by-products in ordinary catalytic hydrogenations. It is noteworthy that the amines were obtained as their hydrochlorides, the chloride anion presumably being supplied from ppt-Ni. 2-Cyanopyridine characteristically afforded a metal complex of the amine when treated with water in the presence of ppt-Ni or ppt-Cu, while 3- and 4-cyanopyridine gave only the corresponding amine hydrochlorides. *m*-Nitrobenzaldehyde was converted to *m*-methylaniline by a Clemmensen-type reduction, whereas benzaldehyde afforded only benzyl alcohol, no appreciable amount of the expected formation of toluene being observed.

The Reduction of Organic Compounds in the Presence of Ppt-Ni, Al. Another type of ppt-Ni (denoted as ppt-Ni,Al) was prepared using aluminum grains of 40—80 meshes instead of zinc dust. The U-Ni-BA,[8] prepared from the ppt-Ni,Al, has already been reported to be a good catalyst for the hydrogenation of aromatic nuclei. The X-ray diffraction pattern of ppt-Ni,Al showed sharp, proper peaks of nickel at 38.7°, 44.7°, 51.7°, and 76.5° in 2θ, whereas in ppt-Ni the peaks of nickel were little observed.

The results of the reduction in the presence of ppt-Ni,Al are given in Table 2. The activity of the ppt-Ni,Al was found to be high enough to reduce phenol to cyclohexanone and cyclohexanol. However, in the reduction of *o*- and *m*-cresol, most of the

TABLE 2. THE REDUCTION OF ORGANIC COMPOUNDS BY WATER IN THE PRESENCE OF PRECIPITATED NICKEL, PPT-Ni, Al

Exp. No.	Compound		Nickel content of catalyst	Solvent		Reaction time	Product[a]		Recovered
		g	g		ml	hr		%	%
1	Phenol	8	1	Water	70	15	Cyclohexanol Cyclohexanone[b]	60 1.4	38.6
2	*o*-Cresol	10	2	Water	100	12	2-Methylcyclohexanol	5	95
3	*m*-Cresol	8	1	Water	70	7	3-Methylcyclohexanol	2	98
4	Styrene	8	1	Water	100	12	Ethylbenzene	29	77
5	Benzaldehyde	8	1	Water	100	12	Toluene Benzyl alcohol	Trace 94	6
6	Acetophenone[c]	8	1	Water	70	7	Ethylbenzene 1-Phenylethanol	4 36	60
7	Benzophenone	5	1	Water Methanol	40 20	7	Diphenylmethane	33	67

a) The yields were calculated from the results of gas chromatographic analysis.
b) Cyclohexanone was derived to oxime, mp 86—89°C (lit. 89—90°C).
c) Products were identified by infrared spectra after the isolation by gas chromatography.

5) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, **1962**, 3880.
6) E. L. Martin, "Organic Reactions," Vol. 1, p. 155 (1942).
7) M. Rosenblum, "Chemistry of Iron Group Metallocenes," John Wiley & Sons, New Yok (1965), p. 120.
8) K. Hata, S. Taira and I. Motoyama, This Bulletin, **31**, 776 (1958); I. Motoyama, *ibid.*, **33**, 232 (1960).

phenols were recovered unchanged. The results of the reduction of acetophenone, benzophenone, styrene, and benzaldehyde were very similar to those obtained with the ordinary ppt-Ni.

Features of the Precipitated Metals. It has been reported[9,10] that ppt-Ni contains Ni, Zn, ZnO, Zn(OH)Cl, and $Zn(OH)_2$, and that the zinc in ppt-Ni is gradually oxidized to zinc oxide with the progress of the catalytic reaction in the presence of ppt-Ni; thus, the zinc not only acts as a carrier, but also protects the nickel from oxidation.

Since the behavior of zinc might be assumed to contribute greatly to the function of ppt-Ni, we tried to determine to what extent a variation in the Zn/Ni ratio in ppt-Ni affects the reaction. In Fig. 1 the correlation is expressed in terms of the yield of cyclohexanol obtained by the reduction of cyclohexanone. As Fig. 1 shows, the maximum yield of cyclohexanol was attained by a catalyst whose Zn/Ni ratio was 10. This ratio coincides with that of the ppt-Ni, from which the U-Ni catalyst with the highest activity was prepared. It might be concluded from this finding that zinc participates in the reaction by interacting with nickel as well as with water.

From these considerations, some other precipitated metals produced by treating a certain metal chloride with zinc may be

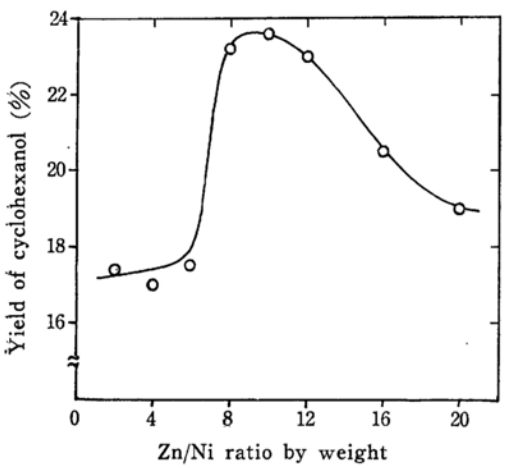

Fig. 1. The correlation between the ratio of zinc to nickel and the yield of cyclohexanol in the catalytic reduction with precipitated nickel.
Cyclohexanone 1g, catalyst 0.3g, water 1ml, heated to 111—115°C for 24 hr in a sealed tube.

9) Y. Urushibara, S. Yamaguchi and M. Kobayashi, *ibid.*, **29**, 815 (1956).

10) Y. Urushibara, M. Kobayashi, S. Nishimura and H. Uebara, *Shokubai* (*Catalyst*) (Tokyo), **12**, 111 (1956).

TABLE 3. THE RELATIVE ACTIVITIES OF THE PRECIPITATED METALS

Cyclohexanone 1 g, catalyst 0.3 g, water 1 ml, heated to 111—114°C for 12 hr in a sealed tube.

Exp. No.	Catalyst	Composition of the reaction product[a] (%)	
		Cyclohexanol	Cyclohexanone
1	Ppt-Ni	15.3	84.7
		15.0	85.0
2	Ppt-Co	10.0	90.0
3	Ppt-Cu	3.5	96.5
4	Ppt-Fe	3.4	96.6
5	Ppt-Ni-Co	17.7	82.3
6	Ppt-Ni-Cu	5.5	94.5
7	Ppt-Ni-Fe	15.2	84.8

a) Products were determined by gas chromatography; column 1.5 m, silicone grease DC 550 on Celite 30—40 meshes; temp., *ca.* 150°C; flow rate, 60 cc/min; carrier gas, H_2.

expected to be more reactive than the ppt-Ni. Thus, the following precipitated metals were prepared: ppt-Co, ppt-Cu, ppt-Fe, and mixed precipitated metals, such as ppt-Ni-Co, ppt-Ni-Cu, and ppt-Ni-Fe. The relative activities of these precipitated metals were then examined in the reduction of cyclohexanone. The results of representative experiments, shown in Table 3, exhibit the relative activities in the following order: ppt-Ni-Co > ppt-Ni > ppt-Ni-Fe > ppt-Co > ppt-Ni-Cu > ppt-Cu > ppt-Fe. This indicates that the activity of precipitated metal may be increased by a proper combination of metals.

The behavior of ppt-Ni contrasts with that of ordinary hydrogenation catalysts. Thus, a rapid decomposition of hydrogen peroxide was observed in the presence of U-Ni, "Stabilized nickel," copper chromite, or zinc chromite, but it could not be observed with ppt-Ni. On the other hand, the effective reduction of the cited compounds by water was observed only in the presence of the "precipitated metals," whereas U-Ni, Raney-Ni, and other hydrogenation catalysts were very feeble. The difference between them is reflected in the X-ray diffraction diagrams. The results of X-ray diffraction analysis, suggest[11] that the surface of ppt-Ni never consists of nickel itself, but rather is convered with alloy-like layers composed of nickel and zinc, contaminated with OH^- and Cl^-.

Some of the experimental results are compatible with this view. Thus, it was found that the reduction of nitriles in the presence

11) S. Taira, "Shokubai Kogaku Koza (Catalytic Engineering)," Vol. 10, Chijinshokan & Co., Tokyo (1967), p. 498.

of ppt-Ni produced amine hydrochlorides, while scarcely any free amines were detectable. When the ppt-Ni was soaked in water, a silver nitrate test for chloride anion was negative after 24 hr and only slightly positive after 72 hr. However, when the ppt-Ni was digested in hot water for 72 hr, a distinct deposit of silver chloride was observed in a silver nitrate test of the solution. Consequently, the surface of the ppt-Ni may be assumed to be relatively acidic as a result of coexisting chloride ions, which might participate in the catalytic reaction.

The Acidity and Acid Strength[12] of the Surface of Ppt-Ni. To measure the acidity and acid strength of the surface of ppt-Ni, *n*-butylamine titration was applied to the ppt-Ni in benzene, using Methyl Red as an indicator (pK_a 4.8). Though Methyl Red generally turns into a red acidic form when it reacts with an acidic solid, the dark gray color of the ppt-Ni makes it impossible to detect any color change in the adsorbed indicator on the solid surface. Therefore, the point of neutralization was determined by noting the change in color on anhydrous magnesium sulfate, which had previously been mixed with the ppt-Ni. The relation between the weight of the ppt-Ni used and the amounts of the *n*-butylamine adsorbed is shown in Fig. 2. From the slope of the line in Fig 2, the acidity of ppt-Ni was calculated to be 1.05×10^{-5} (eq/g) at pK_a 4.8. On the other hand, the acidity of ppt-Ni was nearly zero when Methyl Yellow was used as an indicator (pK_a 3.3). These results imply that the acid strength of the surface is at least more acidic than pK_a 4.8, while the number of acid sites is comparatively small.

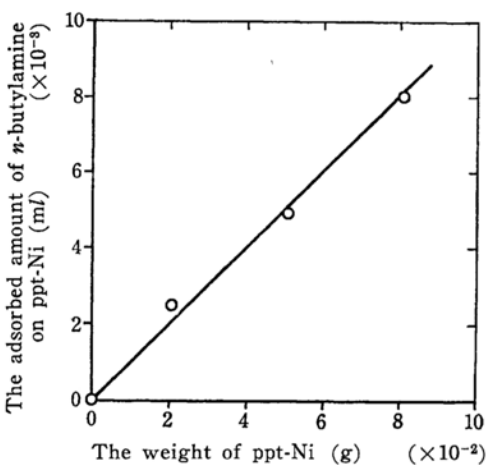

Fig. 2. *n*-Butylamine titration of the precipitated nickel.

Discussion

It is well known that both zinc amalgam[6] and zinc itself[13] can be used for reduction in acidic, basic, or neutral solutions. However, the reduction generally requires the cooperation of acid to increase the yield of the reaction product, and subsequent undesirable side-reactions due to the acid are inevitable. A unique characteristic of the reduction with ppt-Ni is the use of water as a hydrogen donor, thus making the use of any acid generally unnecessary. Consequently, the reduction can be performed under practically neutral conditions.

The results shown in Table 1 suggest that the reduction may proceed in a manner somewhat similar to that in the Clemmensen reduction. However, there are some differences between these two reduction reactions. The Clemmensen reduction of a ketone often results in the formation of alcohol, saturated hydrocarbon, olefin, and a dimerization or rearrangement product; for example, benzophenone yields benzhydrol, diphenylmethane, tetraphenylethylene, and benzopinacol. In regard to the formation of the pinacol, a radical intermediate has been proposed for the mechanism of the Clemmensen reduction.[14] On the other hand, the reduction of benzophenone in the presence of the ppt-Ni affords only benzhydrol and diphenylmethane. A radical mechanism may be excluded on the base of the fact that no formation of the pinacol was observed. The presence of a large quantity of water as a solvent also supports this presumption.

Among three analogous α,β-unsaturated ketones $RC(CH_3)=CHCOR$ ($R=CH_3$, C_6H_5, ferrocenyl), the reduction of carbonyl to methylene was observed only in dypnone ($R=C_6H_5$). It has been reported[15] that the carbonyl group in mesityl oxide also remains unaffected by the Clemmensen reduction, the reason being discussed by postulating the intermediacy of a cyclopropanol form. On the other hand, Rinehart *et al.*[16] have pointed out the differ-

12) O. Johnson, *J. Phys. Chem.*, **59** 827 (1955); H. A. Benesi, *J. Am. Chem. Soc.*, **78**, 5496 (1956).

13) Y. Ogata, "Oxidation and Reduction of Organic Compounds" (in Japanese), Nankodo, Tokyo (1963), p. 656.

14) W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923).

15) B. R. Davis and P. D. Woodgate, *J. Chem. Soc.* (C), **1966**, 2006.

16) L. Rinehart, Jr., J. Curby, Jr., H. Gustafson, K.G.Harrison, R.E. Bozak and D.E.Bublity, *J. Am. Chem. Soc.*, **84**, 3263 (1962).

ence in behavior between 1,3-diferrocenyl-2-buten-1-one and dypnone toward reaction with methylmagnesium bromide, the former not bringing about either the 1,4- or 1,2-addition of the Grignard reagent, whereas the latter does so. The present results on the reduction in the presence of ppt-Ni are compatible with these observations.

Bradlow *et al.*[17] have examined the substituent effect in the Clemmensen reduction of benzophenone derivatives; they found that substituents in the ortho position or electron-withdrawing substituents facilitate the formation of diphenylmethanes, whereas electron-donating substituents promote the formation of pinacols. In the present reduction of carbonyl groups, the trend of the reaction must be affected not only by the electronic factor but also by the steric factor. A molecule of dypnone can take a planar conformation in which the C=C, C=O, and two phenyl groups lie on a common plane, as is indicated by a molecular model. The planar conformation may facilitate the approach of the molecule toward the catalyst metal, resulting in the reduction of both ethylenic and carbonyl groups. On the other hand, a voluminous ferrocenyl group is assumed to hinder the approach of the carbonyl group toward the catalyst metal, thus preventing the catalytic reduction.

At any rate, the ppt-metal catalyzed reaction has been found to be relatively complex, and it is difficult to explain the function of ppt-metal in terms of the electrode potential of the metals. It was found that the ppt-Ni prepared with a 0.25 M sodium chloride solution instead of water increased the yield of the product, and the X-ray diffraction analysis has indicated an increase in the amount of Zn(OH)Cl in this particular ppt-Ni.

Though the mechanism of the ppt-metal-catalyzed reaction has not yet been sufficiently elucidated, the reaction may be assumed to involve at least two processes—the decomposition of water and the reduction of substrates, and the reduction may follow a course similar to that in an ordinary hydrogenation reaction. A more detailed discussion of the mechanism of this reaction will, however, be reported in a subsequent paper.

Experimental

Catalysts. *Precipitated Metals.* Zinc dust (10 g) and distilled water (3 m*l*) were placed in an Erlenmeyer flask and heated on a water bath. An aqueous solution (10 m*l*) containing either 4.04 g of nickel(II) chloride ($NiCl_2 \cdot 6H_2O$),[2] 4.04 g of cobalt(II) chloride ($CoCl_2 \cdot 6H_2O$), 2.69 g of copper(II) chloride ($CuCl_2 \cdot 2H_2O$), or 4.84 g of iron(III) chloride (anhydrous), previously heated to 60°C, was added to the heated zinc dust mud with vigorous shaking. A violent exchange reaction took place, depositing nickel on the surface of the zink dust. The whole solid was collected on a glass filter by suction, washed with water three times and then with methanol and ether, and dried under reduced pressure. The precipitated metal thus obtained contains about 1 g of each metal, supported on the zinc dust.

Mixed Precipitated Metals. Ppt-Ni-Co, ppt-Ni-Cu, and ppt-Ni-Fe were prepared by the same procedure using a mixture of 2 g of nickel(II) chloride and either 2 g of $CoCl_2 \cdot 6H_2O$, 1.5 g of $CuCl_2 \cdot 2H_2O$, or 1.4 g of $FeCl_3$, instead of 4.04 g of nickel chloride alone.

Ppt-Ni,Al. Aluminum grains of 40—80 meshes (50 g) were washed with 250 m*l* of a 3% sodium hydroxide solution and then with water. The aluminum grains were placed in a 300-m*l* Erlenmeyer flask along with a small quantity of water, and were heated on a water bath. An aqueous solution of nickel chloride (100 m*l*) containing 40 g of $NiCl_2 \cdot 6H_2O$, previously heated to 80°C, was poured on the aluminum grains. Occasional stirring with a glass rod was continued until the slushy reaction mixture became nearly solid. The solid was then washed three times with water and then with methanol and ether, and dried under reduced pressure.

The Reduction of Styrene. A suspension of styrene (10 g) in 100 m*l* of water was refluxed vigorously in the presence of the ppt-Ni containing 4 g of nickel. After the solution had been refluxed for 12 hr, the ppt-Ni was separated by filtration while hot, and washed with water and with ether. The filtrate and the washings were combined and extracted with ether. The extract was dried over anhydrous magnesium sulfate, and the ether was carefully evaporated away on a water bath. The residue was analyzed by gas chromatography (column, 30% Carbowax 1500 on Celite 30—40 meshes; length, 2 m; column temp., *ca.* 180°C; flow rate, 14—20 cm/sec; carrier gas, H_2). The yield of ethylbenzene was 81.4%. The ethylbenzene (bp 129—131°C) was identified by infrared spectrum analysis.

The Reduction of Benzonitrile. The reaction procedure was almost the same as that described above. After the reaction, the ppt-Ni was filtered off. The filtrate was carefully evaporated to dryness under reduced pressure, and the residue was extracted with ether. The evaporation of the ether extract gave a small quantity of a white solid which was identified as benzamide. A major part of the product, which consisted of a white solid insoluble in ether, was recrystallized from hot water (mp >240°C). It was identified as benzylamine hydrochloride by IR analysis (ν_{max}^{KBr} 3012, 1520, 1500, 750, and 695 cm^{-1}) and by NMR analysis (benzene ring protons τ 2.55, methylene protons τ 5.8 in D_2O). The hydrochloride (yield, *ca.* 90%) liberated benzyl-

17) H. L. Bradlow and C. A. van der Werf, *J. Am. Chem. Soc.*, **69**, 1254 (1948).

amine when treated with sodium hydroxide.

The Reduction of Formylferrocene.[18] After the reaction had been conducted in a similar manner, the ppt-Ni was separated and the product was obtained by extraction with ether. The gas chromatographic analysis (column, 20% APL on Celite 30—40 meshes; length, 2 m; column temp., *ca.* 180°C; flow rate, 20—15 cm/sec; carrier gas, H_2) indicated a sole compound as the reduction product. The crude product was dissolved in benzene and separated by column chromatography on active alumina (*ca.* 100—200 meshes), using *n*-hexane for elution. A careful evaporation of the yellow elute afforded yellow crystals of methylferrocene (yield, *ca.* 80%), mp 34.9—35.2°C (lit. 35.5—36.5°C). This substance was identified by comparing its infrared spectrum with that of an authentic specimen. A successive elution of the column chromatography exhibited a small quantity of a yellow crystalline product, which could not be detected on gas chromatography and which was assumed to be 1-methyl-2-(ferrocenylmethyl)ferrocene on the basis of its NMR spectrum.

The Reduction of 2-Cyanopyridine. 2-Cyanopyridine (0.3 g) and water (10 m*l*) were refluxed vigorously in the presence of ppt-Ni or ppt-Cu (containing 0.4 g of the catalyst metal) for 10 hr. After the ppt-Ni or ppt-Cu had then been filtered off, the filtrate was carefully evaporated to dryness on a water bath; a green solid was thus obtained. The solid was washed with ether, dissolved in ethanol, and separated by column chromatography on active alumina. The evaporation of the solvent from the elute gave a greenish-blue solid. Recrystallization from hot water afforded a nickel or copper chelate in the form of greenish-blue (nickel) or pale blue (copper) needles. Elementary analyses were carried out with samples dried at 56°C under reduced pressure for 1 hr.

Nickel complex, Found: C, 49.67; H, 5.52; N, 17.68%. Calcd for $C_{36}H_{50}O_5N_{11}ClNi_2$: C, 49.7; H, 5.75; N, 17.7%.

Copper complex, Found: C, 31.09; H, 3.91; N, 12.42%. Calcd for $C_6H_8N_2Cl_2Cu$: C, 29.7; H, 3.30, N, 11.5%.

These metal complexes were confirmed to be metal chelates of 2-pyridylmethylamine by means of their infrared and ultraviolet spectra.[19] The composition of the nickel chelate corresponds to the formula. $Ni_2(C_5H_5NCH_2NH_2)_5(C_5H_5NCO_2H)(H_2O)_3Cl$ Nickel complex: IR, ν_{max}^{KBr} 3220,2924,1670(s), 1608 cm^{-1} UV, $\lambda_{max}^{H_2O}$ 267,261,254 mμ. Copper complex: IR, ν_{max}^{KBr} 3220, 2924, 1604 cm^{-1}. UV, $\lambda_{max}^{H_2O}$ 253, 247, 240 mμ.

Acid Strength Measurement[12] **of Ppt-Ni.** The ppt-N powder was completely dried for an hour at 80°C under reduced pressure. A sample of the ppt-Ni (0.0215 g) was then placed in a 50-m*l* Erlenmeyer flask, together with 0.500 g of anhydrous magnesium sulfate. Dry benzene (5 m*l*) and a drop of a 0.1% benzene solution of Methyl Red (pK_a 4.8) were added to the mixture. The indicator immediately gave a red color on the magnesium sulfate. Then, a 0.0999 N benzene solution of *n*-butylamine was added, drop by drop, through a micropipet until a color change from red to yellow was observed on the surface of the magnesium sulfate. Referring to a blank test in order to evaluate the acid strength of the magnesium sulfate itself, the amount of *n*-butylamine adsorbed on the acid sites of the ppt-Ni was then calculated. Similar titrations were made with 0.0516 g and 0.0817 g of ppt-Ni; the results are plotted on Fig. 2.

Using Methyl Yellow as an indicator, the same titration method was applied to measure the acid strength of ppt-Ni in pK_a 3.3. In order to ensure that no excess of amine was present on the solid at the end point, a drop of 0.05 N trichloroacetic acid in benzene was added; the red color then reappeared.

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18) Formylferrocene was prepared by a modified method of the Vilsmeyer reaction: M. Sato, H. Kono, M. Shiga, I. Motoyama and K. Hata, This Bulletin, **41**, 252 (1968).

19) S. Utsuno and K. Sone, *ibid.*, **37**, 1038 (1964).