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Formation of *n*-Butyldiazoate by Reaction of $[M(CN)_5NO]^{2-}$ ($M = Fe, Ru, Os$) with Lithium *n*-Butylamide

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Summary: The reactions of $[M(CN)_5NO]^{2-}$ ($M = Fe, Ru, Os$) with lithium n-butylamide are reported for the first time. Free (E)-n-butyldiazoate was found as the only product arising from the amide. This result and the reinvestigation of the reactions of n-butylamine with $[Fe(CN)_5NO]^{2-}$ and $[Ru(bpy)_2(NO)Cl]^{2+}$ give a strong indication that diazoates (and/or diazoic acids) are intermediates in the reactions of amines with these nitrosyl complexes.

Our group is exploring the possibility of obtaining stabilized diazonium ions by reaction of primary amines with coordinated nitrosyl ligands. This route was first pointed out by Meyer et al.,[1] who obtained aromatic diazonium salts stabilized by coordination to ruthenium through the reaction of $[Ru(bpy)_2(NO)Cl]^{2+}$ with aniline and other aromatic amines.

In previous works we have studied the reaction of *n*-butylamine, benzylamine, and other aliphatic amines with $[Fe(CN)_5NO]^{2-}$ and $[Ru(bpy)_2(NO)Cl]^{2+}$ (bpy is 2,2'-bipyridyl),[2-5] finding evidence for the stabilization by coordination of the corresponding diazonium salts. In this work we have explored for the first time the reaction of lithium *n*-butylamide with $[M(CN)_5NO]^{2-}$ ($M = Fe, Ru, Os$). *n*-Butylamide has the advantage over *n*-butylamine of being a much more potent nucleophile. This not only accelerates a nucleophilic attack to NO but also brings up the possibility of using nitrosyl complexes which are not electrophilic enough for reacting with amines.

Although in previous works[1-5] diazoates ($RN{=}NO^-$) and diazoic acids were proposed as intermediates for the formation of diazonium salts in reactions of amines with these nitrosyl complexes, there was no evidence supporting this suggestion. In this work we provide strong evidence indicating that the formation of diazonium salts in these reactions occurs via the corresponding diazoates.

When a THF solution of lithium *n*-butylamide[6] was added at 0 °C to a pyridine solution of $(tba)_2[Fe(CN)_5NO]$ (tba is the tetra-*n*-butylammonium ion), the initially pale yellow solution turned brown immediately. ^{13}C NMR of the reaction mixture in pyridine−THF−C_6D_6 showed four signals of almost equal intensity at δ (ppm) 14.1, 20.7, 30.0, and 54.1, corresponding to (*E*)-*n*-butyldiazoate.[9] The only other observed product was

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(4) Doctorovich, F.; Granara, M.; Di Salvo, F., *Transition Met. Chem.* **2001**, *26*, 505.

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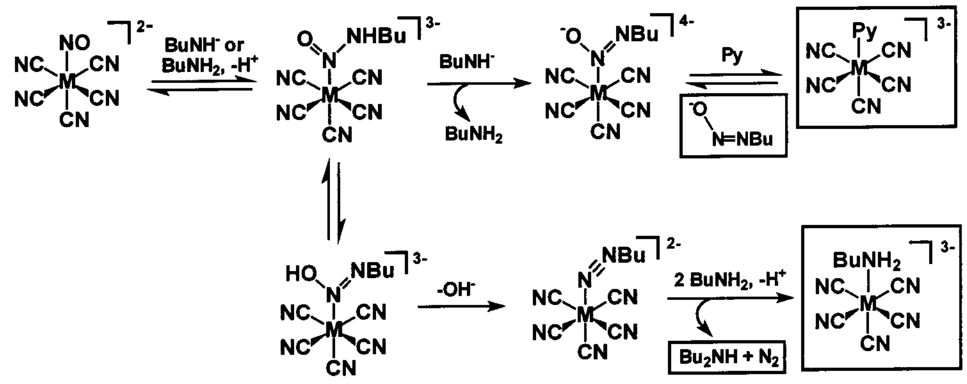
Scheme 1. Proposed Mechanism for the Reactions of Lithium *n*-Butylamide and *n*-Butylamine with $[M(CN)_5NO]^{2-}$ (M = Fe, Ru, Os)



n-butylamine in a 1:1 ratio with respect to the diazoate, as indicated by the height of the corresponding ^{13}C NMR signals. The yield of (*E*)-*n*-butyldiazoate was 80%, as determined by treatment of the reaction mixture with aqueous HCl, followed by GC quantitation of the resulting *n*-butanol. No rearrangement products (2-butanol and butenes) derived from the intermediate diazonium ion were observed by GC or ^{13}C NMR. Although only 40−50% of *n*-butanol is expected to be produced by hydrolysis of (*E*)-*n*-butyldiazoate, due to rearrangement of the butyldiazonium intermediate,[12] it is likely that under the present conditions the small amount of diazoate complex in equilibrium with the pyridine complex (see Scheme 1) decomposes faster—or at a higher pH—than the free diazoate due to the strong back-donation induced by the negative $[Fe(CN)_5]^{3-}$ moiety, which probably makes the diazoate less acidic. Therefore, the diazonium ion produced by hydrolysis is probably coordinated to the metal and it is attacked by OH^- before rearrangement takes place. We have demonstrated in previous works[2,3] that $n\text{-}BuN_2^+$ is strongly stabilized by coordination to the $[Fe(CN)_5]^{3-}$ moiety. At this point we should make clear that, although the diazoate complex is most likely formed as drawn in Scheme 1, the nitrogen atom attached to the metal is the least basic and it is possible that after being released from the metal it will coordinate back through the other nitrogen atom (the one α to the carbon atom) and/or the oxygen atom.

A precipitate was observed when the reaction with lithium *n*-butylamide was carried out at concentrations of complex higher than 0.1 M. FTIR analysis of the precipitate showed a signal at 2052 cm^{-1}, characteristic of cyanides corresponding to a $[Fe(CN)_5]^{3-}$ moiety. The UV−visible spectrum of the precipitate after addition of pyrazine showed bands corresponding to $[Fe(CN)_5(pz)]^{3-}$ (pz = pyrazine),[11] indicating the presence in the reaction mixture of a $[Fe(CN)_5L]^{3-}$ complex with L being a labile ligand. The supernatant showed ^{13}C NMR signals corresponding to (*E*)-*n*-butyldiazoate. These facts confirmed that (*E*)-*n*-butyldiazoate was not coordinated to iron. The same behavior was observed even at low amide to complex ratios (such as 0.2:1), suggesting that the diazoate is labile enough as a ligand to be replaced not only by the highly nucleophilic amide but also by pyridine present as solvent.

FTIR inspection of the reaction mixtures at amide to complex ratios varying from 0.2:1 up to 4:1 showed that the nitrosyl signal at 1880 cm^{-1} disappeared completely at a ratio between 2:1 and 3:1. The yield of diazoate increased linearly as the amount of *n*-butylamide increased up to a stoichiometric amide to complex ratio of ≅2:1, as semiquantitatively determined by comparing the height of the ^{13}C NMR signals due to diazoate with the height of the signals corresponding to tba. This is consistent with a mechanism (Scheme 1) in which 1 equiv of amide adds nucleophilically to the nitrosyl, while a second equivalent rapidly abstracts a proton from the diazoic acid before its decomposition (which produces a diazonium ion)[12] takes place. A third equivalent of amide could replace the resulting diazoate, although pyridine competes favorably in this step due to its high concentration.

When the reaction was carried out with $(tba)_2[Ru(CN)_5NO]$ and $(tba)_2[Os(CN)_5NO]$, signals attributable to *n*-butyldiazoate were observed again by ^{13}C NMR. Addition of pyrazine in the case of the Ru complex showed UV−visible bands corresponding to $[Ru(CN)_5(pz)]^{3-}$,[11] while in the case of the Os complex the bands corresponding to $[Os(CN)_5(py)]^{3-}$ were observed even after dilution with water.[11] $[Os(CN)_5(py)]^{3-}$ was quanti-

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(6) Lithium *n*-butylamide was prepared by following the method suggested by Collum.[7] Dropwise addition at −78 °C of 5 mL of 1 M *n*-butyllithium in hexane to 5 mL of a 1 M solution of *n*-butylamine in hexane produced a white precipitate of lithium *n*-butylamide. After a few minutes the precipitate was centrifuged and washed several times with anhydrous hexane. The hexane layer was separated by means of a syringe, and the remaining solid was dried under vacuum immediately prior to use. The amide can be kept at −18 °C for 2 weeks before noticeable decomposition takes place. A ^{13}C NMR spectrum was obtained in hexane−THF−C_6D_6: δ (ppm) 14.6, 21.3, 42.9, 48.5. Reactions of lithium *n*-butylamide with nitrosyl complexes: lithium *n*-butylamide dissolved in anhydrous THF and titrated with *tert*-amyl alcohol using phenanthroline as an indicator[8] was added to a 2 M pyridine solution of the corresponding complex and allowed to react at 0 °C protected from light. The reaction was instantaneous, as judged by the color change. The complex to amide ratios studied ranged from 1:0.2 to 1:4.

(7) Aubrecht, K. B.; Lucht, B. L.; Collum, D. B. *Organometallics* **1999**, *18*, 2981.

(8) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(9) The product was compared with an authentic sample obtained following the method by Thiele,[10] as described in the Supporting Information. The ^{13}C NMR shifts are slightly different due to the change in solvent and counterion. Several unsuccessful attempts were made to dissolve the independently prepared sodium (*E*)-*n*-butyldiazoate in a THF−pyridine mixture with/without the addition of tetrabutylammonium salts or crown ethers. Presumably, the (*E*)-*n*-butyldiazoate formed in the reaction is kept in solution by the presence of the tetrabutylammonium counterion.

(10) Thiele, J. *Chem. Ber.* **1908**, *41*, 2806.

(11) Baraldo, L. M.; Forlano, P.; Parise, A. R.; Slep, L.; Olabe, J. A. *Coord. Chem. Rev.* **2001**, *219−221*, 881.

(12) Ho, J.; Fishbein, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 6611.

fied by measuring its UV−vis band at 318 nm (yield 96%). These results indicate that the diazoate complex is labile enough as to be substituted by pyridine even in the case of the inert osmium complex. To observe the intermediate diazoate complex, reactions with $(tba)_2[Ru(CN)_5NO]$ and $(tba)_2[Os(CN)_5NO]$ were carried out at −45 °C (minimum temperature before pyridine solidifies) and were followed by UV−visible spectroscopy. However, no intermediates were observed under these conditions, indicating that coordinated diazoate is replaced rapidly by other ligands (less than a few seconds).

The formation of *n*-butyldiazoate by reaction of $[Fe(CN)_5(NO)]^{2-}$ with lithium *n*-butylamide contrasts with the formation of dibutylamine as the main product in the reaction of the same complex with *n*-butylamine.[2] This can be explained if the diazoic/diazoate equilibrium shown in Scheme 1 is shifted to the left far enough to form a diazenido species by loss of hydroxide. Attack of *n*-butylamine on the α-carbon of the diazenido moiety produces dibutylamine. Although the reaction of $[Fe(CN)_5(NO)]^{2-}$ with *n*-butylamine was reinvestigated to look for the presence of *n*-butyldiazoate as an intermediate, no indication of its presence was found by NMR. However, when the diazotization reaction of *n*-butylamine with $[Ru(bpy)_2(NO)Cl]^{2+}$—which also yields products derived from an *n*-butyldiazenido species[3]—was studied at amine:complex = 3:1, the ^{13}C NMR spectrum of the reaction mixture at short times showed among other signals those corresponding to free (*E*)-*n*-butyldiazoate, indicating that the corresponding diazoic acid is an intermediate for the formation of *n*-butyldiazonium ion. A signal at 3.53 ppm corresponding to the methylene α to the diazoate group was observed by ^1H NMR. The ^{15}N NMR spectrum of the reaction mixture obtained starting with $[Ru(bpy)_2(^{15}NO)Cl]^{2+}$ showed a signal at 154 ppm (reference CH_3NO_2) corresponding to ^{15}N-(*E*)-*n*-butyldiazoate.[13] *n*-Butylamine is basic enough to abstract the proton from the diazoic acid, producing diazoate,[14] although the diazoic/diazoate equilibrium is not shifted toward the diazoate as far as in the case of the highly basic amide (Scheme 1), and therefore, products arising from the decomposition of the diazonium ion are observed.[3] In the case of the less electrophilic moiety $[Fe(CN)_5]^{3-}$ the acidity of the coordinated diazoic acid is decreased due to back-donation from the electron-rich metal center, and in the reaction of $[Fe(CN)_5(NO)]^{2-}$ with *n*-butylamine the diazoic acid/diazoate equilibrium is shifted toward the diazoic acid, which rapidly loses hydroxide ion to form the *n*-butyldiazonium salt.

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Supporting Information Available: Text giving experimental procedures not contained in this work and a figure showing the ^{13}C NMR spectrum of the reaction mixture. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Lown, J. W.; Chauhan, S. M. S.; Koganty, R. R.; Sapse A.-N. *J. Am. Chem. Soc.* **1984**, *106*, 6401.

[14] The pK_a for *n*-butyldiazoate is 8.77.[12]