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New Effective Nickel(II) Catalysts for the Cross-coupling of an Aryl Grignard Reagent with Aryl Halide

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Synopsis. It has been found that seventeen nickel complexes of the Ni–O_4, Ni–S_4, Ni–O_2N_2, Ni–O_3N_3, Ni–N_4, Ni–N_6, and Ni–$(C_5)_2$ types exhibit a high catalytic activity for the selective cross-coupling reaction of an aryl Grignard reagent with aryl iodide, which make possible the synthesis of unsymmetrical aromatics of a high purity and in a high yield.

In connection with the search for an effective method of C_{ar}–C_{ar} bond formation, Corriu and Masse[1] have reported that bis(acetylacetonato)nickel(II) catalyzes the selective cross-coupling reaction between aromatic Grignard reagents and aryl or alkenyl halides. Tamao *et al.*[2] have independently found a high catalytic activity of nickel-phosphine complexes for similar cross-coupling reactions. The present study was undertaken in order to develop a new, efficient catalyst for the synthesis of unsymmetrical biaryls by means of a Kharasch-type reaction.

The catalytic activity of a variety of nickel complexes was examined using a cross-coupling reaction of phenylmagnesium bromide with 2-iodobiphenyl as a model under a standard set of conditions. The activities of seventeen complexes and those of the four known representative catalysts, determined as the yield of *o*-terphenyl[I], are given in Table 1. The seventeen complexes showed a fairly high activity (a 70—90% yield of I), eleven of them exhibiting an activity superior to that of the four known catalysts used for comparison (57—78%; **12**, **19**, **20**, and **21**). Although in all cases, I was accompanied by 16—43% of biphenyl[II] and no, or only a small amount of, *o*-quaterphenyl[III]. I could easily be separated from these contaminants. Thus, the seventeen complexes, particularly eleven of them, were found to be preferential catalysts for the synthetic production of unsymmetrical aromatics of a high purity and in a high yield.

The seventeen new catalysts are classified briefly into the following groups: i) the Ni–O_4 complexes of the β-diketones and aldehyde ligands (**2**, **10**, **14**, **16**, and **8**); ii) the Ni–S_4 complex of the β-dithioketone ligand (**11**); iii) the Ni–O_2N_2 complexes of the β-keto imines and Schiff-base ligands (**1**, **6**, and **4**); iv) the Ni–O_3N_3 complex of the amino acid ligand (**9**); v) the Ni–N_4 and Ni–N_6 complexes of substituted amides, dioxime, and the diamine ligands (**3** and **5**; **15**; **17**, **13**, and **18**), and vi) the Ni–$(C_5)_2$ complex of the carbanion ligand (**7**). Although most of the new catalysts are diamagnetic square-planar complexes of bis-bidentate or quadridentate ligands (**1**,[3] **2**,[4] **3**,[5] **4**,[6a] **5**,[5] **11**,[6b] and **15**), a few octahedral complexes of tris-bidentate ligands (**9**,[6c] **13**, and **18**) as well as strongly paramagnetic complexes (**7**[7] and **8**[8]) are also included in the new catalysts. In contrast to the trimeric octahedral structure of **12**[9a,b] and **14**[9c] in solution, **2** has been reported to exist as a monomeric structure, presumably because of the steric hindrance of the ligand.[4a] It seems of interest to note that the catalytic activity of coordinately saturated complexes (**9**, **13**, and **18**) is nearly comparable to that of unsaturated ones. Another result of considerable significance is the observation that the activities of a series of four closely related complexes (**10**, **12**, **14**, and **16**), the logarithms of their formation constants,[10] and the negative logarithms of the acid dissociation constants of the ligands[10] show a rather fair correlation, as is shown in Table 2.

The foregoing results suggest that the catalytic activity of the complexes has no remarkable relation with such factors as the kind and number of coordinate atoms, the size and number of chelate rings, the aggregation degree of complexes, and the steric effect of the ligands, or, consequently, with the configuration and magnetic susceptibility of the complexes. Ultimately, for the excellent catalytic activity of the complexes, the presence of Ni(II) as the central metal can be regarded

TABLE 1. CATALYTIC ACTIVITY OF VARIOUS NICKEL COMPLEXES FOR THE CROSS-COUPLING OF C_6H_5MgBr WITH 2-I·C_6H_4·C_6H_5 (Ar′I)[a]

Catalyst	x[b] %	[I][c] %	[III][c] %	[II][d] %
none	15	2	0	19
Ni(dpm)$_2$ (**2**)	100	90	0	16
Ni(tfa)$_2$ (**10**)	100	86	4	16
Ni(acac)$_2$ (**12**)	100 100	78 80[e]	1 2[e]	31 27[e]
Ni(ba)$_2$·H_2O (**14**)	94	75	4	33
Ni(dbm)$_2$ (**16**)	99	71	1	34
Ni(sal)$_2$·2H_2O (**8**)	100	86	2	24
Ni(SacSac)$_2$ (**11**)	100	83	3	26
Ni(acaen) (**1**)	100	90	0	22
Ni(acNH)$_2$ (**6**)	100	87	1	29
Ni(H-sal-fum)$_2$ (**4**)	100	89	2	43
K[Ni(L-pro)$_3$]·3H_2O (**9**)	100	86	0	24
Ni(pc$_{1,3}$-pn)·H_2O (**3**)	100	89	2	23
Ni(pc$_{1,2}$-pn)·3H_2O (**5**)	100	87	0	25
Ni(dgH)$_2$ (**15**)	92	72	4	27
Ni(en)$_2$Cl$_2$ (**17**)	100	70	4	37
Ni(en)$_3$Cl$_2$·2H_2O (**13**)	100	79	3	32
Ni(bpy)$_3$Cl$_2$·7H_2O (**18**)	100	70	17	35
Ni(C_5H_5)$_2$ (**7**)	100	87	4	26
Ni(dppp)Cl$_2$ (**19**)	88	63	14	40
Ni(Ph_3P)$_2$Cl$_2$ (**20**)	83	58	5	27
Ni(dppe)Cl$_2$ (**21**)	81	57	15	39

a) The mean value of the duplicate runs is presented. b) x: Conversion of Ar′I, 100% implies all the 2-I·C_6H_4·C_6H_5 is consumed. c) Based on the 2-I·C_6H_4·C_6H_5 used. d) Based on the C_6H_5MgBr used. e) Isolated yield.

Table 2. Correlation of the catalytic activity with the formation constant of the complexes and with the acid dissociation constant of the ligands

Complex	Activity yield of [I] %	log K_f(av)[a]	pK_D[a]
10	86	7.1	8.7
12	78	8.69	12.70
14	75	9.00	12.85
16	71	10.09	13.75

a) Ref. 10; 75 vol% dioxane-25 vol% water.

as essential,[11] and an appropriate range of stability may be attributable to one of the invaluable factors.

Experimental

Instruments. The melting points were determined with a Mettler FP-51 or FP-52 apparatus. The UV spectra were measured on a Shimadzu MPS-50L spectrophotometer in cyclohexane solutions. The ^{1}H NMR spectra were obtained with a Varian A-60A spectrometer in a $CDCl_3$ solution, using TMS as an internal standard. Quantitative GLPC was performed on a Shimadzu GC-5APTF gas chromatograph using a 1 m×3 mmϕ glass column 3% Dexsil 300GC or Silicone OV-17 on Chromosorb W AW-DMCS.

Materials. The following complexes used as catalysts, except those available commercially (**7**, **12**, and **15**), were prepared according to the references or by known methods, and all gave satisfactory physical data and acceptable results in elemental analyses.

N,N′-Bis(1-methyl-3-oxobutylidene)ethylenediaminatonickel(II)[3c] (**1**), bis(dipivaloylmethanato)nickel(II)[4b] (**2**), *N,N′*-dipicolinoyl-1,3-propanediaminatonickel(II) hydrate[5] (**3**), bis[*N*-(2-furylmethyl)salicylideneaminato]nickel(II)[6a] (**4**), *N,N′*-dipicolinoyl-1,2-propanediaminatonickel(II) trihydrate[5] (**5**), bis(4-imino-2-pentanonato)nickel(II)[12b] (**6**), bis(η-cyclopentadienyl)nickel(II) (**7**), bis(salicylaldehydato)nickel(II) dihydrate[8] (**8**), potassium tris(L-prolinato)niccolate(II) trihydrate[6c] (**9**), bis(trifluoroacetylacetonato)nickel(II) (**10**), bis(dithioacetylacetonato)nickel(II)[6b] (**11**), bis(acetylacetonato)nickel(II) (**12**), tris(ethylenediamine)nickel(II) chloride dihydrate[12a] (**13**), bis(benzoylacetonato)nickel(II) hydrate[13] (**14**), bis(dimethylglyoximato)nickel(II) (**15**), bis(dibenzoylmethanato)nickel(II)[14] (**16**), dichloro[bis(ethylenediamine)]nickel(II)[15] (**17**), tris(bipyridine)nickel(II) chloride heptahydrate[16] (**18**), dichloro[1,3-bis(diphenylphosphino)propane]nickel(II)[17] (**19**), dichloro[bis(triphenylphosphine)]nickel(II)[18a] (**20**), dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II)[17] (**21**).

Coupling Reactions. To an ethereal solution of phenylmagnesium bromide (20 mmol), prepared in the usual manner, we added, all at once, a mixture of 2-iodobiphenyl[18b] (10 mmol) and a catalyst **12** (0.5% of C_6H_5MgBr) in benzene at 0 °C under a nitrogen atmosphere. The mixture was stirred for 1 h, refluxed for 3 h, and hydrolyzed, and then the product was extracted with benzene. The organic layer was separated, washed with water, and then dried. Upon the withdrawal of a tenth part of the solution for analysis, the remainder was subjected to the isolation of the products. After the removal of the solvent, the resulting solid was separated into three fractions by chromatography on alumina, with cyclohexane as the eluent. Upon the evaporation of the solvent, the fractions afforded II, I, and III, which were identified by means of mixed-melting-point measurements and by means of a spectral comparison with each of the authentic samples.

o-*Terphenyl*[*I*]: Mp 56.7 °C (lit,[19] mp 56—57 °C); yield, 1.65 g (79.7%). NMR: δ 7.16 (10H, s, C_6H_5), 7.40 (4H, s, C_6H_4). UV: λ_{max} (ε) 197 (48300), 207 (46500), 233 (29100), 251 nm (sh) (13300).

Biphenyl[*II*]: Mp 69.4 °C; yield, 0.37 g (26.7%). NMR: δ 7.16—7.70 (10H, m, C_6H_5).

o-*Quaterphenyl*[*III*]: Mp 118 °C (lit,[18b] mp 118—119 °C); yield, 0.03 g (2.2%). UV: λ_{max} (ε) 201 (60600), 230 (34100), 245 nm (sh) (25600).

The yields of the coupling products were determined by quantitative GLPC, using *m*-terphenyl as an internal standard calibrated against the pure samples.

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11) In the preliminary experiments of the present coupling reaction, five complexes of $M(acac)_n$ (where M=Co(II), Fe(III), Fe(II), Mn(III), and Cr(III)) showed only a slight activity (18, 25, 24, 20, and 18% yields of I respectively). In the cases of the other analogous complexes (M=Co(III), Li(I), Cu(II), Be(II), Mg(II), Zn(II), Al(III), Zr(IV), Th(IV), and Mn(II)), only a trace of I or none was observed.

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