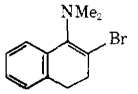
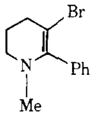
Table I. β-Lithioenamines. Synthesis and Reactions

β-Bromoenamines **1**	Conditions of Br—Li exchange using n-BuLi: Temp, °C	h	E (reagent)	Enamines **3**: % yield[a]	Bp, °C (mmHg)
$EtCBr{=}CHNC_4H_8O$ (**1a**)[b]	−70	1.5	Me (MeI)	45[c]	78 (20)
t-$BuCBr{=}CHNC_4H_8O$ (**1b**)[d]	−70	1.5	H (H_2O)	70[e]	87 (15)
			D (D_2O)	70[e]	87 (15)
			Me (MeI)	64[e]	96 (15)
			Et (EtI)	45[e]	68 (15)
t-$BuCBr{=}CHNEt_2$ (1c)[d]	−20	2.5	Me (MeI)	45[e]	65 (23)
t-$BuC(NC_4H_8O){=}CHBr$ (1d)[b]	−70	10 min[f]	Me (MeI)	75[g]	62 (0.75)
			n-Bu (n-BuI)	50[g]	92 (0.7)
			I (I_2)	50[g,h]	[h]
			MeCHOH— (MeCHO)	50[g]	95 (0.7)
$PhC(NMe_2){=}CHBr$ (1e)[i]	−70	0.5	Me (MeI)	60[c,j]	92 (15)[j]
			Et (EtI)	40[c]	80 (0.65)
			n-Bu (n-BuI)	45[c]	88 (0.8)
 (1f)[b]	−70	1	Me (MeI)	55[c]	96 (0.7)
 (1g)[b]	−70	1.5	Me (MeI)	65[c]	90 (0.6)
			n-Bu (n-BuI)	55[c]	105 (0.7)

[a] Yields of distilled products are given except where noted. The IR, NMR, and mass spectral data are fully compatible with the structures shown; purity was established by gas chromatography. [b] Prepared from the parent enamine according to the procedure of ref 2; the crude bromoenamine was used after filtration and removal of the solvents. Bromoenamine 1g and its parent enamine have already been reported: L. Duhamel and J. M. Poirier, *Tetrahedron Lett.*, 2437 (1976). [c] Based on parent nonhalogenated enamine. [d] Prepared from the bromoaldehyde according to the procedure cited in ref 1. [e] Based on distilled bromoenamine. [f] The quantitative bromine—lithium exchange was also observed with t-BuLi after 30 mn at −70 °C. [g] Based on crude bromoenamine. [h] The β-iodoenamine was decomposed by distillation. [i] Bromine (1.6 g, 10 mmol) in 10 mL of THF was added at −60 °C under nitrogen to dimethylamino 1-phenyl-1-ethylene (1.47 g, 10 mmol) in 25 mL of THF. The reaction mixture was allowed to warm up to 0 °C, and then 18 mL (23 mmol) of n-BuLi (1.3 M in ether solution) was added at −70 °C. [j] Based on 1-phenyl-1-propanone obtained by hydrolysis.

β-Bromoenamines are readily available either by reaction of secondary amines with α-halocarbonyl compounds,[1] or by bromination of the parent enamines and subsequent addition of 1 equiv of base to the intermediate α-bromoiminium salt.[2] If the base was a tertiary amine, such as triethylamine, the crude bromoenamine was used without distillation after filtering the triethylamine hydrobromide and removing the solvent under reduced pressure. When the base used was n-butyllithium, the β-lithioenamine was prepared in a one-pot reaction directly from the parent enamine, as indicated by the following equation.

$$PhC(NMe_2){=}CH_2 \xrightarrow[\text{2.2 equiv of } n\text{-BuLi, } -70°]{\text{1.1 equiv of } Br_2\text{, THF, } -60\ °C} PhC(NMe_2){=}CHLi$$

Bromine-lithium exchange reactions have been observed with various β-bromoenamines: open-chain aldo- and ketoenamines, **1a–d**, and cyclic and heterocyclic enamines, **1f** and **1g**. The ease of exchange decreases with crowding;[3] thus, at −70 °C, the halogen-metal exchange was complete with bromoenamine **1d** after a reaction period of only 10 min, whereas, with the more crowded isomeric β-bromoenamine **1b**, it was only 60% complete after 10 min. With the very crowded enamine **1c**, reaction was only 30% complete after 4.5 h at −70 °C; in this last case, the reaction rate was greatly accelerated by adding small amounts of HMPA (9:1 THF:HMPA, 70% after 4.5 h at −70 °C), or when the temperature was raised (100% after 2.5 h at − 20 °C).

Thus we have in hand β-lithioenamines which can serve in synthesis as equivalents of delocalized anions $^{-}CC{=}Z \leftrightarrow C{=}CZ^{-}$ (Z = O,[4] NR,[5-7] N-NMe$_2$[8]).

Several characteristic advantages of these reagents should be mentioned: (1) their formation is quantitative and rapid even from quite hindered bromoenamines; (2) their reactions with electrophiles are rapid even at very low temperature; (3) alkylation takes place without competitive N-alkylation or polysubstitution; (4) the resulting products are enamines which can be isolated or easily transformed into the corresponding carbonyl compounds.

References and Notes

(1) L. Duhamel, P. Duhamel, and J. M. Poirier, *Bull. Soc. Chim. Fr.*, 221 (1972).

(2) L. Duhamel, P. Duhamel, and J. M. Poirier, *Tetrahedron Lett.*, 4237 (1973).

(3) The yields of exchange were determined by alkylation with CH_3I, followed by VPC and NMR analysis.

(4) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 546–570.

(5) G. Stork and S. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963).

(6) (a) G. Wittig, H. Frommeld, and P. Suchanek, *Angew. Chem., Int. Ed. Engl.*, **2**, 683 (1963); (b) G. Wittig and H. Reiff, *ibid.*, **7**, 7 (1968).

(7) (a) T. Cuvigny and H. Normant, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 1380 (1969); (b) T. Cuvigny and H. Normant, *Bull. Soc. Chim. Fr.*, 3976 (1970).

(8) E. J. Corey and D. Enders, *Tetrahedron Lett.*, 3 (1976).

Lucette Duhamel,* Jean-Marie Poirier

Laboratoire de Chimie Organique de la Faculté des
Sciences et des Techniques de Rouen
76130 Mont Saint Aignan, France

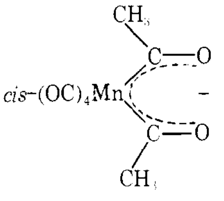
Received June 16, 1977

Reactions of Coordinated Molecules.
15. Preparation and Coordination of the Metallo Analogue of the Triacetylmethanide Anion, *fac*-$(OC)_3Re(CH_3CO)_3^{2-}$

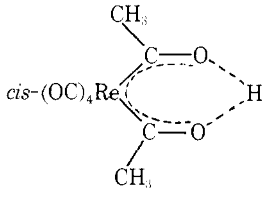
Sir:

We recently reported the preparation of the metallo acetylacetonate anion, **1**, and its coordination to aluminum(III) ion affording the neutral, tris-chelate complex analogous to

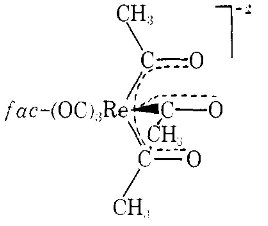
Al(acac)$_3$.[1] The rhenium analogue to the anion, **1**, was formed similarly. This anion also coordinates to metal ions, and it can be protonated at −78 °C using HCl/Et$_2$O affording the first example of a metallo acetylacetone molecule, **2**.[2,3] Several examples of these coordination complexes and metallo β-diketone molecules have been reported.[2,4] The anion, **1**, and the enol tautomer, **2**, are metallo analogues of the corresponding β-diketone species where the M(CO)$_4$ moiety replaces formally the methine group of the organic analogue.



1



2



3

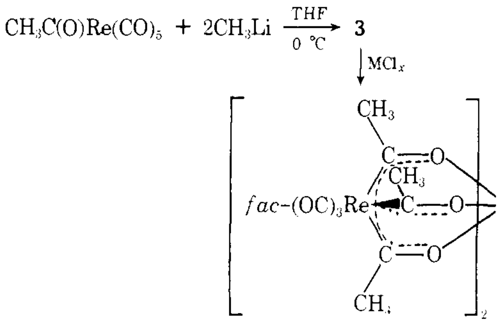
We wish to report the preparation of the *fac*-triacetyltricarbonylrhenate dianion, **3**, and the coordination of this dianion to the aluminum(III) and hafnium(IV) ions affording octahedral coordination complexes.

To a stirred solution of 0.51 g (1.38 mmol) of acetylpentacarbonylrhenium[2] in 50 mL of THF at 0 °C under argon was added dropwise 2.05 mL (3.49 mmol) of a 1.7 M solution of methyllithium in ether. The resulting reddish orange reaction solution was stirred for 90 min and then was treated with a solution of 0.22 g (0.69 mmol) of HfCl$_4$ in 13 mL of THF. The reaction solution was stirred for an additional 1 h at 0 °C and then for 1 h at 25 °C. During this period the solution changed gradually to an amber color. The solvent was removed at reduced pressure, and the residue was extracted with 80 mL of benzene. The mixture was filtered, and the solvent was removed from the filtrate at reduced pressure. Repeating the extraction procedure with 130 mL of toluene, followed by washing the filtrate residue with 3-8-mL portions of pentane, afforded 0.29 g (43%) of the product, [*fac*-(OC)$_3$Re(CH$_3$CO)$_3$]$_2$Hf, as a pale yellow solid: mp 120-200 °C dec; IR (CH$_2$Cl$_2$, in cm^{-1}) ν(CO) 2020 (s), 1925 (vs), ν(C$\cdots$O) 1465 (m); ^{1}H NMR (acetone-d_6 vs. TMS) τ 7.54 (s, CH$_3$).[5] Anal. Calcd for C$_{18}$H$_{18}$O$_{12}$Re$_2$Hf: C, 22.12; H, 1.86; Re, 38.11. Found: C, 22.02; H, 2.16; Re, 37.05.[6]

To a solution of the dianion **3** which was prepared by the above procedure using 0.15 g (0.41 mmol) of acetylpentacarbonylrhenium in 20 mL of THF and 0.94 mmol of the methyllithium solution and stirring for 45 min at 0 °C was added a solution of 0.03 g (0.22 mmol) of anhydrous AlCl$_3$ in 1 mL of THF. The reaction solution was stirred for 2 h at 0 °C and then was treated with 0.13 g (0.21 mmol) of bis(triphenylphosphine)iminium (PPN) tetrafluoroborate.[7] After the mixture was stirred for 20 min, the solvent was removed at reduced pressure. The residue was extracted with 40 mL of methylene chloride and was crystallized from a methylene chloride–heptane (4:1) solution at −20 °C affording 0.06 g (21%) of the product, (PPN)([*fac*-(OC)$_3$Re(CH$_3$CO)$_3$]$_2$Al), as a pale yellow solid: mp 240-265 °C dec; IR (CH$_2$Cl$_2$, in cm^{-1}) ν(CO) 1990 (s), 1900 (vs), ν(C$\cdots$O) 1485 (m); ^{1}H NMR (CD$_2$Cl$_2$ vs. TMS) τ 7.49 (s, 18, CH$_3$), 2.41 (m, 30, C$_6$H$_5$). Anal. Calcd for C$_{54}$H$_{48}$O$_{12}$NP$_2$Re$_2$Al: C, 47.54; H, 3.55; N, 1.03; Re, 27.29; Al, 1.98. Found: C, 46.47; H, 3.56; N. 0.80; Re, 27.03; Al, 2.06.

The tetramethylammonium salt of the above aluminum complex, (Me$_4$N)([*fac*-(OC)$_3$Re(CH$_3$CO)$_3$]$_2$Al), was isolated in 20% yield using the above procedure and substituting (Me$_4$N)BF$_4$ for (PPN)BF$_4$: mp >205 °C dec; IR (CH$_2$Cl$_2$, in cm^{-1}) ν(CO) 1990 (s), 1900 (vs), ν(C$\cdots$O) 1485 (m); ^{1}H NMR (acetone-d_6 vs. TMS) τ 7.49 (s, 18, CCH$_3$), 6.82 (s, 12, NCH$_3$). Anal. Calcd for C$_{22}$H$_{30}$O$_{12}$NRe$_2$Al: C, 29.36; H, 3.36; N, 1.56. Found: C, 29.22; H, 3.45; N, 1.15.

When acetylpentacarbonylrhenium is treated with 2 molar equiv of methyllithium in THF solution, the dianion, **3**, is formed as shown. This stoichiometric reaction is followed easily by IR. During the slow addition of the methyllithium solution, the carbonyl and acyl C–O stretching vibrations of the acetyl complex disappear with the concomitant appearance of the bands expected for the monoanionic rhenium analogue of **1**.[2] The reaction solution is yellow at this point, but the continued addition of another molar equivalent of methyllithium produces a reddish orange color change and the appearance of a two-band ν(CO) pattern at 1957 and 1857 cm^{-1} having a relative intensity of 1:2, respectively. This is the spectrum of the terminal carbonyl ligands of the dianion, **3**.[8] The acyl C–O stretching vibration of **3** appears at 1532 cm^{-1}. The corresponding acyl band of the rhenium analogue of the monoanion **1** appears at 1585 cm^{-1}. The lower frequencies for the carbonyl and acyl bands of dianion **3** are consistent with the increased negative charge of the complex.[10]



4, M = Hf; x = 4; n = 0
5, M = Al, x = 3; n = −1

The dianion **3** coordinates to hafnium(IV) and aluminum(III) ions affording the bis-chelate neutral complex, **4**, and the anionic complex **5**. Both **4** and **5** exhibit the two-band ν(CO) spectrum expected for a *fac*-(OC)$_3$M group. These bands all occur at frequencies higher than the analogous bands of the dianion **3**, and the bands of the neutral hafnium complex, **4**, appear at higher energy than the bands of the anionic aluminum complex, **5**. However, the frequency of the acyl ligands drops from 1532 cm^{-1} in **3** to 1465 and 1485 cm^{-1} in the complexes **4** and **5**, respectively. A similar change is observed when the monoanions of type **1** are complexed to aluminum(III) or gallium(III).[2,4]

The single ^{1}H NMR resonance for the methyl substituents of **4** and **5** indicates that the six methyl groups of each complex are equivalent. This is consistent with the dianion, **3**, acting as a tridentate, chelating ligand which forms bis-chelate, octahedral coordination complexes having idealized D_{3d} symmetry. The methyl resonances of **4** and **5** occur at ~0.32 ppm to higher field than the methyl resonance of the tris-chelate aluminum complex of the rhenium metallo acac ligand, [*cis*-(OC)$_4$Re(CH$_3$CO)$_2$]$_3$Al. This shift may reflect an increase in the electron density located on the acyl ligands in going from a four-carbonyl to a three-carbonyl metallo fragment.

Anion **3** represents formally the metallo analogue of the triacetylmethanide anion, (CH$_3$CO)$_3$C$^-$, where the carbanion is replaced by the isoelectronic *fac*-(OC)$_3$Re^{-2} moiety. When a THF solution of **3** is treated with 2 equiv of HCl/ether at −78 °C, the product obtained by ether extraction shows a two-line ν(CO) pattern at 1990 and 1895 cm^{-1}. This species may be the dienol analogue of complex **2**, although further characterization is needed. Such a complex would not possess a direct, formal carbon analogue.

The preparation and complexation of the dianion **3** and its derivatives and the synthesis of the neutral, dienol complexes are being pursued actively.

Acknowledgment. We thank the University Research Council of Vanderbilt University and the National Science Foundation (Grant No. CHE-76-14304) for support of this research.

References and Notes

(1) C. M. Lukehart, G. P. Torrence, and J. V. Zeile, *J. Am. Chem. Soc.*, **97**, 6903 (1975). The preparation of a similar anion, *cis*-$(OC)_4Mn(CH_3CO)(C_6H_5CO)^-$, was reported earlier; see C. P. Casey and C. A. Bunnell, *J. Chem. Soc., Chem. Commun.*, 733 (1974).

(2) C. M. Lukehart, G. P. Torrence, and J. V. Zeile, *Inorg. Chem.*, **15**, 2393 (1976).

(3) C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, **98**, 2365 (1976).

(4) C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, **99**, 4368 (1977).

(5) Infrared and ^1H NMR spectra were recorded on Perkin-Elmer 727 and JOEL MH-100 spectrometers, respectively. Microanalyses were performed by Galbraith Laboratories, Inc. Knoxville, Tenn.

(6) Hafnium could not be analyzed in the presence of rhenium.

(7) $(PPN)BF_4$ was prepared by the metathesis reaction of (PPN)Cl and $AgBF_4$ in acetone solution in 95% yield.

(8) This dianion is very similar to the dianion $[fac\text{-}(PhCH_2CO)_3Mn(CO)_3]^{-2}$ prepared by M. Y. Darensbourg et al.[9] However, this manganese dianion was prepared quantitatively using a 20-fold excess of $PhCH_2MgCl$. Presumably such an excess of the alkylating reagent would inhibit the successful coordination or protonation of this dianion.

(9) D. Drew, M. Y. Darensbourg, and D. J. Darensbourg, *J. Organomet. Chem.*, **85**, 73 (1975).

(10) The rapid addition of the methyllithium produces **3** directly. If unreacted acetyl complex is present, the dianion **3** will react with it producing the rhenium monoanion analogous to **1**.

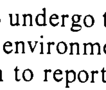
David T. Hobbs, C. M. Lukehart*
Department of Chemistry, Vanderbilt University
Nashville, Tennessee 37235

Received July 26, 1977

Cobalt(II) Induced Amine Deprotonation in Aqueous Solution in the Near Basic pH Range

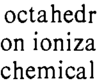
Sir:

There are three major types of N–H bonds generally found in proteins: amide (i), imidazole (ii), and amino ($-NH_2$). Metal



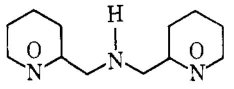
$\overset{O}{\overset{\|}{-C}}-\overset{H}{\overset{|}{N}}-$

i

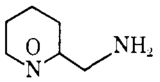


ii

ions have been reported to induce both amide[1] and imidazole[2] proton ionizations which are often accompanied by concomitant stereochemical changes about the metal ion; e.g., the nickel(II) complex of the triglycine undergoes a change from octahedral to square-planar geometry upon amide proton ionization[1c] and the bis(histidinato)cobalt(II) chelate is reported to undergo transformation from an octahedral to tetrahedral environment upon imidazole proton ionization. We now wish to report the first case of stereochemical changes induced in cobalt(II) chelates upon amino proton ionization in aqueous solution near the physiological pH range. We chose to study the colbalt(II) complexes of tridentate bis(2,2′-pyridylmethyl)amine (DPA) (I)[3] and bidentate 2-aminomethylpyridine (AMP) (II)[4] because of possible charge stabilization due to dispersal from the ionized amino group through the metal ion into the pyridine rings via "d"–π^* orbital interactions.[5]



I



II

Potentiometric formation curves of 1:1, DPA·3HCl to cobalt(II), solutions have an inflection at $a = 3$, moles of base per mole of ligand, indicating the formation of $[Co(DPA)(H_2O)_3{}^{2+}]$.[6] At pH 8.5, a second buffer zone with slow equilibrium times (up to 15 min/titration point) is found, indicating that a reaction other than that of a simple deprotonation (usually quite fast) is occurring. The color of the solution turns from pink to deep blue as the deprotonation reaction occurs, indicating a change in cobalt(II) stereochemistry.[7-10] Computer treatment of the titration data indicate that there are two proton ionizations in the second buffer region.[11] Infrared spectra (KBr disk) of the isolated blue compound,-$[Co(H_{-1}DPA)OH]\cdot 3H_2O$[12] indicated the lack of a N–H band. Upon recrystallization from MeOH, the infrared spectrum (KBr disk) of $[Co(H_{-1}DPA)OH]$ (III) contained no N–H band and a sharp strong band at 3640 cm^{-1}, indicating a nonhydrogen-bonded OH group.[13,14] The conductivity of III (9.7×10^{-4} M) in CH_3NO_2 was measured to be 5.4 $\Omega\ cm^2/mol$,[15] and the molecular weight of III obtained by vapor pressure osmometry in MeOH was determined as 265 ± 5. The above indicate that III is a nonionic monomeric metal complex. This together with infrared and visible spectral data supports the formulation of III as $[Co(H_{-1}DPA)OH]$. DPA was found not to undergo amine proton ionization in the presence of Zn^{2+}, Ni^{2+}, or Cu^{2+}.

Potentiometric formation curves of 1:1 and 2:1, *N*-methylbis(2,2′-pyridylmethyl)amine (MeDPA) to cobalt(II), solutions have an inflection at $a = 3$, indicating the formation of $[Co(MeDPA)(H_2O)_3{}^{2+}]$ and $[Co(MeDPA)_2{}^{2+}]$, respectively.[16] In both systems, the color of the solutions remained pink above pH 10, the equilibria times above pH 8 were fast, and there was no near basic buffer zone as in the Co:DPA formation curves. The above indicates that the replacement of the amino hydrogen in DPA by a methyl group drastically alters the solution chemistry of Co^{2+}; i.e., there is no proton ionization in the near basic pH range and there appears to be no change in the stereochemistry of Co^{2+}. The above further supports the ionization of the amino proton in $[Co(DPA)(H_2O)_3{}^{2+}]$.

Potentiometric formation curves of 2:1, AMP·2HCl to cobalt(II), solutions had an inflection at $a = 2$, indicating the formation of $[Co(AMP)_2(H_2O)_2{}^{2+}]$, followed by a second buffer zone similar in nature (long equilibrium times) to that of the 1:1, $Co^{2+}\cdot$DPA, system.[17] Again two protons were liberated in the second buffer zone as the solution turned deep blue, indicating the formation of $[Co(H_{-1}AMP)_2]$.[18] It is interesting to note that $Co(DPA)^{2+}$ with two pyridyl donors per amine undergoes deprotonation at a lower pH value (0.3 unit) than does $Co(AMP)_2{}^{2+}$ with only one pyridyl residue/amine nitrogen. This suggests that the aromatic ring possibly acts as an electron density sink for the deprotonated amine, where charge is dispersed through the "d" orbitals of the metal into the π^*-antibonding orbitals of the pyridine rings. This would also explain why similar amine deprotonation reactions have not been reported in diethylenetriamine or other polyalkylenepolyamine complexes of Co^{2+}.

The biological consequences of the above are possibly great. Deprotonation reactions observed in the metal ion binding of peptides and proteins, often thought to be due to the ionization of peptide protons, could in some cases be due to amino proton ionization. $[Co(DPA)(H_2O)_3{}^{2+}]$ begins to deprotonate at pH 8.5, a pH value similar to that at which bis(glycylglycinato)cobalt(II) starts to undergo amide proton ionization.[19] The