Addition compounds of alkali-metal hydrides.
25. Facile reaction of borinic esters with lithium monoethoxyaluminohydride to form lithium dialkylborohydrides

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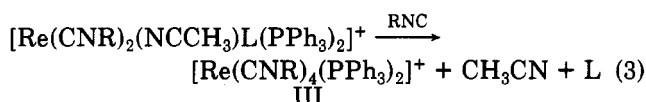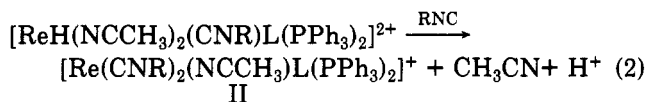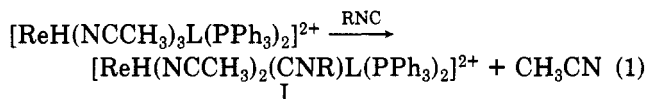
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[ReH(NCCH₃)₃L(PPh₃)₂](BF₄)₂, where L = CH₃CN or py, was reacted with *tert*-butyl isocyanide in refluxing ethanol for 3 h (85% yield). Thus it appears that in the reaction of RNC ligands with [ReH(NCCH₃)₃L(PPh₃)₂](BF₄)₂, where L = CH₃CN, py, C₆H₁₁NH₂, and *t*-BuNH₂, the following steps occur:

$$[\text{ReH(NCCH}_3)_3\text{L(PPh}_3)_2]^{2+} \xrightarrow{\text{RNC}}$$
$$[\text{ReH(NCCH}_3)_2(\text{CNR})\text{L(PPh}_3)_2]^{2+} + \text{CH}_3\text{CN} \quad (1)$$
$$\text{I}$$

$$[\text{ReH(NCCH}_3)_2(\text{CNR})\text{L(PPh}_3)_2]^{2+} \xrightarrow{\text{RNC}}$$
$$[\text{Re(CNR)}_2(\text{NCCH}_3)\text{L(PPh}_3)_2]^{+} + \text{CH}_3\text{CN} + \text{H}^{+} \quad (2)$$
$$\text{II}$$

$$[\text{Re(CNR)}_2(\text{NCCH}_3)\text{L(PPh}_3)_2]^{+} \xrightarrow{\text{RNC}}$$
$$[\text{Re(CNR)}_4(\text{PPh}_3)_2]^{+} + \text{CH}_3\text{CN} + \text{L} \quad (3)$$
$$\text{III}$$

Depending upon the reaction conditions (solvent, temperature) and the nature of L, these reactions can afford products I, II, or III. This sequence of steps ((1)–(3)) was confirmed upon monitoring the reaction between [ReH-(NCCH₃)₃(H₂NC₆H₁₁)(PPh₃)₂](BF₄)₂ and *t*-BuNC by cyclic voltammetry. By this means we obtained electrochemical evidence for the sequential formation of I, II, and III. Note that in the reactions which produce II, significant quantities of the 17-electron dicationic analogues [Re(CNR)₂-(NCCH₃)L(PPh₃)₂](BF₄)₂ are always produced. We believe

that this oxidation is brought about through the reaction of II with the HBF₄ that is released in step 2. Separate experiments (e.g., the addition of HBF₄ to CH₂Cl₂ solutions of [Re(CN-*i*-Pr)₂(NCCH₃)py(PPh₃)₂](BF₄) have confirmed that such an oxidation indeed occurs.

Addition Compounds of Alkali-Metal Hydrides. 26. Facile Reaction of Borinic Esters with Lithium Monoethoxyaluminohydride To Form Lithium Dialkylborohydrides[1]

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Addition of 1 mol equiv of borinic esters to lithium monoethoxyaluminohydride in ethyl ether at 0 °C results in a facile and rapid precipitation of the dialkoxyalane as a solid, producing the corresponding lithium dialkylborohydride in quantitative yield. The reaction is quite general, applicable to borinic esters of widely varied structural requirements. These derivatives are very stable and can be stored under nitrogen at 25 °C without hydride loss and either redistribution or isomerization of the alkyl groups. Methyl iodide or acids readily and quantitatively removes metal hydride from these dialkylborohydrides, generating the free dialkylboranes for further use. Thus the present study provides a simple method for preparing a wide variety of lithium dialkylborohydrides under mild conditions, valuable intermediates for storing dialkylboranes for extended periods of time, and a simple procedure for generating pure dialkylboranes as required for further application.

The utility of trialkylborohydrides as powerful selective reducing agents in organic synthesis is well-known.[3] Recently several routes to synthesize hindered and highly hindered trialkylborohydrides have been developed.[4] In contrast, very little is known about lithium borohydrides

with less than three alkyl groups on boron.[5,6] In large part, this deficiency can be attributed to the marked lability of dialkylboranes and the lack of general procedures for preparing them. Moreover, the synthetic routes that are well established for the synthesis of trialkylborohydrides are not applicable to the preparation of dialkylboro-hydrides.[6,7] For example, the most elegant synthesis of

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Table I. Lithium Dialkylborohydrides Prepared from Borinic Esters

borinic esters R₂BOMe₂	lithium dialkylboro-hydride LiR₂BH₂, R	isolated yield,[a] %	^{11}B NMR chem shift, δ (multiplicity)	J_{BH}, Hz	IR ν_{B-H}, cm^{-1}
methyl di-*n*-butylborinate	*n*-butyl	90	−16.4 (t)	67	2032
methyl di-*n*-hexylborinate	*n*-hexyl	78	−16.4 (t)	67	2027
methyl bis(2-methyl-1-propyl)borinate	2-methyl-1-propyl	88	−19.1 (t)	67	2092
methyl bis(3-methyl-2-butyl)borinate	3-methyl-2-butyl	75	−12.3 (t)	68	2095
methyl dicyclohexylborinate	cyclohexyl	84	−9.3 (t)	67	2009
B-methoxyboralane	tetramethylene	78	−20.2 (t)	71	2183
B-methoxyborinane	pentamethylene	80	−18.9 (t)	68	2102

[a] Determined by hydride analysis. See Experimental Section.

lithium trialkylborohydrides is the reaction of *tert*-butyllithium with trialkylboranes (eq 1).[8]

$$R_3B + (CH_3)_3CLi \xrightarrow{\text{THF, −78 °C}} LiR_3BH + (CH_3)_2C{=}CH_2 \quad (1)$$
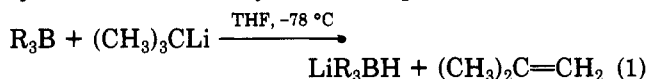
Unfortunately, dialkylboranes react with *tert*-butyllithium to yield a mixture of products.[7] We recently reported a synthetically useful preparation of pure lithium dialkylborohydrides.[5] Thus, triethylenediamine–dialkylborane complexes (TED·BHR₂) were treated with lithium aluminum hydride (LiAlH₄) to give lithium dialkylborohydride (LiR₂BH₂) in quantitative yield (eq 2). However, this method is limited to those dialkylboranes that can be readily prepared by hydroboration of hindered olefins.[9]

$$TED \cdot BHR_2 + LiAlH_4 \xrightarrow[\text{0.5 h}]{\text{EE, 0 °C}} LiR_2BH_2 + TED \cdot AlH_3 \downarrow \quad (2)$$
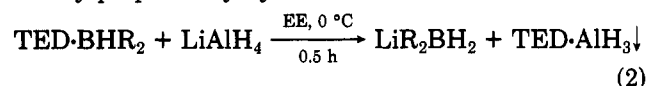
We previously demonstrated that the reaction of methyl dialkylborinates with LiAlH₄ in the presence of olefins gives mixed trialkylboranes in high yields.[10] Presumably, the dialkylborane, produced in situ, is rapidly captured by the olefin to give the desired product (eq 3). When this

$$3R_2BOMe + LiAlH_4 + 3\text{olefin} \rightarrow$$
$$R_2BR^1 + LiAlH(OMe)_3 \quad (3)$$

reaction was performed in the absence of olefin, a heterogeneous mixture resulted, from which the dialkylborane could not be separated.[11] In the course of our reappraisal of this reaction, we discovered that LiAlH₄ and R₂BOMe, in 1:1 ratio, cleanly produced the corresponding lithium dialkylborohydrides (eq 4). Encouraged by this result, we undertook to examine the reaction of LiAlH₄ with a representative series of borinic esters.

$$R_2BOMe + LiAlH_4 \xrightarrow[\text{0.5 h}]{\text{THF, 25 °C}} LiR_2BH_2 + AlH_2(OMe) \quad (4)$$
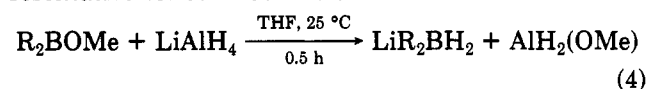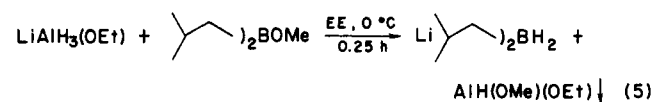
Results and Discussion

Addition of a tetrahydrofuran (THF) solution of LiAlH₄ to methyl di-*n*-hexylborinate in THF at 0 °C resulted in a moderately exothermic reaction. Examination of the clear solution by ^{11}B NMR revealed a triplet (δ −16.4 (*J* = 67 Hz)) attributed to the clean formation of lithium di-*n*-hexylborohydride. The same solution showed an aluminum signal in the ^{27}Al NMR spectrum. Evidently, the byproduct alkoxyalane is readily soluble in THF. We carried out this reaction in ethyl ether (EE) and in *n*-

pentane, but similar results were obtained. These results indicated that a clean synthesis of lithium dialkylborohydride might be achieved if the aluminum-containing byproduct could be completely removed from the solution. We had recently observed that both trialkoxyalane and dialkoxyalane precipitate quantitatively from ether solvents.[1,12] Accordingly, we examined the reaction of borinic esters with lithium diethoxyaluminohydride (LDEA) and lithium monoethoxyaluminohydride (LMEA) in EE.

Both LDEA and LMEA were prepared from LiAlH₄ and ethyl acetate following published procedure.[13] An EE solution (0.5 M) of methyl diisobutylborinate was added to a slurry of LDEA in EE at 0 °C. A white solid separated from the solution. Following the addition, the reaction mixture was well mixed and centrifuged. Examination of the clear supernatant solution by ^{11}B NMR showed the presence of lithium diisobutylborohydride together with a minor amount of unreacted borinic ester. Analyses by ^{27}Al NMR and IR spectroscopy revealed the solution to be free of any aluminum-containing product. However, this reaction, while interesting, is not useful for the preparation of lithium dialkylborohydride since it is not quantitative.

Addition of a 0.5 M EE solution of methyl diisobutylborinate to LMEA in EE at 0 °C resulted in a mildly exothermic reaction with the formation of a white precipitate. The reaction mixture was centrifuged. Examination of the clear supernatant solution by ^{11}B NMR showed the clean formation of the desired lithium dialkylborohydride. Analyses by ^{27}Al NMR and IR spectroscopy revealed the solution to be free of any aluminum containing compound. Evidently, the reaction proceeds as shown in eq 5. We then applied this reaction to various other borinic esters. All of these compounds underwent rapid and essentially quantitative reaction. The reaction is exceedingly rapid, essentially complete in 0.25 h at 0 °C.

$$LiAlH_3(OEt) + (\diagdown\diagup)_2BOMe \xrightarrow[\text{0.25 h}]{\text{EE, 0 °C}} Li(\diagdown\diagup)_2BH_2 +$$
$$AlH(OMe)(OEt) \downarrow \quad (5)$$

The borohydrides were isolated and dissolved in a known amount of solvent, and the concentration was estimated by hydrolysis.[9] The yields were then calculated from the molarity of the solution. The purity of the dialkylborohydrides was determined by its ^{11}B NMR, ^{27}Al NMR, and IR spectra. The results are summarized in Table I.

One of the intriguing problems in borane chemistry has been the relative instability of dialkylboranes.[9] Workers in this area have usually been acutely aware of the possibilities for isomerization and redistribution. On the other

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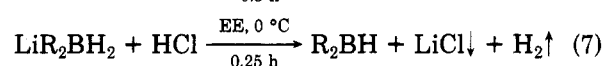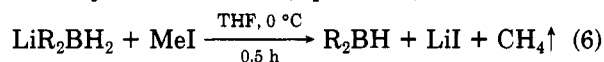
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hand, these lithium dialkylborohydrides are very stable and can be stored under nitrogen even at 25 °C without any hydride loss and either redistribution or isomerization of the alkyl groups. Consequently, it is now possible to store these dialkylboranes as their lithium borohydrides for extended periods of time, converting them into the corresponding free dialkylboranes when needed by a convenient simple reaction, treatment either with methyl iodide or hydrochloric acid (eq 6 and 7).

$$LiR_2BH_2 + MeI \xrightarrow[0.5 \text{ h}]{\text{THF, 0 °C}} R_2BH + LiI + CH_4\uparrow \quad (6)$$

$$LiR_2BH_2 + HCl \xrightarrow[0.25 \text{ h}]{\text{EE, 0 °C}} R_2BH + LiCl\downarrow + H_2\uparrow \quad (7)$$

We encountered no difficulty in generating these dialkylboranes nor in utilizing them for typical organoborane applications.

Application of Lithium Disiamylborohydride for the Selective Hydroboration of Vinylcyclohexene. 4-Vinylcyclohexene and lithium disiamylborohydride (LiSia$_2$BH$_2$) in THF were mixed together at 0 °C. The free disiamylborane was liberated by adding excess methyl iodide. The reaction was complete within 2 h. The reaction mixture was then washed with water to remove lithium iodide and then oxidized. The usual workup[14] afforded 2-(4-cyclohexenyl)ethanol in 84% GC yield (eq 8).
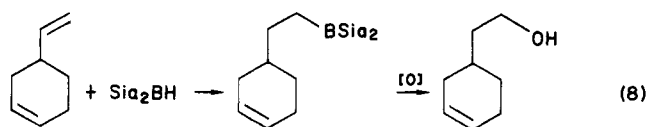
Application of Lithium Pentamethyleneborohydride in the Zweifel Cycloalkylidene Synthesis. Lithium pentamethyleneborohydride was reacted with methyl iodide at 0 °C to generate free borinane. The borinane thus prepared was utilized in the Zweifel cycloalkylidine synthesis using 1-iodo-1-hexyne.[15] The pentylidinecyclohexane was isolated in 60% yield (eq 9).
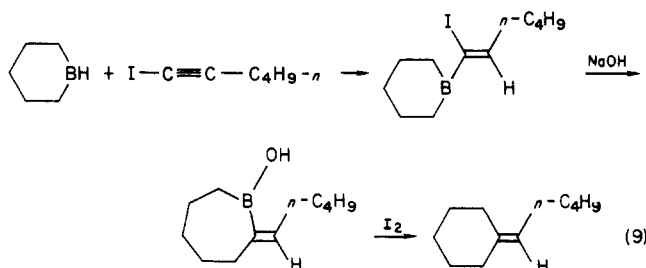
Application of Lithium Dicyclohexylborohydride in the Zweifel Cis Olefin Synthesis.[16] Dicyclohexylborane was precipitated in THF from lithium dicyclohexylborohydride by using methyl iodide, and 1-hexyne was added to it at 0 °C. The vinylborane thus formed was treated with aqueous sodium hydroxide and iodine to yield *cis*-1-cyclohexyl-1-hexene (68% isolated yield) (eq 10).

Conclusion

Lithium monoethoxyaluminohydride reacts rapidly and quantitatively with all of the borinic esters examined to give the corresponding lithium dialkylborohydrides. Under the reaction conditions, the byproduct, presumably the dialkoxyalane, precipitates quantitatively from the solution. The borinic esters are readily available from the
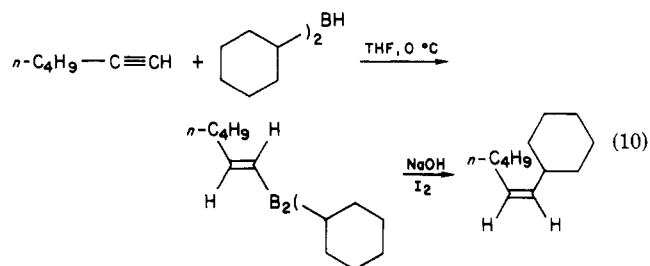
corresponding dialkylhaloboranes.[17] Consequently, this procedure provides a convenient entry into lithium dialkylborohydrides. Furthermore, reaction of methyl iodide with these dialkylborohydrides provides a rapid and quantitative means of generating the corresponding dialkylborane for further study and utilization.

Experimental Section

All operations were carried out under a nitrogen atmosphere with oven-dried glassware.[9] The spectra were obtained in an inert atmosphere. The infrared spectra were obtained with a Perkin-Elmer 1420 spectrometer using sealed cells and a two-syringe technique. The ^{11}B NMR and ^{27}Al NMR spectra were recorded on a Varian FT-80A spectrometer. The ^{11}B NMR chemical shifts are in δ relative to EE·BF$_3$ with chemical shifts downfield from EE·BF$_3$ assigned as positive. The ^{27}Al NMR chemical shifts are in δ relative to Al(NO$_3$)$_3$.

Materials. Tetrahydrofuran (THF) was distilled from LiAlH$_4$ and stored under nitrogen. Anhydrous ethyl ether (EE) was purchased from Mallinckrodt, Inc., and used directly. Lithium monoethoxyaluminohydride (LMEA) and lithium diethoxyaluminohydride (LDEA) were prepared from LiAlH$_4$ and ethyl acetate in EE following literature procedure.[13] All of the borinic esters were prepared by published procedures.[17] LiAlH$_4$ (1.0 M) in EE was purchased from Aldrich Chemical Co.

Reaction of Borinic Esters with Lithium Monoethoxyaluminohydride. The following procedure for the preparation of lithium diisobutylborohydride is typical. A 50-mL centrifuge vial fitted with a rubber septum and a magnetic stirring bar was charged with 10 mL of a 1.0 M EE solution of LiAlH$_4$. To this was added a 1.0 M EE solution of ethyl acetate (5 mL, 5 mmol) at 25 °C with stirring. The resulting LMEA was cooled to 0 °C, and a 0.5 M EE solution of methyl diisobutylborinate (20 mL, 10 mmol) was added with constant stirring. After the addition, the reaction mixture was mixed well and then centrifuged. The clear supernatant solution was transferred via double-ended needle to another vial. The solid dialkoxyalane was washed with EE (2 × 5 mL), and the washings were combined with the supernatant solution. The solvent EE was evaporated under reduced pressure (12 mmHg). The residue (2.0 g) was dissolved in THF (18 mL), and the resulting solution was estimated by hydride analysis:[9] 0.44 M; 8.8 mmol (88% yield); ^{11}B NMR δ -19.1 (t, J = 67 Hz); IR ν 2092 cm^{-1}. No signal attributable to the presence of aluminum compounds in the solution could be detected either in ^{27}Al NMR or in the IR spectrum.

Application of Lithium Disiamylborohydride. Selective Hydroboration of 4-Vinylcyclohexene. Free disiamylborane (5 mmol) was generated from lithium disiamylborohydride (5 mmol) by treating it with methyl iodide (7 mmol) in THF at 0 °C. Hydroboration of 4-vinylcyclohexene (6 mmol) was carried out, by using this reagent, as recommended in the literature.[14] The resulting trialkylborane was washed with water (2 × 2 mL) to remove lithium iodide. After the usual oxidation of the hydroboration product, analysis by GC, using n-dodecane as internal standard, showed 84% of 2-(4-cyclohexenyl)ethanol.

Application of Lithium Pentamethyleneborohydride in the Zweifel Cycloalkylidene Synthesis. To a 1.0 M THF solution of lithium pentamethyleneborohydride (15 mmol) cooled to 0 °C was added methyl iodide (25 mmol) with constant stirring. Borinane was generated quantitatively within 1 h. The reaction of 1-iodo-1-hexyne (14 mmol) with this reagent was carried out

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following Zweifel's procedure.[15] The product pentylidinecyclohexane was purified by distillation: 1.28 g (60% yield); bp 94–96 °C (12 mmHg).

Application of Lithium Dicyclohexylborohydride. The Zweifel Cis Olefin Synthesis. Dicyclohexylborane was generated from a THF solution of lithium dicyclohexylborohydride (10 mmol) at 0 °C by using methyl iodide (15 mmol). Hydroboration of 1-hexyne (12 mmol) with this reagent produced the vinylborane. The product was treated with iodine following Zweifel's procedure.[16] There was produced *cis*-1-cyclohexyl-1-hexene, purified by distillation: 1.13 g (68% yield); bp 93–95 °C (12 mmHg).

Synthesis from Diamines of Mono- and Dinuclear Cyclopentadienyliron Dicarbonyl Carbamoyl Compounds. Crystal and Molecular Structure of (μ-CONH(CH₂)₂NHCO)[CpFe(CO)₂]₂

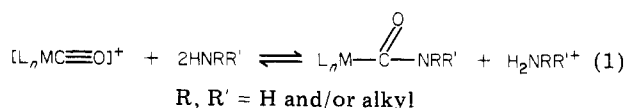Alan J. Lindsay, Sangsoo Kim, Robert A. Jacobson, and Robert J. Angelici*

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The cationic complex [CpFe(CO)₃]PF₆ exhibits three types of reactivity toward diamines. It reacts with the unsymmetrical primary diamine H₂NCH₂CMe₂NH₂ to give the mononuclear cationic carbamoyl complex [CpFe(CO)₂(CONHCH₂CMe₂NH₃)]PF₆ (1); spectroscopic studies indicate relatively strong intermolecular hydrogen bonding between the carbamoyl oxygen and an NH₃⁺ group. Complex 1 is readily deprotonated to yield its neutral analogue CpFe(CO)₂(CONHCH₂CMe₂NH₂) (2) that can be further deprotonated in the presence of [CpFe(CO)₃]PF₆ to form the first reported dinuclear "dicarbamoyl-bridged" complex (μ-CONHCH₂CMe₂NHCO)[CpFe(CO)₂]₂ (3). In addition, [CpFe(CO)₃]PF₆ reacts with the unsymmetrical primary/tertiary diamine H₂N(CH₂)₂NMe₂ and with H₂N(CH₂)₂OH to form exclusively CpFe(CO)₂(CONH(CH₂)₂NMe₂) (4) and CpFe(CO)₂(CONH(CH₂)₂OH) (5), respectively. Finally, [CpFe(CO)₃]PF₆ reacts with symmetrical primary and secondary diamines such as RHN(CH₂)ₓNHR (R = H, x = 2, 3; R = Me, x = 2) and the cyclic diamine piperazine HN(CH₂CH₂)₂NH to yield exclusively the dinuclear dicarbamoyl-bridged complexes (μ-CONR(CH₂)ₓNRCO)[CpFe(CO)₂]₂ (R = H, x = 2 (6); R = H, x = 3 (7); R = Me, x = 2 (8)) and (μ-CON(CH₂CH₂)₂NCO)[CpFe(CO)₂]₂ (9). The molecular structure of complex 6 was determined by X-ray diffraction. The crystals are triclinic of space group P1̄ with two crystallographically independent molecules per unit cell, each having an inversion center, and with cell constants of a = 9.504 (7) Å, b = 8.435 (5) Å, c = 12.989 (9) Å, α = 101.20 (5)°, β = 104.80 (5)°, and γ = 100.49 (5)°. The structure was refined to R = 0.043 and Rw = 0.047 for 1485 independent observed reflections having I ≥ 3.0σ(I). The dimensions of the two crystallographically independent molecules do not differ significantly; the average Fe–C(carbamoyl) distance of 1.99 Å is significantly longer than the average Fe–C(CO) distance of 1.76 Å. The overall geometry of the structure shows the metal centers to be in a transoid orientation about the bridging ligand as dictated by the inversion center, and the central part of the structure adopts a gauche–trans–gauche conformation. Each molecule is connected through weak hydrogen bonds to two others.

Introduction

Many cationic, and to a lesser extent neutral, metal carbonyl complexes are known to react directly with nucleophiles such as ammonia and primary and secondary amines to yield carbamoyl complexes[1–3] (eq 1).

$$[L_nMC{\equiv}O]^+ \; + \; 2HNRR' \; \rightleftharpoons \; L_nM{-}\overset{O}{\overset{\|}{C}}{-}NRR' \; + \; H_2NRR'^+ \quad (1)$$

R, R' = H and/or alkyl

Although an extensive range of amines has been studied in this reaction, no reports involving the analogous reactions with diamines have been noted. In this paper, we report the reaction of [CpFe(CO)₃]PF₆[4] with 2-aminoethanol and a range of diamines to yield both neutral and cationic monomeric carbamoyl complexes, as well as neutral dinuclear dicarbamoyl-bridged compounds. Some of the neutral monomeric complexes have "dangling" NH₂

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