

and Pt(II) does form robust complexes with both adenine and guanine sites. Conclusions which may be drawn from a review of the literature³⁰ would suggest that Pt(II) complexes suffer the same problems as noted for Ru(NH₃)₅(H₂O)²⁺ in the introduction. This problem is that product distributions are kinetically controlled rather than thermodynamically controlled.

The usefulness of most labile metal centers for specific labeling is limited, because compositions respond so rapidly to changes in conditions which often are a concomitant of doing the experiments of locating the metal ions. An advantage of the system we have described is that the high discrimination of the equilibrium labeling can be exploited and the system can then be fixed in this composition by oxidizing [Ru(NH₃)₄SO₂H₂O]²⁺ to the sulfato ruthenium(III) complex. In principle, specificity can be further improved by substituting NH₃ in the cis positions by other groups.

Conclusions

The rate data in Table II demonstrate that equilibrium is established very rapidly in the reaction of *trans*-Ru(NH₃)₄(SO₃)(H₂O) with nitrogen heterocyclic ligands. With 1,9-dimethylguanine at 1 × 10⁻³ M, the pseudo-first-order rate constant is 0.1 s⁻¹. This equilibrium can be "frozen" by oxidation of S(IV) to S(VI) using H₂O₂ as the oxidant at pH ≤ 4. The position of the rapidly established equilibrium is sensitive to the steric and electronic properties of the entering ligand. These facts make this ruthenium ammine system an attractive candidate for labeling biological materials. The strong (>50) discrimination between guanine and adenine binding sites should make it possible to label the guanine sites in DNA specifically, the equilibrium then being frozen by oxidation of S(IV) to S(VI) and Ru(II) to Ru(III). Furthermore, the coordinated SO₄²⁻ can be selectively replaced by a heavy atom as I⁻ in a Ru(II)-catalyzed substitution process.

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Reactions of Coordinated Molecules. 12.

Preparation of *cis*-(OC)₄Re[CH₃C(O)][CH₃CN(C₆H₅)(H)]: the Ketamine Tautomer of a Metallo-β-ketoimine Molecule

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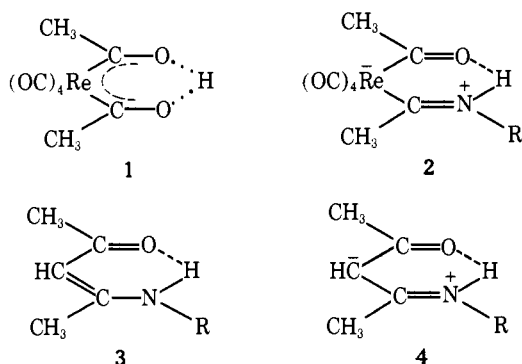
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Abstract: The rhenium metalloacetylacetonate complex, *cis*-(OC)₄Re[C(CH₃)O...H...OC(CH₃)], reacts with two primary aromatic amines, H₂NR (where R is phenyl or *p*-tolyl), affording complexes of the type *cis*-(OC)₄Re[CH₃C(O)][CH₃CN(R)(H)]. The crystal and molecular structure of the *N*-phenyl complex was determined commercially on an Enraf-Nonius CAD4 diffractometer by using Mo Kα radiation: *Pbca*, *a* = 6.838 (2) Å; *b* = 18.807 (5) Å; *c* = 23.729 (5) Å; α = β = γ = 90°; *Z* = 8; *d*_{calcd} = 2.004 g/cm³; *R*₁ = 0.033; *R*₂ = 0.040. The molecular geometry and the spectroscopic data and, especially, the chemical reactivity of the complex are consistent with the chemical formulation of the complex as a metallo-β-ketoimine molecule. The electronic structure is interpreted as a zwitterionic metal complex having a multiple C-N bond. The geometrical isomerization about this bond was followed using ¹H NMR.

In a previous communication, we reported the preparation of the first example of a "metalloacetylacetonate" molecule, **1**.¹ This complex was characterized as the metallo analogue of the symmetrical, enol tautomer of acetylacetonate where the

methine group is replaced formally by the Re(CO)₄ moiety. Several other examples of these "metallob-ketoimine" molecules having various substituents and metallo moieties were prepared recently.² We are currently investigating the simi-

larities in chemical reactivity of complex **1** to that of acetylacetone, and we wish to report that complex **1** condenses with aniline and *p*-toluidine affording the metallo analogues of the corresponding β -ketoimine molecules, **2**.



These complexes represent the metallo analogue of the ketamine tautomer of a β -ketoimine molecule, **3**, where the methine group is replaced formally by the Re(CO)₄ moiety. The molecular structure of the *N*-phenyl complex including the presence of strong intermolecular hydrogen bonding, and, especially, the solution-phase spectroscopic and chemical characterization indicate that this molecule is described best by the zwitterionic ground-state structure, **2**. The analogous nonmetallo structure, **4**, and its various resonance forms presumably account for the greater intrinsic stability of the ketamine tautomer over the enimine or Schiff-base keto tautomers of a β -ketoimine molecule.³

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen. Diethyl ether was dried over Na/K alloy with added benzophenone and methylene chloride was dried over P₂O₅. Both solvents were dried under a nitrogen atmosphere and were freshly distilled before use. All other solvents were dried over 4 Å molecular sieves and were purged with nitrogen before use. The rhenium-enol complex, **1**, was prepared by a literature method.¹

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as solutions in 0.10-mm sodium chloride cavity cells using the solvent as a reference and a polystyrene film as a calibration standard. ¹H NMR spectra were obtained on a JEOL MH-100 NMR spectrometer using Me₄Si as an internal reference, and mass spectra were obtained on a LKB 9000 spectrometer. Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of the β -Ketoimine Complexes. To 0.40 g (1.04 mmol) of complex **1** dissolved in 5 mL of dry chloroform was added dropwise 0.20 mL (2.15 mmol) of aniline at 25 °C. An excess of aniline is used to increase the rate of reaction. After stirring for 24 h the reaction solution was filtered and the solvent was removed at reduced pressure. The crude product was crystallized from distilled ether at -20 °C affording 0.14 g (53%) of the *N*-phenyl analogue of **2** as pale lime-yellow needles: mp 111–112 °C; IR (CH₂Cl₂) ν (CO) 2070 m, 1965 vs, 1935 s, sh, ν (C=O, C=N) 1575 cm⁻¹ m ¹H NMR (CDCl₃ vs. Me₄Si) τ 7.60 (singlet, 3, CH₃CO), 6.79 (singlet, 3, CH₃CN), 2.82–2.56 (complex multiplet, 5, C₆H₅), -1.56 (broad singlet, 1, NH); mass spectrum P (*m/e* 461), ligand fragments predominantly with loss of acetyl and methyl radicals to give (OC)₄ReC(CH₃)-(NHC₆H₅)⁺, base peak (*m/e* 92, C₆H₅NH⁺).

Anal. (C₁₄H₁₂NO₅Re) H, N, C: calcd, 36.52; found, 36.07.

The *N*-*p*-tolyl analogue of **2** is prepared similarly. To 0.30 g (0.78 mmol) of complex **1** dissolved in 5 mL of distilled methylene chloride was added 0.16 g (1.56 mmol) of *p*-toluidine at 25 °C. After stirring for 3 days, the solvent was removed at reduced pressure affording 0.10 g (27%) of the crude product, *cis*-(OC)₄Re[CH₃C(O)]-[CH₃CN(*p*-CH₃-C₆H₄)(H)], which was crystallized from a minimum volume of 10% ether/pentane solution as pale yellow needles: mp 102–104 °C; IR (CH₂Cl₂) ν (CO) 2075 m, 1978 s, sh, 1958 vs, br, 1935 s, ν (C=O, C=N) 1575 cm⁻¹ m; ¹H NMR (CDCl₃ vs. Me₄Si) τ 7.71 (singlet, 3, CH₃), 7.63 (singlet, 3, CH₃CO), 6.94 (singlet, 3, CH₃CN), 2.85 (broad multiplet, 4, C₆H₄), -1.28 (broad singlet, 1,

NH). Anal. (C₁₅H₁₄NO₅Re) H, N, C: calcd, 37.97; found, 38.51.

X-Ray Data, Structure Solution, and Refinement. A 0.05 × 0.05 × 0.07 mm single crystal of *cis*-(OC)₄Re[CH₃C(O)]-[CH₃CN(C₆H₅)(H)] was mounted in a glass capillary on an Enraf-Nonius CAD4 diffractometer by Molecular Structure Corp., College Station, Texas. The crystal and molecular structure was obtained as a commercial, technical service. The automatic centering and angle refinement of 25 reflections (MoK α , λ = 0.71073 Å) yielded the unit cell data: *a* = 6.838 (2) Å, *b* = 18.807 (5) Å, *c* = 23.729 (5) Å, *V* = 3051.6 (10) Å³, *d* (calcd) = 2.004 g/cm³ at 23 °C with *Z* = 8 for the orthorhombic space group *Pbca*.

Intensity data were collected with Mo K α radiation which was filtered by a graphite-crystal incident-beam monochromator. The data were collected with a take-off angle of 5.8° using a θ - 2θ scan of variable scan rate (4–20°/min) for the range of data of 0° < 2θ (Mo K α) < 50° with a scan range of from 2θ (Mo K α_1) - 0.8° to 2θ (Mo K α_2) + 0.8°. Three standard reflections were measured periodically and no significant change was observed. Intensities and standard deviations or intensities were calculated using the formulas

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

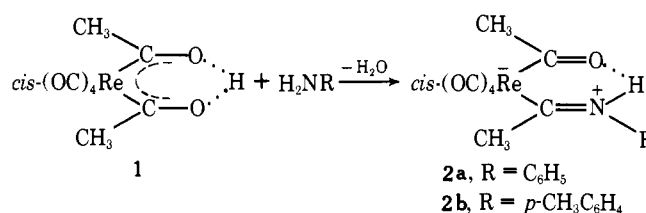
where *S* is the scan rate, *C* is the total integrated peak count, *R* is the ratio of scan time to background counting time, *B* is the total background count, and *p* is a factor introduced to downweight intense reflections and was set at 0.05. Lorentz and polarization corrections were applied to the data. An extinction correction was not necessary and an absorption correction (linear absorption coefficient = 84.36 cm⁻¹) was not necessary owing to the uniform shape of the crystal. Of the 3106 data measured, 1214 had *F*_o² < 3 σ (*F*_o²) and were used in the solution and refinement of the structure.

The structure was solved using the Patterson method. The Patterson map showed the position of the rhenium atom. Least-squares refinement of this atom resulted in agreement factors of *R*₁ = 0.198 and *R*₂ = 0.270 where *R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$ and *R*₂ = $[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. The remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and then refined holding the temperature factors at 4 e Å². The positional parameters of the hydrogen atoms on the phenyl ring were calculated and were not refined. All other hydrogen atoms were located on difference maps. Anisotropic full-matrix least-squares refinement of all nonhydrogen atoms including anomalous scattering contributions for the rhenium atom resulted in final agreement factors of *R*₁ = 0.033 and *R*₂ = 0.040.

The final positional and thermal parameters for all of the atoms are given in Table I. See paragraph at end of the paper regarding supplementary material.

Results and Discussion

A Schiff-base condensation reaction apparently results from treating the rhenium metalloacetylacetone complex, **1**, with a primary aromatic amine as shown below.



The complexes of type **2** are isolated as pale yellow, crystalline solids. These compounds have higher melting points than the metallo- β -diketone complex **1**. This trend in thermal stability is observed also with the organic analogues.

Since the complexes **2** are the first examples of a metallo- β -ketoimine molecule and may, therefore, exhibit extensive reaction and coordination chemistry, we obtained, commercially, an x-ray structure determination of the *N*-phenyl metallo- β -ketoimine complex, **2a**, as a technical service. An ORTEP view of the molecular structure of this complex is shown in Figure 1. Interatomic distances and angles are given in Tables II and III, respectively.

Table I. Final Positional and Thermal Parameters for the Atoms in *cis*-(OC)₄Re[CH₃C(O)][CH₃CN(C₆H₅)(H)]^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	-0.023 41 (7)	0.120 72 (2)	0.125 26 (2)	0.0280 (1)	0.002 02 (1)	0.001 17 (1)	0.0012 (1)	-0.000 51 (8)	0.000 33 (3)
O1	-0.413 (2)	0.1287 (6)	0.1913 (5)	0.041 (3)	0.0055 (5)	0.0030 (3)	0.005 (2)	0.009 (2)	0.0013 (6)
O2	-0.148 (2)	-0.0149 (5)	0.0598 (4)	0.054 (4)	0.0023 (3)	0.0027 (3)	-0.005 (2)	0.005 (2)	-0.0010 (5)
O3	0.178 (2)	0.2417 (6)	0.1940 (5)	0.055 (5)	0.0038 (4)	0.0038 (3)	-0.001 (2)	-0.007 (3)	-0.0018 (6)
O4	0.162 (2)	0.0180 (6)	0.2112 (5)	0.065 (5)	0.0039 (4)	0.0033 (3)	0.007 (3)	-0.006 (2)	0.0022 (6)
O5	0.313 (2)	0.1738 (6)	0.0510 (4)	0.048 (4)	0.0048 (4)	0.0015 (2)	-0.002 (2)	0.001 (2)	0.0022 (5)
N	-0.168 (2)	0.2545 (5)	0.0552 (4)	0.038 (4)	0.0027 (4)	0.0006 (2)	0.006 (2)	0.001 (2)	0.0007 (4)
C1	-0.269 (2)	0.1278 (8)	0.1670 (6)	0.046 (5)	0.0035 (5)	0.0013 (2)	0.002 (3)	0.005 (2)	-0.0011 (8)
C2	-0.107 (2)	0.0362 (7)	0.0826 (6)	0.022 (4)	0.0027 (4)	0.0020 (3)	-0.001 (2)	0.003 (2)	0.0005 (6)
C3	0.099 (2)	0.2006 (7)	0.1672 (6)	0.037 (4)	0.0028 (4)	0.0011 (2)	0.004 (3)	-0.002 (2)	0.0001 (6)
C4	0.091 (3)	0.0564 (7)	0.1796 (6)	0.040 (5)	0.0026 (4)	0.0019 (3)	0.003 (3)	0.001 (2)	0.0018 (6)
C5	-0.118 (2)	0.1891 (7)	0.0553 (5)	0.022 (3)	0.0030 (4)	0.0009 (2)	0.001 (2)	-0.000 (2)	0.0006 (5)
C6	-0.131 (2)	0.1568 (8)	-0.0023 (6)	0.036 (5)	0.0038 (5)	0.0017 (3)	-0.000 (3)	-0.001 (2)	-0.0005 (7)
C7	-0.186 (2)	0.2996 (7)	0.1051 (6)	0.031 (4)	0.0020 (4)	0.0019 (3)	0.003 (2)	-0.002 (2)	0.0002 (6)
C8	-0.052 (2)	0.3509 (7)	0.1168 (7)	0.044 (5)	0.0024 (4)	0.0031 (4)	0.003 (3)	0.006 (3)	0.0009 (8)
C9	-0.086 (3)	0.3972 (8)	0.1587 (7)	0.049 (5)	0.0036 (5)	0.0023 (4)	-0.008 (3)	-0.003 (3)	0.0006 (8)
C10	-0.245 (3)	0.3891 (7)	0.1923 (7)	0.077 (8)	0.0016 (4)	0.0020 (3)	0.001 (3)	-0.003 (3)	-0.0013 (7)
C11	-0.378 (3)	0.3383 (8)	0.1799 (6)	0.055 (6)	0.0035 (5)	0.0021 (4)	0.005 (3)	0.005 (3)	-0.0018 (7)
C12	-0.349 (2)	0.2940 (7)	0.1355 (5)	0.030 (4)	0.0027 (4)	0.0014 (3)	-0.003 (2)	-0.000 (2)	-0.0004 (6)
C13	0.250 (2)	0.1233 (8)	0.0751 (4)	0.044 (4)	0.0042 (5)	0.0002 (2)	0.006 (3)	-0.000 (2)	-0.0007 (8)
C14	0.366 (3)	0.0545 (10)	0.0649 (7)	0.035 (6)	0.0058 (7)	0.0027 (4)	0.002 (4)	-0.003 (3)	-0.0009 (10)
H1	-0.18 (2)	0.272 (5)	0.034 (4)						
H2	-0.25 (2)	0.127 (5)	-0.010 (5)						
H3	-0.13 (2)	0.193 (5)	-0.033 (4)						
H4	-0.01 (1)	0.141 (5)	-0.013 (5)						
H5	0.07 (0)	0.354 (0)	0.095 (0)						
H6	0.00 (0)	0.435 (0)	0.166 (0)						
H7	-0.27 (0)	0.420 (0)	0.224 (0)						
H8	-0.48 (0)	0.332 (0)	0.206 (0)						
H9	-0.44 (0)	0.260 (0)	0.125 (0)						
H10	0.54 (2)	0.048 (6)	0.072 (5)						
H11	0.28 (2)	0.023 (6)	0.050 (4)						
H12	0.36 (2)	0.038 (6)	0.110 (4)						

^a The standard deviations here and in other tables are given in parentheses. The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All hydrogen atoms had isotropic temperature factors of 4.0 Å².

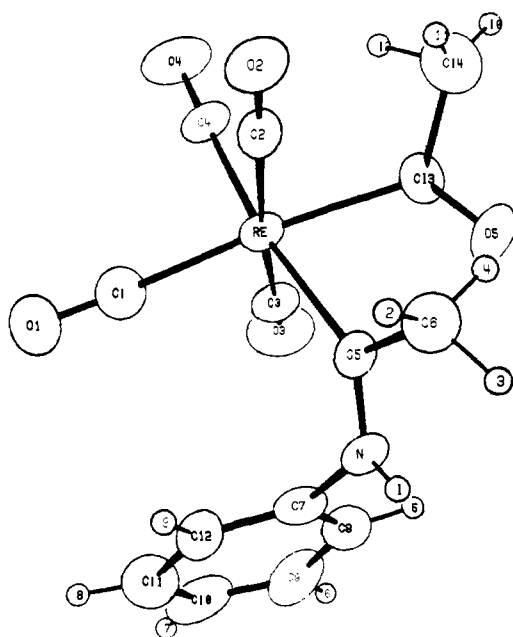


Figure 1. An ORTEP view of *cis*-(OC)₄Re[CH₃C(O)][CH₃CN(C₆H₅)(H)] showing the atomic numbering scheme. The sizes and shapes of the atoms are determined by their final thermal parameters and by their perspective view.

The solid-state structure of **2a** differs from the idealized structure shown above in that the strong intramolecular, unsymmetrical hydrogen bond is actually an intermolecular interaction. This results in a rotation of the imino ligand about

Table II. Interatomic Distances (Å) in *cis*-(OC)₄Re[CH₃C(O)][CH₃CN(C₆H₅)(H)]

Re-C1	1.95 (2)	Re-C2	1.97 (2)	Re-C3	1.99 (2)
Re-C4	1.93 (2)	Re-C5	2.197 (14)	Re-C13	2.22 (2)
O1-C1	1.15 (2)	O2-C2	1.14 (2)	O3-C3	1.14 (2)
O4-C4	1.15 (2)	O5-C13	1.19 (2)	N-C5	1.26 (2)
N-C7	1.47 (2)	C5-C6	1.50 (2)	C7-C8	1.36 (2)
C7-C12	1.33 (2)	C8-C9	1.35 (3)	C9-C10	1.35 (3)
C10-C11	1.35 (3)	C11-C12	1.36 (2)	C13-C14	1.54 (3)
O5-H1	2.26 (15)	N-H1	0.62 (14)	C6-H2	1.03 (11)
C6-H3	1.00 (12)	C6-H4	0.92 (12)	C8-H5	0.96 (2)
C9-H6	0.95 (2)	C10-H7	0.96 (2)	C11-H8	0.96 (2)
C12-H9	0.950 (14)	C14-H10	1.21 (13)	C14-H11	0.93 (14)
C14-H12	1.12 (12)				

the Re-C5 bond. The acyl oxygen atom, O5, is bonded to the enolic proton, H1, of a second molecule generated by the second symmetry operator of the space group while H1 of the reference complex is bonded to the acyl oxygen atom of a third molecule related by the second symmetry operator of the space group and displaced along the *a* axis by -1 unit translation. The O5-H1-N angle is 167 (10)°, and the O5-N contact distance of 2.88 (14) Å indicates the presence of a normal N-H...O type of hydrogen bond.⁴ Also, complex **2a** exists in the solid state as the geometrical isomer of the idealized structure shown above. This isomer is obtained by a 180° rotation about the C-N double bond. However, the isomer shown as **2a** is the predominant species observed in the solution phase (see below).

Other chemically interesting structural features of the molecule follow: (1) The coordination about the Re atom is essentially octahedral (the average value for the angles defining

Table III. Interatomic Angles (deg) in *cis*-(OC)₄Re[CH₃C(O)]-[CH₃CN(C₆H₅)(H)]

C1-Re-C2	93.9 (7)	C1-Re-C3	93.2 (7)
C1-Re-C4	93.1 (7)	C1-Re-C5	95.1 (7)
C1-Re-C13	174.5 (6)	C2-Re-C3	171.8 (6)
C2-Re-C4	87.4 (7)	C2-Re-C5	89.9 (6)
C2-Re-C13	89.2 (6)	C3-Re-C4	88.2 (7)
C3-Re-C5	93.5 (6)	C3-Re-C13	84.1 (6)
C4-Re-C5	171.5 (6)	C4-Re-C13	91.7 (7)
C5-Re-C13	80.3 (5)	C5-N-C7	126. (1)
Re-C1-O1	177. (2)	Re-C2-O2	176. (2)
Re-C3-O3	174. (2)	Re-C4-O4	179. (2)
Re-C5-N	130. (1)	Re-C5-C6	118. (1)
N-C5-C6	112. (1)	N-C7-C8	119. (2)
N-C7-C12	120. (2)	C8-C7-C12	121. (2)
C7-C8-C9	119. (2)	C8-C9-C10	120. (2)
C9-C10-C11	119. (2)	C10-C11-C12	121. (2)
C7-C12-C11	119. (2)	Re-C13-O5	125. (1)
Re-C13-C14	120. (1)	O5-C13-C14	114. (2)
O5-H1-N	167. (10)	C5-N-H1	124. (16)
C7-N-H1	110. (16)	C5-C6-H2	115. (7)
C5-C6-H3	113. (7)	C5-C6-H4	110. (9)
H2-C6-H3	106. (11)	H2-C6-H4	121. (11)
H3-C6-H4	90. (12)	C7-C8-H5	120. (2)
C9-C8-H5	120. (2)	C8-C9-H6	121. (2)
C10-C9-H6	119. (2)	C9-C10-H7	121. (2)
C11-C10-H7	120. (3)	C10-C11-H8	117. (2)
C12-C11-H8	122. (2)	C7-C12-H9	119. (2)
C11-C12-H9	121. (2)	C13-C14-H10	125. (7)
C13-C14-H11	105. (9)	C13-C14-H12	93. (7)
H10-C14-H11	130. (11)	H10-C14-H12	83. (9)
H11-C14-H12	100. (12)		

the principal coordination axes is 172.6°, and the average value of the angles between adjacent coordination sites is 90.8° except for the C5-Re-C13 angle which is 80.3 (5)°. (2) The average values of the terminal carbonyl ligand C-O distance and the Re-C-O angles are 1.145 Å and 176.5°, respectively. (3) The methyl and phenyl substituents of the imino ligand are anti relative to the C5-N bond with the methyl group being closer to the acyl oxygen atom, O5. (4) The sum of the bonding angles about the atoms C5, C13, and N are 360, 359, and 360°, respectively, indicating formalized sp² hybridization. (5) The atoms C5, N, C13, and O5 are essentially coplanar (maximum deviation from planarity is atom C5 of +0.18 Å) with the atoms Re, C6, C14, and H1 being displaced from this plane by -1.13, 1.66, 0.32, and 0.31 (0.10) Å, respectively. (6) The carbon atoms of the phenyl ring are essentially coplanar (maximum atomic deviation from planarity is 0.04 Å), and this plane intersects the C5, N, C13, O5 plane with a dihedral angle of 62.2°.

Although the chemical interpretation of the solid state structure is complicated by the presence of the intermolecular hydrogen bonding and rather large standard deviations of the bond distances, several structural features and, especially, other spectroscopic and chemical evidence indicate strongly that this complex should be formulated *chemically* as a metallo-β-ketoimine complex rather than as an acetyl-aminocarbenoid complex.

The structural features which are consistent with the zwitterionic formulation, **2a**, are, primarily, the intraligand bond distances. The C13-O5 distance of 1.19 (2) Å is more similar to the C-O bond distance (1.22 Å) of normal Re-acetyl ligands⁵ than to the acyl C-O distance of 1.27 (2) Å found in complex **1** where some π-electron delocalization is possible. Also, the C5-N distance of 1.26 (2) Å appears to represent a C-N bond of nearly bond order 2. The value normally accepted for the C-N bond distance within an amide functional group is 1.32 Å,⁸ and the average value of the C(sp²)-N bond distance within seven aminocarbenoid ligands of transition metal

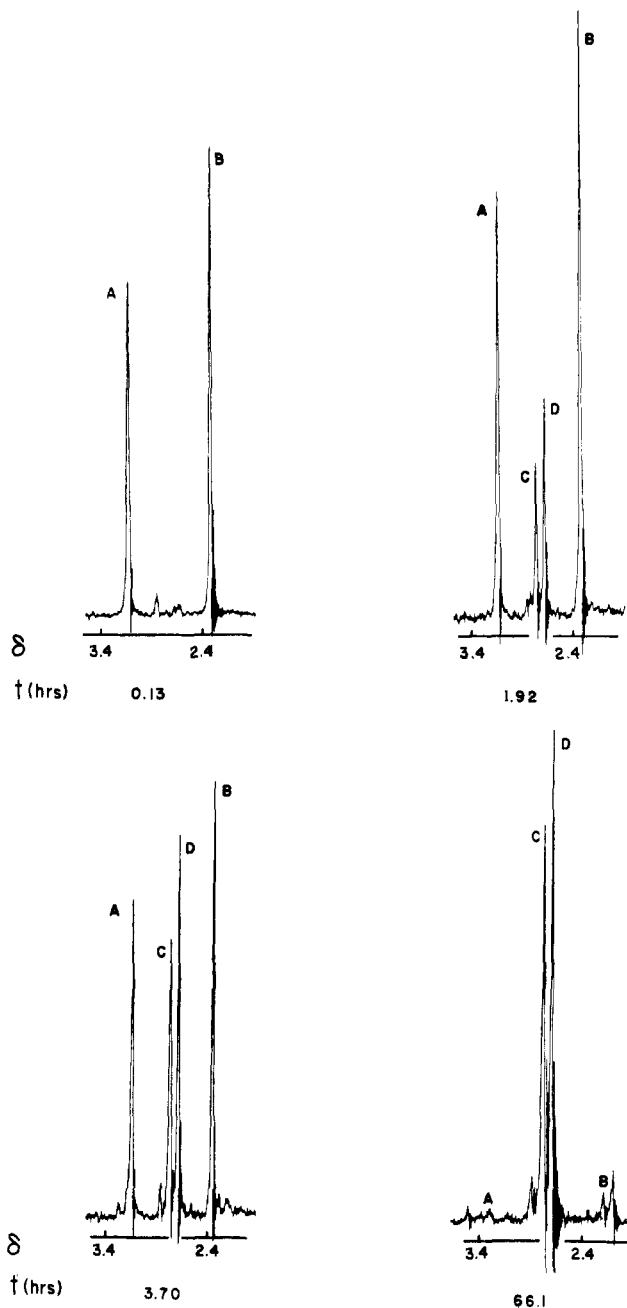


Figure 2. The ¹H NMR spectrum of the methyl region of *cis*-(OC)₄Re[CH₃C(O)][CH₃CN(C₆H₅)(H)] in CDCl₃ vs. Me₄Si at 34 °C showing the geometrical isomerization about the C5-N bond of the intermolecular hydrogen-bonded isomer (resonances A and B) affording the intramolecular hydrogen-bonded isomer (resonances C and D).

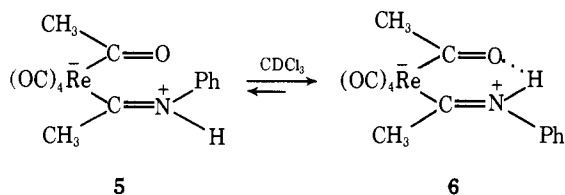
complexes is only 1.33 Å.⁹ Also, the average value of the Re-C5 and Re-C13 distances of 2.21 (1) Å is larger than the corresponding distance in complex **1**, 2.160 (16) Å, and may represent a Re-C(sp²) single bond. The value regarded as an *upper limit* for a Re-C(sp²) single bond is 2.25 Å,⁶ and any extended π-electron delocalization within complex **2a** must be slight since the Re atom lies 1.13 Å below the C5, N, C13, and O5 ligand plane. Steric interactions may favor the observed solid-state conformation which leads to intermolecular hydrogen bonding.

The IR spectrum of **2a** in methylene chloride solution shows only one band in the 1500-1900-cm⁻¹ region at 1575 cm⁻¹. This band appears at 1540 cm⁻¹ as a KBr pellet. This peak is assigned to the C13-O5 and C5-N stretching vibration. The corresponding peak of complex **1** occurs at 1510 cm⁻¹ in methylene chloride solution, and, apparently, at 1598 cm⁻¹

for a CCl_4 solution of *N*-phenylacetylacetoneimine.¹⁰ The most intense terminal carbonyl stretching vibration of both **2a** and **2b** appears at ca. 35 cm^{-1} to lower energy than the analogous band of complex **1**, which is consistent with the greater localization of negative charge on the Re atom of both complexes.

The ^1H NMR and chemical evidence further substantiate the chemical formulation of **2a** as a metallo- β -ketoimine complex. The N-H proton of **2a** resonates at δ 11.56 in CDCl_3 with a width at half-height of 18 Hz. This resonance disappears completely upon adding a drop of methanol- d_4 to the sample solution with no change in the other resonances. The N-H resonances of *N*-phenylacetylacetoneimine and $(\text{OC})_5\text{Cr}[\text{C}(\text{CH}_3)(\text{NHC}_6\text{H}_5)]$ occur at δ 12.6 (CCl_4) and 10.43 (CDCl_3), respectively.^{10,11} The presence of the low-field chemical shift of the N-H proton of a β -ketoimine is considered the best diagnostic evidence for an enolic hydrogen atom.^{10,12}

When a ^1H NMR sample of **2a** in CDCl_3 is placed at $34\text{ }^\circ\text{C}$ for several hours, the spectrum reported above changes with time as shown in Figure 2. The two methyl singlets at δ 3.21 and 2.40 (resonances A and B, respectively) and the enolic N-H resonance at δ 11.56 disappear slowly with the concomitant appearance of two methyl singlets at δ 2.83 and 2.75 (resonances C and D, respectively) and an enolic N-H singlet (15 Hz width at half-height) at δ 15.26. These changes indicate a geometrical isomerization about the C-N double bond of **2a** when going from the solid-state isomer having intermolecular hydrogen bonding, **5**, to the solution-phase isomer having intramolecular hydrogen bonding, **6**.



As expected from the structure of isomer **6** the enolic N-H resonance occurs at very low field,¹ and it disappears completely upon treating with methanol- d_4 with no change in the other resonances. Also, the chemical shift difference between the two methyl resonances of **5** is 81 Hz while the analogous separation in isomer **6** is only 8 Hz even though the respective relative shapes of the methyl resonances of each isomer are identical.

The **5** to **6** isomerization was followed at $34\text{ }^\circ\text{C}$ in CDCl_3 solution using ^1H NMR. The value of the equilibrium constant, K , of 15.86 indicates the nearly complete conversion of **5** into **6** (94% **6** and 6% **5**). Assuming a first-order reaction approaching equilibrium, the value of the overall rate constant, k_t , was calculated to be $4.97 \pm 0.17 \times 10^{-5}\text{ s}^{-1}$. The half-life

of the reaction is 3.86 h.¹³ Apparently, the polarity or hydrogen-bonding properties of the solvent determines the relative thermodynamic stability of the isomers **5** and **6**. The crystallization of **2a** from ether solution affords isomer **5**, while isomer **6** has been crystallized recently from hexane solution as a golden-yellow solid.¹⁴

When a THF solution of **2a** is placed over sodium hydride, the instantaneous evolution of a gas, presumably hydrogen, is observed. An IR spectrum of the resulting solution shows a shift of the terminal carbonyl frequencies by 20 cm^{-1} to lower frequency along with a shift of the C \equiv O and C \equiv O peak by 30 cm^{-1} to lower frequency.¹⁵ This reactivity is nearly identical with that of complex **1**, and indicates the formation of the metallo- β -ketoimine enolate anion. The preparation of other derivatives of complex **2** and the coordination chemistry of the corresponding anions are being pursued.

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Supplementary Material Available: A listing of data, structure factor amplitudes, refinement procedures, least-squares planes, general temperature factor expressions, and root-mean-square amplitudes of thermal vibration (13 pages). Ordering information is given on any current masthead page.

References and Notes

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- (13) Since $K = k_1/k_{-1}$ and $k_t = k_1 + k_{-1}$, then the values of the forward (k_1) and reverse (k_{-1}) rates are calculated to be 4.68×10^{-5} and $2.95 \times 10^{-6}\text{ s}^{-1}$, respectively.
- (14) C. M. Lukehart and G. P. Torrence, unpublished results.
- (15) This peak becomes two closely separated bands of equal intensity in the anion.