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INSERTION OF CARBON DIOXIDE INTO THE Ni-R BOND OF NiR_2(bpy) (R = CH_3, C_2H_5) AND ELIMINATION OF DIETHYL KETONE FROM THE INTERMEDIATE PRODUCT $Ni(C_2H_5)(OCOC_2H_5)$(bpy)

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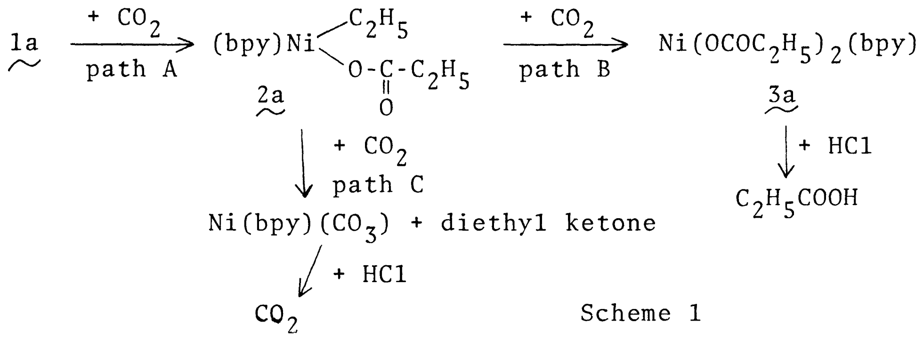
$Ni(C_2H_5)_2$(bpy)(bpy = 2,2'-bipyridine) reacts with CO_2 in benzene at 40-50°C to afford diethyl ketone and nickel propionate. Diethyl ketone seems to be formed through an intramolecular rearrangement in an intermediate product $Ni(C_2H_5)(OCOC_2H_5)$(bpy). A similar reaction of $Ni(CH_3)_2$(bpy) gives nickel acetate.

Insertion of CO_2 into transition metal-carbon bonds is a subject of recent interest. It has been reported that CO_2 can be inserted into several transition metal-carbon bonds including Ti-C,1) Fe-C,2) Co-C,3) and Cu-C,4) but insertion of CO_2 into a Ni-C bond has no precedent. We now report insertion of CO_2 into the Ni-R bond of NiR_2(bpy) (R = CH_3, C_2H_5) and elimination of diethyl ketone from the intermediate product $Ni(C_2H_5)(OCOC_2H_5)$(bpy).

When a benzene (2.2 ml) solution of $Ni(C_2H_5)_2$(bpy)5) 1a (200 mg, 0.73 mmol) was allowed to react with carbon dioxide (1 atm, 2.1 mmol)* in a sealed Schlenk type tube for 12 h at 40-50°C, formation of diethyl ketone (0.68 mol/1a, determined by GC and NMR) was observed. Drying up the reaction mixture gave a green residue, whose acidolysis by dry HCl gave propionic acid (0.24 mol/1a, determined by GC) and carbon dioxide. The IR spectrum of the green residue showed strong bands at 1605, 1535, and 1370 cm^{-1} which are assignable to ν(C=O) and ν(C-O) bands of metal carboxylates or carbonates.

These results can be elucidated by assuming insertion of CO_2 into the $Ni-C_2H_5$ bond (path A) and an intramolecular rearrangement of $Ni(C_2H_5)(OCOC_2H_5)$(bpy) thus produced (path C):



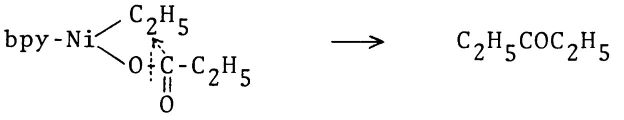
Scheme 1

In order to obtain evidence to support Scheme 1 we prepared 2a by an independent route treating 1a with an equimolar amount of propionic acid in tetrahydrofuran (THF) at -78°C.

$$\underset{\text{deep green}}{\mathbf{1a}} + C_2H_5COOH \longrightarrow \underset{\text{deep red}}{\mathbf{2a}} + C_2H_6\,(0.89\ \text{mmol}/\mathbf{1a}) \qquad (1)$$

Addition of hexane yielded a deep red powder of 2a. Analytical data (Found: C, 57.2; H, 5.0; N, 8.9; C_2H_6/Ni(acidolysis by H_2SO_4) = 0.91. Calcd.: C, 56.8; H, 5.7; N, 8.8) roughly agreed with the structure; Recrystallization of 2a was unsuccessful due to instability of the complex in solutions at room temperature (vide infra). Klein and Karsch[6)] have prepared a monoalkylnickel(II) carboxylate with two PMe_3 ligands.

On standing a THF solution of 2a at room temperature for 1 day, diethyl ketone (52 %/2a) was liberated into the solution. Diethyl ketone seems to be formed through scission of the bond between O and propionyl moiety in the C_2H_5COO group and combination of the propionyl moiety with the ethyl group bonded to nickel:



$$\text{bpy-Ni}(C_2H_5)(OC(O)C_2H_5) \longrightarrow C_2H_5COC_2H_5 \qquad (2)$$

It is known that non-transition metal alkyls such as RLi and RMgX react with carboxylic acids to afford ketones.[7)] However, formation of ketone by a similar reaction of an organotransition metal compound with carboxylic acid has no precedent.

Parallel to the intramolecular rearrangement of 2a a bimolecular disproportionation of 2a occurred to give 1a and $Ni(OCOC_2H_5)_2(bpy)$ (light green):

$$2\ \mathbf{2a} \longrightarrow \mathbf{1a} + Ni(OCOC_2H_5)_2(bpy)\ (\mathbf{3a}) \qquad (3)$$

The visble spectrum of 2a in THF gradually changed to that of 1a. A small amount of precipitate formed turned out to include $Ni(OCOC_2H_5)_2(bpy)$ by comparing its IR spectrum with that of an authentic sample prepared by a 1:2 reaction between 1a and C_2H_5COOH. If we take into account the occurrence of the disproportionation reaction concerning 2a, two reaction pathways are conceivable to yield 3a from 2a in Scheme 1, one being a further insertion of CO_2 into the remaining $Ni-C_2H_5$ bond in 2a and another the disproportionation reaction. Reaction of 1a with 3a did not give diethyl ketone.

In contrast to the reaction of 1a, $Ni(CH_3)_2(bpy)_2$ 1b gave only a trace amount of the corresponding ketone in the reaction with CO_2. The reaction of 1b (0.52 g, 2.1 mmol) with CO_2 (1 atom, 2.8 mmol) for 15 h at 80°C afforded a black precipitate, whose IR spectrum showed bands characteristic of nickel carboxylates. Addition of C_2H_5Br (excess) to the black precipitate gave $CH_3COOC_2H_5$ (0.22 mol/1b). These results indicate that CO_2 insertion into the $Ni-CH_3$ bonds did take place but the intramolecular rearrangement of $NiCH_3(OCOCH_3)(bpy)$ to give acetone (Type 2 reaction) proceeds with difficulty in contrast to its ethyl homolog.

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