

Reactions of Coordinated Molecules. XXIX. A ^{13}C -NMR Study of the Structure and Bonding of Several Metalla- β -ketoimine Molecules

KEVIN P. DARST and C. M. LUKEHART* [1]

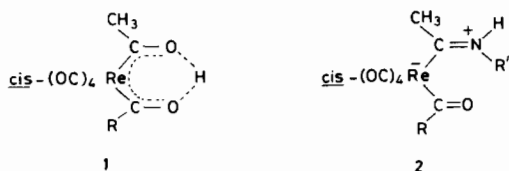
Department of Chemistry, Vanderbilt University, Nashville, Tenn., U.S.A.

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The ^{13}C -NMR spectra of 4-methylamino-3-pentene-2-one and four metalla- β -ketoimine molecules are reported. Spectral comparison permits the assignment of the observed resonances and supports the lack of extensive π -electron delocalization within the zwitterionic metalla- β -ketoimine molecules. The ^{13}C -NMR spectra of the intra- and intermolecularly hydrogen-bonded isomers of the *N*-phenyl rhena-acetylacetonimine complex reveal a significant difference in charge distribution between the two isomers. This charge redistribution may account for the shifts in the ^{13}C and proton NMR resonances which are observed during the intramolecular isomerization.

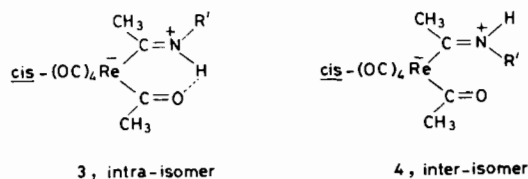
Introduction

We have reported the preparation of several metalla- β -diketone molecules, 1, where R is an alkyl substituent [2]. These complexes are metalla analogues of the enol tautomers of β -diketone molecules where the methine group is formally substituted by the metal complex. The enolate anions of the metalla- β -diketones coordinate to main group and transition metal ions [2–4], and the metalla- β -diketones condense with trigonal boron compounds, BX_2Y , and with primary amines, $\text{H}_2\text{NR}'$, to afford the (metalla- β -diketonato) $\text{B}(\text{X})(\text{Y})$ complexes [5, 6] and the metalla- β -ketoimine molecules, 2, [7, 8], respectively.



Seventeen metalla- β -ketoimine complexes have been prepared, and the X-ray structure of 2, where R' is phenyl, confirms the localized bonding as shown

in the zwitterionic description 2, [7]. Extensive PMR data has verified the geometrical isomerization about the carbon–nitrogen double bond. The two geometrical isomers are referred to as the intramolecularly hydrogen bonded isomer, 3, and the intermolecularly hydrogen bonded isomer 4. The inter-isomers are usually solids, but they isomerize rapidly in solution to the thermodynamically more stable intra-isomers which are usually liquids or low-melting solids.



In a previous ^{13}C -NMR study [9], we examined the solution-phase structures and intramolecular bonding of several metalla- β -diketones and their complexes to aluminum and boron. We wish to report a similar study of the metalla- β -ketoimine molecules, 2, to provide an unambiguous assignment of the ^{13}C -NMR resonances of these molecules, to further examine the unusual electronic structure of this class of compound, and to probe any differences in charge distribution between the intra and inter geometrical isomers 3 and 4.

Experimental

The complexes 2 where R is methyl and R' is hydrogen, 5; R is isopropyl and R' is hydrogen, 6; R and R' are methyl, 7, and where R is methyl and R' is phenyl, 8, and 4-methylamino-3-pentene-2-one were prepared by known procedures [7, 8, 10]. The ^{13}C -NMR spectra were recorded on a Jeol FX90Q Fourier transform NMR spectrometer operating at a frequency of 22.50 MHz as CDCl_3 or d^6 -acetone solutions at 36 °C. The ^2H signal of the solvent was used for locking and a tilt angle of 90° was used. A repetition rate of 1.4 sec was employed to collect 1000–9000 pulses/spectrum. The spectra were proton

*Author to whom all correspondence should be addressed.

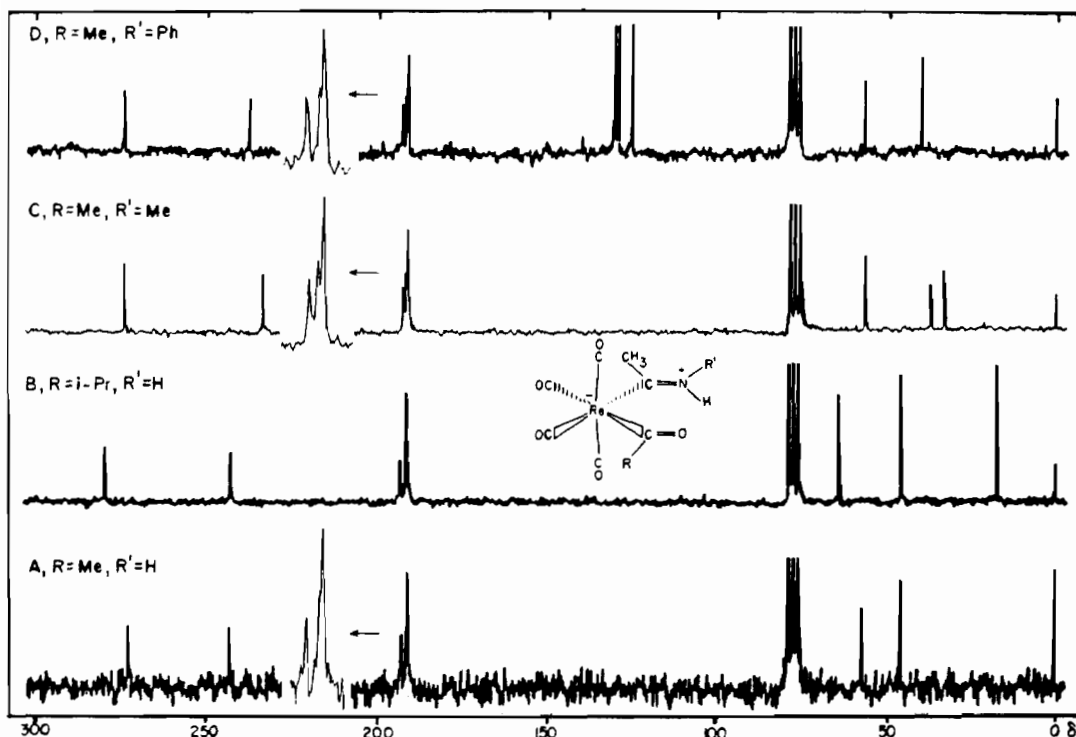


Fig. 1. ^{13}C -NMR spectra of four rhenium- β -ketoimine molecules: (A) *cis*-(OC) $_4$ Re(CH $_3$ CO)(CH $_3$ CNH $_2$), 5; (B) *cis*-(OC) $_4$ Re(*i*-C $_3$ H $_7$ CO)(CH $_3$ CNH $_2$), 6; (C) *cis*-(OC) $_4$ Re(CH $_3$ CO)[CH $_3$ CN(CH $_3$)(H)], 7; (D) *cis*-(OC) $_4$ Re(CH $_3$ CO)[CH $_3$ CN(C $_6$ H $_5$)(H)], 8, in CDCl $_3$ solution. The solvent resonances appear as three peaks centered at δ 77.0 ppm vs. TMS. For the complexes 7 and 8 the spectrum shown is that of the intra-isomer.

decoupled using a 1000 Hz bandwidth. The samples consisted of 25–60 mg of compound and 0.2–0.3 mg of Cr(acac) $_3$ dissolved in 0.4 ml of solvent with TMS as an internal reference. All chemical shifts refer to CDCl $_3$ solution unless stated otherwise. Table I gives the chemical shift values and the peak assignments, and Fig. 1 shows the spectra of complexes 5–8.

Results and Discussion

All spectra were recorded at 36 $^\circ\text{C}$ using CDCl $_3$ as the solvent, unless stated otherwise, and TMS as an internal reference for the ^{13}C -NMR data. Tris(2,4-pentanedionato)chromium, Cr(acac) $_3$, was added to the samples of the organometallic compounds to facilitate the relaxation of the ^{13}C nuclei. The mole percentage of added Cr(acac) $_3$ was *ca.* 1% so an induced shift of the resonances is not expected [11]. The numerical values for the ^{13}C chemical shifts and the assignments of these resonances are provided in Table I.

A general assignment for the ^{13}C -NMR resonances of the metalla- β -ketoimine complexes is provided by comparing the spectra of the parent metalla- β -ketoimine complexes, 5 and 6, which differ only by the substitution of an isopropyl group for a methyl group

on the acyl ligand. In going from the acetyl complex, 5, to the isobutyryl complex, 6, the methyl resonance at 56.7 ppm is lost and is replaced by the methyl and methine carbon resonances of the isopropyl group at 17.1 and 63.6 ppm, respectively, while the methyl resonance at 45.5 ppm remains essentially unchanged. These spectral changes permit the assignment of the two methyl carbon resonances of 5 at 45.5 ppm and 56.7 ppm to the imino- and acetyl-methyl groups, respectively. The acyl carbon resonance at 271.9 ppm in complex 5 is shifted to 279.3 ppm in the isobutyryl complex, 6, which is consistent with an acetyl to isobutyryl ligand conversion [9], while the imino-carbon resonances of 5 and 6 differ by only 0.5 ppm. The imino-methyl and imino-carbon resonances of 5 at 45.5 and 241.7 ppm, respectively, are not significantly shifted in going to the isobutyryl complex, 6, as expected for the presence of the same iminium ligand in each complex.

A comparison of the spectra of the parent imine complex, 5, and its N-methyl analogue, 7, confirms these assignments. These complexes differ only in the N-substitution of the imino ligand which is considered from X-ray structural data to be essentially electronically isolated from the acyl ligand of the molecule [7, 8] in contrast to the high degree of electron delocalization postulated for the metalla- β -

TABLE I. ^{13}C -NMR Data and Peak Assignments for the Complexes $cis\text{-(OC)}_4\text{Re(CO)[CH}_3\text{CN(R')(H)]}^a$.

| Cpd | Isomer | R | R' | CH_3CN | CCO | axial $^{\text{Re-CO}}$ | equatorial | CH_3CN | CCO | Other |
|----------------|--------|---|-------------------------------|------------------------|--------------|-------------------------|----------------|------------------------|--------------|--|
| 5 ^b | — | CH ₃ | H | 45.5 | 56.7 | 189.7 | 190.0 191.5 | 241.7 | 271.9 | — |
| 6 ^b | — | <i>i</i> -C ₃ H ₇ | H | 45.4 | 63.6 | 190.0 | 190.0 192.1 | 241.2 | 279.3 | (CH ₃) ₂ C 17.1 |
| 7 ^b | intra | CH ₃ | CH ₃ | 37.4 | 56.5 | 190.2 | 190.7 191.6 | 232.5 | 273.0 | CH ₃ N 33.3 |
| 8 ^b | intra | CH ₃ | C ₆ H ₅ | 39.7 | 56.4 | 190.1 | 190.4 191.6 | 236.5 | 273.2 | C ₆ H ₅ 124.6, 128.5 129.5, 139.1 |
| 8 ^c | intra | CH ₃ | C ₆ H ₅ | 39.6 | 56.2 | 190.9 | 192.7 | 236.6 | 270.0 | C ₆ H ₅ 125.3, 129.2 130.3 |
| 8 ^c | inter | CH ₃ | C ₆ H ₅ | 55.9 | 44.3 | 190.8 | 191.7 192.8 | 255.5 | 248.0 | C ₆ H ₅ 127.6, 130.1 130.3 |

^aAll chemical shifts in ppm (δ) from TMS. ^bIn CDCl₃ solution. ^cIn d⁶-acetone solution.

diketones [12, 13]. The acetyl-methyl and acyl carbon resonances in complex 7 appear at 56.5 and 273.0 ppm, respectively, representing an average change in chemical shift of less than 0.7 ppm from the corresponding resonances in complex 5. However, the effect of the N-methyl substitution on the imino-methyl and imino-carbon resonances is more pronounced. These resonances appear at 37.4 and 232.5 ppm, respectively, which represent shifts of 8.1 and 9.2 ppm upfield from the corresponding resonances in complex 5. These shifts result from the greater electron donation of the N-methyl substituent as compared to the N-H substituent. The methyl carbon resonance of 7 at 33.3 ppm can be assigned unambiguously to the N-methyl group.

The carbonyl ligands for all of the metalla- β -ketoimine complexes, 5–8, appear between 189.5 and 192.1 ppm in CDCl₃ solution and have a weighted-average chemical shift of 190.4 ppm. The axial-carbonyl resonances for these complexes always appear as a single peak *ca.* 1.0 ppm to higher field from the average value of the equatorial-carbonyl carbon resonances which appear as two separate peaks each having half the relative intensity of the axial-carbonyl resonance. The average anisochronism between these equatorial-carbonyl carbon resonances is 1.3 ppm. The equivalence of the axial-carbonyl carbon atoms and the nonequivalence of the equatorial-carbonyl carbon atoms is consistent with the C_s molecular symmetry of these metalla- β -ketoimine molecules. The equatorial-carbonyl carbon resonances appear at lower field due to the *trans* effect of the acyl and iminium ligands.

It is convenient to compare the ^{13}C -NMR spectrum of 4-methylamino-3-pentene-2-one, CH₃C(O)CH = C(CH₃)N(CH₃)(H), with that of the metalla analogue, $cis\text{-(OC)}_4\text{Re[CH}_3\text{C(O)][CH}_3\text{CN(CH}_3\text{)(H)]}$, 7. In the metalla complex, 7, the N-methyl, imino-

methyl, acyl-methyl, imino and acyl carbon resonances appear at 33.3, 37.4, 56.5, 232.5 and 273.0 ppm, representing a respective downfield shift of 4.2, 19.1, 27.9, 68.8 and 78.7 ppm from the corresponding carbon resonances of the organic β -ketoimine. Similar trends in chemical shifts are observed for the β -diketones and their respective metalla analogues, 1, and are due, presumably, to the substitution of the more electronegative Re(CO)₄ moiety for the methine group of the organic molecules.

When the rhenia-acetylacetone complex, $[cis\text{-(OC)}_4\text{Re(CH}_3\text{CO)}_2\text{)]H}$, 1 where R is methyl, is converted to the metalla- β -ketoimine complex $cis\text{-(OC)}_4\text{Re[CH}_3\text{C(O)][CH}_3\text{CN(CH}_3\text{)(H)]}$, 7, which exists as the intramolecularly hydrogen-bonded isomer 3, the metal carbonyl carbon resonances are shifted downfield an average of only 1.1 ppm. However, the acetyl carbonyl carbon resonance shifts upfield 24.9 ppm, from 297.9 to 273.0 in complex 7, and the imino-carbon atom resonance of 7 appears at 232.5 ppm, which is 65.4 ppm upfield from the acetyl carbonyl carbon resonance in the rhenia-acetylacetone molecule. These large and dissimilar upfield shifts for the acetyl carbonyl and imino carbon resonances of 7 reflect the effect of the incorporation of the more electropositive imino nitrogen atom into the metalla molecule and a lack of extensive pi-electron delocalization throughout the framework of the metalla- β -ketoimine molecule.

The X-ray structure of complex 8 indicates that the rhenium-carbon bonds to the acyl and iminium ligands are essentially single bonds, and the ^{13}C -NMR spectrum should reflect this bonding if it can be shown that the acyl and imine ligands are nearly electronically insulated. When comparing the isostructural metalla- β -ketoimines, $cis\text{-(OC)}_4\text{Re[CH}_3\text{CO][CH}_3\text{CN(R)(H)]}$, where R = H (5), CH₃ (7) and C₆H₅ (8), the methyl-imino and imino-carbon atom

resonances vary from 45.5 and 241.7 ppm to 37.4 and 232.5 ppm to 39.7 and 236.5 ppm, respectively. The acetyl-methyl and acetyl carbonyl carbon atom resonances of these complexes, however, vary less than 0.2 and 0.8 ppm from the average values of 56.5 and 272.7 ppm, respectively. Only very slight variations in chemical shift are observed for the carbon resonances of the metal carbonyl ligands within this series of compounds, also. Clearly, the electronic affects generated by changing the N-substituent is localized predominately within the iminium ligand.

The acetyl carbonyl carbon resonance of complex 7 appears at 273.0 ppm, which is nearly midway between the corresponding resonances of acetyl-pentacarbonylrhenium (244.7 ppm) and the rhenia-acetyl-acetone molecule 1 where R is CH₃ (297.9 ppm). This chemical shift probably reflects the lack of extensive pi-electron delocalization in 7, and the greater electron donation to the rhenium atom from a σ -iminium ligand than from a carbonyl ligand.

The imino-carbon resonance of the N-methyl complex, 7, appears at 232.5 ppm, which is 24.7 ppm upfield from the resonance of the carbenoid carbon atom in the (methylamino)(methyl)-carbene complex, (OC)₅W(CH₃)[N(CH₃)(H)], [14]. We believe that this shift is a greater upfield shift than would be predicted solely from the greater shielding by the more electron-rich rhenium atom, and that it supports the chemical formulation of complex 7 as a metalla- β -ketoimine complex rather than as an acetyl-(methylamino)(methyl)-carbene complex.

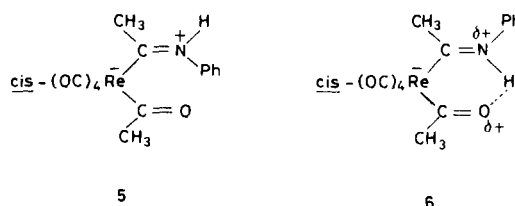
Repeated attempts to record the ¹³C-NMR spectrum of the intermolecularly (inter-isomer) hydrogen bonded isomer of complex 8 in both CDCl₃ and CD₂Cl₂ solutions were thwarted by the rapid isomerization of this isomer to the intramolecularly (intra-isomer) hydrogen-bonded isomer and by the inherent low solubility of this complex in these solvents which precluded short acquisition times. However, both isomers could be observed in d⁶-acetone solution due to the greater solubility in this solvent.

The ¹³C-NMR spectra of the intra-isomer of 8 in CDCl₃ and d⁶-acetone are virtually identical with the greatest difference being that the equatorial metal carbonyl carbon resonances are not noticeably split in the d⁶-acetone solution.

The spectrum of the inter-isomer of 8 shows significant differences from that of the intra-isomer. Specifically, the acetyl, imino and methyl carbon resonances undergo large shifts during the isomerization, while the metal carbonyl and phenyl carbon resonances remain essentially unchanged. Based on relative intensities it appears that the highest field methyl carbon resonance of the inter-isomer should be assigned to the acetyl methyl group and the lower field methyl carbon resonance to the imino methyl group. This assignment requires that during the inter-

to intra-isomer conversion the acetyl methyl carbon resonance shifts to lower field by 11.9 ppm while the imino methyl carbon resonance shifts 16.3 ppm to higher field. These shifts parallel those observed in the well-characterized PMR spectra which were recorded during the isomerization process [7, 8]. Presumably the imino and acetyl carbonyl carbon resonances shift similarly, and also cross past each other affording a reversed assignment of these resonances for the two isomers.

Apparently the charge distribution must differ considerably between the inter- and intra-isomers. The structure of the inter-isomer of 8 has been determined [7], and the intramolecular bond distances are consistent with the idealized structure 5. The above ¹³C-NMR data indicate that the atomic charge on the



rhenium atom is very similar in each complex, but that the acetyl ligand of 5 becomes more electron deficient while the imino ligand of 5 becomes more electron rich upon conversion to the intra-isomer. We suggest that the intramolecular hydrogen bond within the intra-isomer will facilitate a charge redistribution as shown in 6. A complete transfer of the N-H hydrogen atom to the acetyl oxygen atom seems less likely since this does not occur in the organic analogues. This strong O...H hydrogen bond and the resulting charge redistribution may account for the unusual chemical shifts observed for the carbon resonances of the acetyl and imino ligands within each isomer.

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