Synthesis of *cis*-Bis(heteroaryl)nickel(II) Complexes and Reductive Elimination of Bis(heteroaryl) Products Induced by Protic Acid

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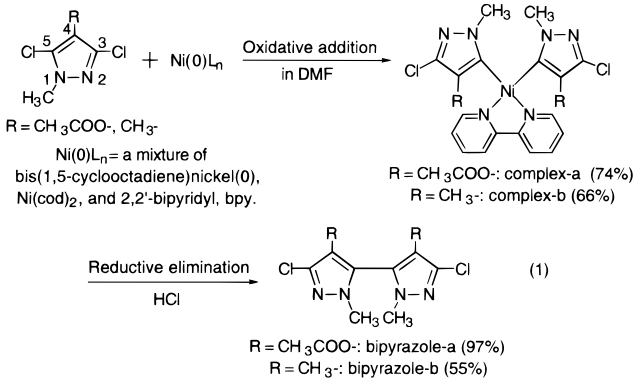
Introduction. Diarylnickel(II) complexes are usually observed in the trans configuration,[1] the *cis*-diarylnickel(II) complexes being unstable.[2] A few examples of *cis*-diarylnickel-(II) complexes with highly electron-withdrawing aryl groups have been reported.[3]

In the course of our research on Ni(0)-complex-promoted polycondensation of dihaloaromatic compounds,[4] we have found (i) that the reaction of a Ni(0) complex with 3,5-dichloropyrazoles gives new thermally stable *cis*-type bis(heteroaryl)nickel-(II) complexes and (ii) that the bis(heteroaryl)nickel(II) complexes undergo unique acid-promoted reductive elimination of the heteroaryl groups to give bipyrazoles.

Results and Discussion. Reactions of the 3,5-dichloro-1-methylpyrazoles[5] shown in eq 1 with a mixture of bis(1,5-cyclooctadiene)nickel(0)[6] ($Ni(cod)_2$: 1.5 mol/mol of dichloro-1-methylpyrazole) and 2,2′-bipyridyl (bpy: 1.5 mol/mol of dichloro-1-methylpyrazole) in DMF for 24 h at 60 °C afford complexes **a** and **b**, respectively. These are considered to be formed through oxidative addition of the C(5)−Cl bond to the Ni(0) complex followed by disproportionation of the NiCl(Ar)-Ln type oxidative addition product, similar to the formation of $Ni(C_6F_5)_2(bpy)$ from a Ni(0) complex and C_6F_6.[3c]



^{1}H NMR data and mass spectroscopic and elemental analyses (Supporting Information) agree with the structure of the complexes.

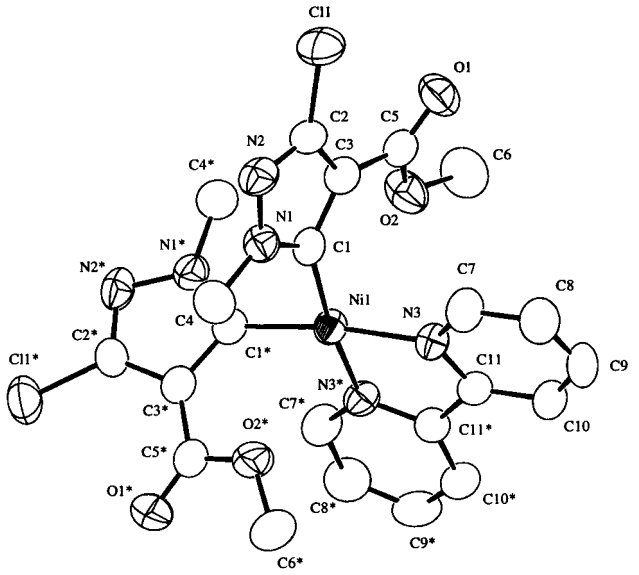


Figure 1. Perspective drawing of complex **a**. Selected bond lengths (Å) and angles (deg): Ni(1)−C(1) 1.886(4), Ni(1)−N(3) 1.947(3); C(1)−Ni(1)−C(1) 87.8, N(3)−Ni(1)−N(3) 82.6, N(3)−Ni(1)−C(1) 95.3.

X-ray crystallography of complex **a**[7] unequivocally confirms the *cis*-type square planar structure as depicted in Figure 1. The Ni−C (1.886 Å) and Ni−N (1.947 Å) bond distances are comparable to those (1.905 and 1.937 Å, respectively)[8] of an analogous bpy−Ni(II) complex with the highly electron-accepting C_6F_5 group: $Ni(C_6F_5)_2(bpy)$.[3c] The complex is the first example of an isolated *cis*-bis(heteroaryl)nickel(II) complex.

The obtained complexes show highly thermal stability in TGA analysis. For example, complexes **a** and **b** are stable up to 306 and 178 °C under N_2, respectively, and start decomposition at these respective temperatures. They are soluble in various organic solvents including $CHCl_3$, Me_2SO, and DMF, and they are highly stable even in the solution under air. For example, no chemical change is observed after heating the DMF solution of the complexes at 60 °C for 5 h under air; drying the solution recovers the original complex as proved by ^{1}H NMR spectroscopy. In addition, the complexes are inert during workup using various reagents such as ammonia and EDTA.

The following two factors seem to contribute to the high stability of the complexes. First, the 5-pyrazoyl group is considered to have an electron-withdrawing nature due to its containing both electron-withdrawing imine C═N nitrogen[4,9] and the Cl substituent; the electron-withdrawing nature of the

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(7) A crystal of complex **a** suitable for crystallography was obtained by recrystallization from chloroform/hexane. The crystal was mounted in a glass capillary tube. The IR spectrum of the crystal is identical to that of the main product of the reaction expressed by eq 1. The compound crystallizes in monoclinic space group *C*2/*c* (No. 15), with $a = 11.712(5)$ Å, $b = 13.896(5)$ Å, $c = 14.875(8)$ Å, $V = 2404(1)$ Å^3, $Z = 4$, and $\beta = 96.70(4)°$. The calculated density and total number of electrons in the cell are 1.553 g cm^{-3} and $F(000) = 1152$. $R = 4.3\%$; $R_w = 3.3\%$.

(8) Unreported data.

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5-pyrazolyl group may be comparable to that of the C_6F_5 group as judged from the analogous geometries around the Ni atoms of complex **a** and $Ni(C_6F_5)_2(bpy)$ (see above). Second, substituents at the 2- (or *o*-) position of the aryl ligand usually contribute to the stabilization of the Ni−aryl bond significantly,[10] presumably by blocking the reaction site, and such an effect in the present complexes is also conceivable.

The C−Cl bond in complexes **a** and **b** is inert toward added Ni(0) complexes, and dehalogenative polycondensation[4] of the complex to give a polymer complex has not been successful. Similar inertness of C−halogen bonds in ligands (e.g., aryl ligand) of Ni complexes toward added Ni(0) complexes has been reported.[11] Complexes **a** and **b** show negligible conductivity (smaller than that of $Ni(PPh_3)_4$) in DMF (at 5.0×10^{-3} M). Complex **b** is considered to have a *cis*-bis(heteroaryl)nickel(II) structure similar to that of complex **a**.

The highly stable complexes, however, smoothly undergo reductive elimination on treatment with acids such as hydrochloric acid (6 M) or nitric acid (6 M), evolving bipyrazole by reductive elimination. In the case of the reaction of complex **a**, analytically pure bipyrazole-a (eq 1) is obtained in 97% yield. On the other hand, the crude product obtained from complex **b** needs purification by column chromatography: bipyrazole-b is thus isolated in a 55% yield.

The Ni−R bond is normally cleaved by protic acid to give RH; however, such a product was not obtained. Although the reductive elimination of R−R from the *cis*-type Ni complex NiR_2Ln or activation of the Ni−R bond proceeds under various conditions,[12] occurrence of the reductive elimination by the interaction with protic acid is unique. A detailed mechanism for the reductive elimination has not been clarified; however, enhancement of the reductive elimination by the interaction of the Ni center with protic acid is conceivable, similar to the enhancement of the reductive elimination by interaction with a π-acid or a Lewis acid.[12]

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Supporting Information Available: Text describing the experimental details of this work (2 pages). An X-ray crystallographic file, in CIF format, for complex **a** is available on the Internet only. Ordering and access information is given on any current masthead page.

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