Control of Reductive Elimination and Acidolysis of Diarylnickel(II) Complexes by the Kind of Brønsted Acid and the Presence of Oxygen

Takakazu Yamamoto,* Yasuharu Murakami, and Mahmut Abla
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

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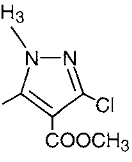
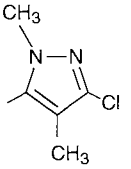
Reaction of NiAr$_2$(bpy) (Ar = electron withdrawing aryl group, bpy = 2,2'-bipypridyl) with Brønsted acids leads to reductive elimination of Ar-Ar from NiAr$_2$(bpy). The reaction also causes acidolysis of the Ni complex depending on the kind of the acid and reaction conditions.

Reaction of organometallic compounds having a M-R bond with Brønsted acid HY usually causes acidolysis of the M-R bond to liberate RH.[1] However, we have recently found that reaction of NiAr$_2$(bpy) with the acids such as aqueous solutions of H_2SO_4 and HNO_3 leads to reductive elimination of Ar$_2$ from the Ni complex when the Ar group is an electron-withdrawing 3-chloro-1-methylpyrazole-5-yl ligand.[2] We here report that such an effect of the Brønsted acid on the reductive elimination can be also observed with another NiAr$_2$(bpy) type complex and that the product of the reaction of NiAr$_2$(bpy) with HY depends on the kind of Brønsted acid and the presence or absence of O_2. Table 1 summarizes products of the reactions of NiAr$_2$(bpy) with the acids.

Although usual diorganonickel(II) complexes with aryl ligand(s) are thermally unstable,[3] selection of highly electron-withdrawing aryl ligands such as C_6F_5[4] and 3-chloro-1-methylpyrazole-5-yl[2] affords thermally stable NiAr$_2$(bpy), **1**-**3**; they are also stable under air.

Ar = C_6F_5 (**1**),


(**2**),


(**3**)

Such thermally stable NiAr$_2$(bpy), however, receives the reductive elimination by the interaction with the Brønsted acid HY as shown in Table 1. The reaction of **1**, which is stable even at 150 °C under air, with trifluoroacetic acid at room temperature causes the reductive elimination under air to liberate decafluorobiphenyl quantitatively (No. 1 in Table 1). Kinetic studies by UV-vis spectroscopy reveal that the rate of the reaction is proportional to both concentrations of **1** and CF_3COOH. These results indicate that the Brønsted acid-induced reductive elimination under air is not specific for the 3-chloro-1-methylpyrazole-5-yl complexes (**2** and **3**) but it proceeds generally with the NiAr$_2$(bpy) complexes with the electron-withdrawing Ar groups. The reductive elimination of diorganonickel(II) complexes proceeds under various conditions,[4,5] and coordination of π-acids[4,5a] and Lewis acids[5c] enhances the reductive elimination. Consequently similar enhancement effect of H^+ or HY by coordination to Ni is conceivable. Interaction of HCl with an organoplatinum complex has recently been reported.[1b] Hydrochloric acid shows a lower enhancement effect for the reductive elimination of **1**. It does not causes the reductive elimination at room temperature, and elevation of the temperasture is needed for the reductive elimination (No. 2 in Table 1).

Table 1. Products of the reactions of NiAr$_2$(bpy) with HY[a]

No.	Complex	HY[b]	N_2, Air, or O_2	Temp[c] °C	Product/%[d] Ar-Ar	Product/%[d] ArH
1	1	TFA (1.1 M)	Air	r.t.	100	0
2	1	HCl (1.0 M)	Air	100	100	0
3	1	TFA (neat)	N_2	r.t.	0	50
4	1	TFA (neat)	Air	r.t.	95	0
5[e]	2	HNO_3 (6.0 M)	Air	r.t.	97	0
6	3	HNO_3 (0.3 M)	Air	30	83	15
7	3	HCl (0.3 M)	O_2	30	72	23
8	3	HCl (0.3 M)	Air	r.t.	29	67
9	3	HCl (0.3 M)	N_2	50	0	ca.100
10	3	HBr (0.3 M)	Air	30	ca.100	tr[f]
11	3	HBr (0.3 M)	N_2	50	ca.100	tr[f]

[a] In DMSO except for Nos. 3 and 4. Reaction time = 10 - 24 h. [b]TFA = trifluoroacetic acid. Concentration is given in the parentheses. [c] r.t. = room temperature. [d] determined by GLC and/or NMR. [e] From ref. 2. [f] tr = trace.

However, the reductive elimination reaction of **1** apparently requirs the presence of oxygen. Under an atmosphere of N_2, the rate of the reaction of **1** with CF_3COOH (1.1 M) in DMSO was very slow and formation of only a trace amount of ArH (pentafluorobenzene) was observed; the reductive elimination product was not formed in the reaction under N_2 at room temperature. By using neat CF_3COOH at room temperature, the yield of the acidolysis product is increased (No. 3), although even in neat CF_3COOH the reductive elimination is preferred under air (No. 4).

A similar acceleration effect of O_2 on the acid-induced reductive elimination is clearly observed for the reaction of **3** with HCl (Nos. 7-9). The role of oxygen is not clear at the moment. However, recently effects of O_2 on the reductive elimination reaction of nickel complexes have been demonstrated,[6] and the reductive elimination reaction of NiAr$_2$(bpy) may be enhanced by simultaneous coordination of the Brønsted acid and O_2 to nickel. As described above, $NiAr_2$(bpy) is stable under air in the absence of HY.

In the case of HBr, it causes the reductive elimination both in the presence and in the absence of O_2 (Nos. 10 and 11 in Table 1). UV-visible spectroscopic studies indicate that the reactions under air and N_2 proceed with a clear isosbestic point at 313 nm. The above shown results reveal that the new type of acceleration of the reductive elimination by HY can occur with various $NiAr_2$(bpy)-type complexes and it is affected by the kind of HY and the reaction conditions.

References and Notes

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