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(15) Abbreviations used: phen = 1,10-phenanthroline; bpy = 2,2′-bipyridyl; ox = oxalate; dien = diethylenetriamine = H_2N–CH_2CH_2–$NHCH_2$–CH_2–NH_2; medien = 4-methyldiethylenetriamine = 2,2′-methyliminobis(ethylamine) = H_2N–CH_2CH_2–NMe–CH_2CH_2–NH_2; en = ethylenediamine; pn = propane-1,2-diamine; trenen = 4-(aminoethyl)-1,4,7,10-tetraazadecane; cyclam = 1,4,8,11-tetraazacyclotetradecane; edta = ethylenediaminetetraacetato.
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Reactions of Coordinated Molecules. 16. Preparation and Characterization of Several Metalla-β-ketoimine Molecules as the Ketamine Tautomers

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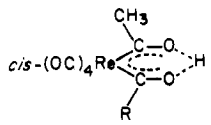
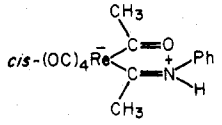
The reaction of the metalla-β-diketone molecules *cis*-$(OC)_4Re[C(CH_3)O\cdots H\cdots OC(R)]$, where R is either methyl or isopropyl, with anhydrous ammonia or with several primary aliphatic or aromatic amines H_2NR', where R′ is phenyl, *p*-tolyl, methyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, cyclohexyl, or benzyl, or with ethylenediamine or propylenediamine affords the metalla-β-ketoimine molecules *cis*-$(OC)_4Re[RC(O)][CH_3CN(R')(H)]$ as the ketamine tautomers. Seventeen such complexes are reported. The structure and chemical reactivity of these molecules is discussed. Both structural and geometrical isomerism is observed.

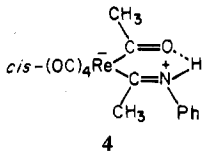
We reported recently the reaction of the metallaacetylacetone molecule, **1** (3,3,3,3-tetracarbonyl-3λ^6-rhena-2,4-pentanedione), with aniline and *p*-toluidine affording the metalla analogues of the corresponding β-ketoimine molecules.[1,2] The X-ray structure of the *N*-phenyl complex, **3**, indicates that the molecule is described best as the zwitterionic ketamine tautomer.[1] Two geometrical isomers, **3** and **4**, of this molecule are observed. Isomer **3** is isolated by crystallization from ether solution as an extended intermolecular hydrogen-bonded structure. When **3** is dissolved in $CDCl_3$ solution at 34 °C, it isomerizes slowly and nearly completely (6:94) to another isomer, **4**, which is presumed to be the isomer having intramolecular hydrogen bonding. Isomer **4** can be isolated pure by crystallization from hexane solution.



1, R = CH_3
2, R = $(CH_3)_2CH$



3



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In this paper we report the preparation and characterization of 17 metalla-β-ketoimine molecules. In many cases the geometrical isomerization about the C–N multiple bond is observed. When the unsymmetrical metalla-β-diketone, **2**, is used, the condensation reaction of the amine occurs predominantly at the acetyl ligand, although the other structural isomer is observed for some molecules. Both the presence of coupling between the α protons of the R′ group and the enolic NH proton and the facile deuterium exchange of the enolic NH proton further substantiate the solution-phase structures of these molecules. These metalla-β-ketoimine complexes represent a new class of compounds which are derivatives of well-known organic molecules.

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25 °C. Diethyl ether and pentane were dried over Na–K alloy with added benzophenone, and methylene chloride was dried over P_2O_5. These solvents were dried under a nitrogen atmosphere and were freshly distilled before use. Cyclohexylamine was distilled over calcium hydride before use. Other amines were used as purchased.

Infrared spectra were recorded on a Perkin-Elmer 727 spectrophotometer as solutions in 0.10-mm sodium chloride cavity cells using the solvent as a reference and a polystyrene film as a calibration

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standard. Band frequencies are reported in cm^{-1}. Proton NMR spectra were obtained on a Jeol MH-100 NMR spectrometer using Me_4Si as an internal reference. Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The complexes *cis*-$(OC)_4Re[C(CH_3)O\cdots H\cdots OC(CH_3)]$, **1**, and *cis*-$(OC)_4Re\{C(CH_3)O\cdots H\cdots OC[C(H)(CH_3)_2]\}$, **2**, were prepared by literature methods.[3,4]

General Preparation of the *N*-Alkylmetalla-β-ketoimine Molecules. To 0.20 g of the appropriate metalla enol complex (**1** or **2**) dissolved in 5 mL of methylene chloride was added 1.5 molar equiv of the primary amine. The reaction solution was allowed to stir for several hours. After this time the solvent was removed at reduced pressure (15 mm). The reaction residue was extracted with an appropriate solvent. This solution was filtered and was placed at −20 °C affording the product as a pale yellow solid or liquid. The detailed procedure and characterization for each complex are provided below.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_3)(H)]$, 6. The addition of the methylamine to the reaction solution was performed at 0 °C. After 1 h of stirring at 25 °C, the solvent was removed at reduced pressure. Crystallization from 10% ether–pentane afforded 0.02 g (10%) of the product as a pale yellow solid: mp 97–98 °C; IR (CH_2Cl_2) (cm^{-1}) ν(CO) 2073 (m), 1984 (s, sh), 1968 (vs), 1945 (s), ν(C⋯O, C⋯N) 1585 (m); ^1H NMR ($CDCl_3$) τ 7.41 (singlet, 3, CH_3CO), 7.17 (singlet, 3, CH_3CN), 6.33 (doublet, 3, CH_3N, J = 5 Hz), 0.18 (broad singlet, 1, NH, width at half-height = 33 Hz). Anal. Calcd for $C_9H_{10}NO_5Re$: C, 27.13; H, 2.54; N, 3.52. Found: C, 27.36; H, 2.61; N, 3.14.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2CH_2CH_3)(H)]$, 7. The reaction solution was stirred for 1 h at 25 °C. Crystallization from hexane solution afforded 0.064 g (29%) of the product as dark yellow hexagonal crystals: mp 96–97 °C; IR (C_6H_{12}) (cm^{-1}) ν(CO) 2070 (m), 1977 (s), 1965 (vs), 1945 (s), ν(C⋯O, C⋯N) 1564 (m); ^1H NMR ($CDCl_3$) τ 9.02 (triplet, 3, CH_3CH_2, J = 7 Hz), 8.25 (septet, 2, CH_3CH_2, J = 7 Hz), 7.50 (singlet, 3, CH_3CO), 7.20 (singlet, 3, CH_3CN), 6.35 (quintet, 2, CH_2N, J = 7 Hz), 0.50 (broad singlet, 1, NH, width at half-height = 24 Hz). Anal. Calcd for $C_{11}H_{14}NO_5Re$: C, 30.98; H, 3.32; N, 3.29. Found: C, 30.63; H, 3.43; N, 3.10.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2CH_2CH_2CH_3)(H)]$, 8. The reaction solution was stirred for 1 h, and the product was crystallized from hexane solution as bright yellow hexagonal crystals affording 0.053 g (23%): mp 68.5–69.5 °C; IR (C_6H_{12}) (cm^{-1}) ν(CO) 2075 (m), 1975 (s), 1965 (vs), 1948 (s), ν(C⋯O, C⋯N) 1568 (m); ^1H NMR ($CDCl_3$) τ 9.00 (triplet, 3, CH_3CH_2, J = 7 Hz), 8.64–8.10 (multiplet, 4, $(CH_2)_2$), 7.43 (singlet, CH_3CO), 7.15 (singlet, 3, CH_3CN), 6.23 (multiplet, 2, CH_2N), 0.62 (broad singlet, 1, NH, width at half-height = 36 Hz). Anal. Calcd for $C_{12}H_{16}NO_5Re$: C, 32.72; H, 3.67; N, 3.18. Found: C, 32.66; H, 3.66; N, 3.16.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)]\{CH_3CN[CH_2C(H)(CH_3)_2][H]\}$, 9. The reaction solution was stirred for 10 min and the product was crystallized from ether solution affording 0.11 g (48%) of **9** as a pale yellow solid: mp 101–103 °C; IR (CH_2Cl_2) (cm^{-1}) ν(CO) 2075 (m), 1975 (s, sh), 1960 (vs), 1938 (s), ν(C⋯O, C⋯N) 1578 (m); ^1H NMR ($CDCl_3$) τ 8.90 (doublet, 6, $(CH_3)_2C$, J = 7 Hz), 7.83 (complex multiplet, 1, CH), 7.42 (singlet, 3, CH_3CO), 7.10 (singlet, 3, CH_3CN), 6.39 (complex triplet, 2, CH_2N, J = 7 Hz), 0.43 (broad singlet, 1, NH, width at half-height = 42 Hz). Anal. Calcd for $C_{12}H_{16}NO_5Re$: C, 32.72; H, 3.67; N, 3.18. Found: C, 32.60; H, 3.83; N, 3.21.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(C_6H_{11})(H)]$, 10. The reaction solution was stirred for 1 h, and the product was crystallized from 10% ether–pentane solution affording 0.016 g (16%) of **10** as a pale yellow solid: mp 115–117 °C; IR (CH_2Cl_2) (cm^{-1}) ν(CO) 2075 (m), 1973 (s, sh), 1955 (vs), 1930 (s), ν(C⋯O, C⋯N) 1573 (m); ^1H NMR ($CDCl_3$) τ 8.80–7.83 (complex multiplet, 11, C_6H_{11}), 7.46 (singlet, 3, CH_3CO), 7.16 (singlet, 3, CH_3CN), 1.09 (broad singlet, 1, NH, width at half-height = 42 Hz). Anal. Calcd for $C_{14}H_{18}NO_5Re$: C, 36.04; H, 3.90; N, 3.00. Found: C, 36.21; H, 3.98; N, 2.92.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2C_6H_5)(H)]$, 11. To a solution of 0.3 g of **1** in 6 mL of methylene chloride was added 0.12 g of benzylamine. The reaction solution was stirred for 90 min, and the product was crystallized from hexane solution as a pale yellow solid affording 0.069 g (20%): mp 97–98 °C; IR (C_6H_{12}) (cm^{-1}) ν(CO) 2077 (m), 1980 (s, sh), 1970 (vs, br), 1949 (s), ν(C⋯O, C⋯N) 1560 (m); ^1H NMR ($CDCl_3$) τ 7.39 (singlet, 3, CH_3CO), 7.21 (singlet, 3, CH_3CN), 5.31 (doublet, 2, CH_2, J = 5 Hz), 2.74 (complex multiplet, 5, C_6H_5), −3.47 (broad singlet, 1, NH, width at half-height = 36 Hz). Anal. Calcd for $C_{15}H_{14}NO_5Re$: C, 37.97; H, 2.97; N, 2.95. Found: C, 37.80; H, 3.17; N, 2.79.

Preparation of *cis*-$(OC)_4Re[[(CH_3)_2(H)CC(O)][CH_3CN(CH_3)(H)]]$, 12. The reaction solution was stirred for 4.5 h, and the product was crystallized from 10% ether–pentane solution affording 0.16 g (78%) of a yellow liquid. The liquid was then distilled in vacuo (62 °C (5 mm)) onto a −78 °C probe for further purification: IR (C_6H_{12}) (cm^{-1}) ν(CO) 2075 (m), 1980 (s), 1970 (vs), 1940 (s), ν(C⋯O, C⋯N) 1560 (m); ^1H NMR ($CDCl_3$) τ 9.07 (doublet, 6, $(CH_3)_2C$, J = 7 Hz), 7.24 (singlet, 3, CH_3CN), 6.85 (complex multiplet, 1, CH, $J \approx$ 7 Hz), 6.78 (doublet, 3, CH_3N, J = 6 Hz), −3.50 (broad singlet, 1, NH, width at half-height = 54 Hz). Anal. Calcd for $C_{11}H_{14}NO_5Re$: C, 30.98; H, 3.32; N, 3.29. Found: C, 30.47; H, 3.31; N, 3.54.

Preparation of *cis*-$(OC)_4Re\{[(CH_3)_2(H)CC(O)][CH_3CN(CH_2CH_2CH_3)(H)]\}$, 13. The reaction solution was stirred for 22 h. The solvent was removed at reduced pressure affording 0.096 g (44%) of the crude product as a golden liquid. This liquid was purified further by vacuum distillation (58 °C (5 mm)) onto a 25 °C probe: IR (C_6H_{12}) (cm^{-1}) ν(CO) 2080 (m), 1980 (s), 1975 (vs), 1940 (s), ν(C⋯O, C⋯N) 1560 (m); ^1H NMR ($CDCl_3$) τ 9.19, 9.17 (2 doublets, 6, $(CH_3)_2C$, $J \approx$ 7 Hz), 9.02, 8.99 (2 triplets, 3, CH_3CH_2, $J \approx$ 7 Hz), 8.21 (septet, 2, CH_2, $J \approx$ 7 Hz), 7.31, 7.20 (2 singlets, 3, CH_3CN), 6.84 (complex multiplet, 1, CH, $J \approx$ 7 Hz), 6.51 (complex multiplet, 2, NCH_2, $J \approx$ 7 Hz), 0.54, −3.26 (2 broad singlets, 1, NH, width at half-height of 33 and 42 Hz, respectively). Anal. Calcd for $C_{13}H_{18}NO_5Re$: C, 34.35; H, 4.00; N, 3.08. Found: C, 34.06; H, 4.06; N, 3.43.

Preparation of *cis*-$(OC)_4Re\{[(CH_3)_2(H)CC(O)][CH_3CN(CH_2CH_2CH_2CH_3)(H)]\}$, 14. The reaction solution was stirred for 22 h, and the product was crystallized from pentane solution affording 0.070 g (30%) of **14** as yellow needles: mp 106–108 °C; IR (C_6H_{12}) (cm^{-1}) ν(CO) 2080 (m), 1983 (s), 1973 (vs), 1940 (s), ν(C⋯O, C⋯N) 1568 (m); ^1H NMR ($CDCl_3$) τ 9.09 (doublet, 6, $(CH_3)_2C$, J = 7 Hz), 8.92 (triplet, 3, CH_3CH_2, J = 7 Hz), 8.50 (complex multiplet, 2, CH_3CH_2), 8.17 (complex multiplet, 2, CH_2), 7.24, 7.13 (2 singlets, 3, CH_3CN), 6.78 (complex multiplet, 1, CH), 6.41, 6.20 (2 quintets, 2, CH_2N, $J \approx$ 7 Hz), 0.68, −3.35 (broad singlets, 1, NH, widths at half-height = 24 and 51 Hz, respectively). Anal. Calcd for $C_{14}H_{20}NO_5Re$: C, 35.89; H, 4.31; N, 2.99. Found: C, 35.38; H, 4.43; N, 2.99.

Preparation of *cis*-$(OC)_4Re\{[(CH_3)_2(H)CC(O)][CH_3CN(CH_2C(H)(CH_3)_2)(H)]\}$, 15. The reaction solution was stirred for 20 h affording 0.092 g (41%) of the product as a yellow liquid after removing the solvent. This liquid was distilled in vacuo (58 °C (5 mm)) onto a −78 °C probe for further purification: IR (C_6H_{12}) ν(CO) (cm^{-1}) 2080 (m), 1980 (s, sh), 1970 (vs), 1940 (s), ν(C⋯O, C⋯N) 1560; ^1H NMR ($CDCl_3$) τ 9.22, 9.19 (2 doublets, 6, $(CH_3)_2C$, $J \approx$ 7 Hz), 9.19, 9.16 (2 doublets, 6, $(CH_3)_2C$ of isobutyl, $J \approx$ 7 Hz), 7.87 (complex multiplet, 1, CH of isobutyl, $J \approx$ 7 Hz), 7.26, 7.12 (2 singlets, 3, CH_3CN), 6.86 (complex multiplet, 1, CH of isopropyl), 6.69, 6.53 (2 quartets, NCH_2, $J \approx$ 7 Hz), 0.43, −3.31 (broad singlets, 1, NH, widths at half-height = 27 and 36 Hz, respectively). Anal. Calcd for $C_{12}H_{20}NO_5Re$: C, 35.89; H, 4.31; N, 2.99. Found: C, 35.84; H, 4.47; N, 2.60.

Preparation of *cis*-$(OC)_4Re\{[(CH_3)_2(H)CC(O)][CH_3CN(CH_2C_6H_5)(H)]\}$, 16. The reaction solution was stirred for 20 h, and the product was crystallized from hexane solution affording 0.060 g (25%) of **16** as a pale yellow solid: mp 104.5–105.5 °C; IR (C_6H_{12}) (cm^{-1}) ν(CO) 2070 (m), 1968 (s, sh), 1960 (vs), 1945 (s), ν(C⋯O, C⋯N) 1560 (m); ^1H NMR ($CDCl_3$) τ 9.10 (doublet, 6, $(CH_3)_2C$, J = 7 Hz), 7.22 (singlet, 3, CH_3CN), 6.86 (septet, 1, CH, J = 7 Hz), 4.99 (doublet, 2, CH_2, J = 6 Hz), 2.40 (complex multiplet, 5, C_6H_5), 0.84 (broad singlet, 1, NH, width at half-height = 18 Hz). Anal. Calcd for $C_{17}H_{18}NO_5Re$: C, 40.63; H, 3.62; N, 2.79. Found: C, 40.41; H, 3.60; N, 2.78.

Preparation of the Metalladiimine Molecules

Preparation of $\{cis$-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2)(H)]\}_2$, 17. To a solution of 0.2 g (0.5 mmol) of **1** in 5 mL of methylene chloride was added 0.022 mL (0.3 mmol) of ethylenediamine. The reaction solution was stirred for 28 h, and then the solvent was removed at reduced pressure. The reaction residue was extracted with 2.5 mL of ether. This mixture was filtered, and the filtrate was placed at

–20 °C affording 0.090 g (38%) of the crystallized product as a yellow solid: mp 132–133 °C; IR (CH_2Cl_2) (cm^{-1}) ν(CO) 2075 (m), 1970 (vs, br), 1935 (s), ν(C⋯O, C⋯N) 1550 (m); ^1H NMR ($CDCl_3$) τ 7.46, 7.35 (2 singlets, 6, CH_3CO), 7.20, 7.03 (2 singlets, 6, CH_3CN), 6.97, 5.70 (2 complex multiplets, 4, 2 CH_2), –0.05, –3.16 (broad singlets, 2, NH, widths at half-height = 24 and 42 Hz, respectively). Anal. Calcd for $C_{18}H_{18}N_2O_{10}Re_2$: C, 27.20; H, 2.29; N, 3.53. Found: C, 27.13; H, 2.33; N, 3.67.

Preparation of {*cis*-(OC)$_4$Re[CH$_3$C(O)][CH$_3$CN(CH$_2$)(H)]}$_2$CH$_2$, 18. To a solution of 0.5 g (1.3 mmol) of **1** in 5 mL of methylene chloride was added 0.05 mL (0.60 mmol) of 1,3-diaminopropane. The reaction solution was stirred for 1 day, and then hexane was added until a small amount of precipitate formed. This solution was filtered, and the filtrate was placed at –20 °C after the addition of ca. 1 mL more of hexane to afford 0.18 g (34%) of the product as a pale yellow solid: mp 118–119 °C; IR (CH_2Cl_2) (cm^{-1}) ν(CO) 2080 (m), 1985 (s, sh), 1975 (vs), 1940 (s), ν(C⋯O, C⋯N) 1555 (m); ^1H NMR ($CDCl_3$) τ 7.68 (complex multiplet, 2, CH_2), 7.42, 7.32 (2 singlets, 6, CH_3CO), 7.22, 7.11 (2 singlets, 6, CH_3CN), 6.24, 5.94 (2 complex multiplets, 4, NCH_2), –0.22, –3.33 (broad singlets, 2, NH, widths at half-height = 51 and 30 Hz, respectively). Anal. Calcd for $C_{19}H_{20}N_2O_{10}Re_2$: C, 28.21; H, 2.50; N, 3.46. Found: C, 28.81; H, 2.52; N, 3.41.

Separation of the Geometrical Isomers of the *N*-Alkylmetalla-β-ketoimine Molecules. The higher melting geometrical isomer was isolated by crystallization from solution at –20 °C. Usually, the lower melting isomer, which was frequently a liquid, was present in the supernatant solution, and it was isolated by vacuum distillation. For example, the higher melting isomer of the complexes **11** and **14** was obtained by crystallization from hexane solution. The lower melting isomer of complex **15** was isolated by vacuum distillation at 58 °C (5 mm) onto a –78 °C probe. One of the symmetrical isomers of the metallaethylenediimine complex, **17**, was obtained pure after two crystallizations from ether solution.

Preparation of the Parent Metalla-β-ketoimine Complexes

Preparation of *cis*-(OC)$_4$Re[CH$_3$C(O)][CH$_3$CNH$_2$], 19. An excess of anhydrous ammonia gas was bubbled into a stirred solution of 0.30 g of **1** in 10 mL of dry methylene chloride at 0 °C. An off-white precipitate formed immediately, and the addition of the ammonia was completed within 1 min. The reaction mixture was warmed to 25 °C during which time the precipitate dissolved. After an additional 1 h of stirring, the solvent was removed at reduced pressure affording 0.20 g (67%) of the crude product as a pale yellow solid. The product was crystallized from hexane solution as a colorless solid: mp 94–96 °C; IR (C_6H_{12}) (cm^{-1}) ν(CO) 2080 (m), 1985 (s, sh), 1978 (vs), 1945 (s), ν(C⋯O, C⋯N) 1555 (m); ^1H NMR ($CDCl_3$) τ 7.32 (singlet, 3, CH_3CO), 7.14 (singlet, 3, CH_3CN), 0.89 (broad singlet, 1, NH, width at half-height = 84 Hz), –3.43 (broad singlet, 1, NH, width at half-height = 84 Hz). Anal. Calcd for $C_8H_8O_5NRe$: C, 25.00; H, 2.10; N, 3.64. Found: C, 24.65; H, 2.25; N, 3.69.

Preparation of *cis*-(OC)$_4$Re[(CH$_3$)$_2$(H)CC(O)][CH$_3$CNH$_2$], 20. An excess of anhydrous ammonia gas was bubbled at a moderate rate for 1 min into a stirred solution of 0.20 g (0.48 mmol) of **2** in 10 mL of dry methylene chloride at 0 °C. The reaction solution was stirred for 1 h at 25 °C, and then the solvent was removed at reduced pressure. The product was extracted into 5 mL of hexane and was crystallized from the hexane solution at –20 °C affording 0.11 g (55%) of **20** as pale lemon yellow needles: mp 89–91 °C; IR (C_6H_{12}) (cm^{-1}) ν(CO) 2080 (m), 1985 (s, sh), 1978 (vs), 1945 (s), ν(C⋯O, C⋯N) 1555 (m); ^1H NMR ($CDCl_3$) τ 9.15 (doublet, 6, $(CH_3)_2C$, $J \approx 7$ Hz), 7.19 (singlet, 3, CH_3CN), 6.80 (septet, 1, CH, $J \approx 7$ Hz), 0.95 (broad singlet, 1, NH, width at half-height = 51 Hz), –3.58 (broad singlet, 1, NH, width at half-height = 91 Hz). Anal. Calcd for $C_{10}H_{12}O_5NRe$: C, 29.12; H, 2.94; N, 3.40. Found: C, 29.63; H, 3.01; N, 3.23.

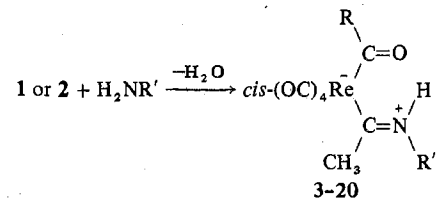
Preparation of Amine Adducts of 1

Preparation of 1·H$_2$NC$_6$H$_{11}$, 21. The reaction solution described above was stirred for only 1 h. The product crystallized from 6 mL of ether solution affording 0.15 g (60%) of **21** as pale green needles: mp 108–109 °C; IR (CH_2Cl_2) (cm^{-1}) ν(CO) 2080 (m), 1985 (vs, br), 1950 (s), ν(C⋯O) 1510 (m); ^1H NMR ($CDCl_3$) τ 8.89–7.95 (complex multiplet, 11, C_6H_{11}), 7.25 (singlet, 6, CH_3), 2.81 (broad singlet, 3, O_2H and NH_2, width at half-height = 42 Hz). Anal. Calcd for $C_{14}H_{20}NO_6Re$: C, 34.70; H, 4.17; N, 2.89. Found: C, 35.19; H, 4.44; N, 3.15.

Preparation of 1·H$_2$NCH$_2$C(H)(CH$_3$)$_2$, 22. The reaction solution described above was stirred for only 10 min. The product crystallized from 1 mL of ether solution affording 0.019 g (8%) of **22** as dark yellow crystals: mp 87–89 °C; IR (CH_2Cl_2) (cm^{-1}) ν(CO) 2070 (m), 1975 (s, sh), 1960 (vs), 1938 (s, sh), ν(C⋯O) 1570; ^1H NMR ($CDCl_3$) τ 9.06 (doublet, 6 $(CH_3)_2C$, $J \approx 7$ Hz), 8.06 (septet, 1, CH, $J \approx 7$ Hz), 7.34 (complex multiplet, 2, CH_2N), 7.23 (singlet, 6, CH_3C), 3.00 (broad singlet, 3, O_2H and NH_2, width at half-height = 33 Hz). Anal. Calcd for $C_{12}H_{18}NO_6Re$: C, 31.43; H, 3.97; N, 3.06. Found: C, 31.59; H, 4.01; N, 3.27.

Results and Discussion

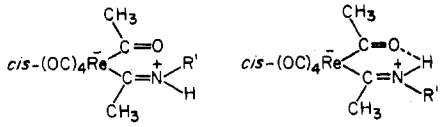
A Schiff base condensation reaction apparently results when the rhenium metalla-β-diketone molecules **1** and **2** are treated with ammonia or a primary amine as shown, where R′ is hydrogen or an alkyl or aromatic substituent.



3-20

The complete characterization (including the X-ray structure determination) of complex **3**, where R is methyl and R′ is phenyl, indicates that these complexes are the ketamine tautomers of metalla-β-ketoimine molecules where the methine group of the organic analogue is replaced formally by the *cis*-(OC)$_4$Re moiety. The detailed intramolecular bonding is represented best by the zwitterionic electronic structure. This formulation is supported also by spectroscopic data.[1]

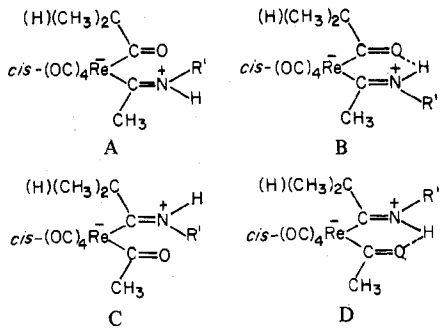
When R is methyl, two geometrical isomers are possible resulting from a 180° rotation about the C–N multiple bond (if R′ is not a hydrogen atom). These isomers are shown as A and B. Both isomers have been isolated for the complex



A B

where R′ is phenyl. These isomers are shown as **3** and **4**, and the rate of isomerization of **3** to **4** in chloroform solution at 34 °C is (4.97 ± 0.17) × 10^{-5} s^{-1}.[1]

When R is isopropyl, two structural isomers are possible depending upon the site of condensation, and each of these isomers may exhibit the above geometrical isomerization as shown in A–D



A B C D

The metalla-β-ketoimine molecules reported here are prepared in moderate to good yield as nearly colorless yellow solids or liquids. These complexes have excellent solubility in organic solvents, and they are air stable for at least several hours. In general, the metalla-β-ketoimine molecules have greater thermal stability than the metalla-β-diketone molecules. This trend parallels that of the organic analogues.[5]

Table I. Relevant ^{1}H NMR Data for the A and B Isomers of *cis*-$(OC)_4Re[RC(O)][CH_3CN(R')(H)]$[a]

			isomer A				isomer B			
complex	R	R'	δ-($CH_3C(N)$)	δ-($CH_3C(O)$)	δ(NH)	%	δ-($CH_3C(N)$)	δ-($CH_3C(O)$)	δ(NH)	%
3 and **4**	CH_3	C_6H_5	3.21	2.40	11.56	*b*	2.83	2.75	15.26	*b*
5	CH_3	*p*-tolyl	3.06	2.37	11.28		*c*			
6	CH_3	CH_3	2.83	2.59	9.82	*b*	2.71	2.63	13.06	*b*
7	CH_3	*n*-propyl	2.80	2.50	9.50	90	2.69	2.60		10
8	CH_3	*n*-butyl	2.85	2.57	9.38		*c*			
9	CH_3	isobutyl	2.90	2.58	9.57	95	2.74	2.65		5
10	CH_3	C_6H_{11}	2.84	2.54	8.91		*c*			
11	CH_3	benzyl	2.88	2.51	9.41	*b*	2.79	2.61	13.47	*b*
12	*i*-Pr	CH_3	2.88			18	2.76		13.50	82
13	*i*-Pr	*n*-propyl[d]	2.80		9.46	30	2.69		13.26	56
14	*i*-Pr	*n*-butyl[d]	2.87		9.32	32	2.76		13.35	58
15	*i*-Pr	isobutyl[d]	2.88		9.57	*b*	2.74		13.31	*b*
16	*i*-Pr	benzyl[d]	2.78		9.16	89	*c*			
19	CH_3	H[e]	2.96	2.68	9.11	anti NH			13.43	syn NH
20	*i*-Pr	H[e]	2.81		9.05	anti NH			13.58	syn NH

[a] All chemical shifts are reported for $CDCl_3$ solutions vs. Me_4Si. [b] Both isomers were isolated nearly pure (usually >95%). [c] Other isomer not observed during routine handling. [d] Small amounts of isomers C and D were observed. [e] Geometrical isomerism about the C–N bond is not defined.

The solution-phase IR spectra indicate the cis-substitution geometry about the rhenium atom. Also, the most intense terminal carbonyl stretching vibrations of these complexes appear at ca. 25 cm^{-1} lower energy than the analogous bands of the metalla-β-diketone complexes, **1** and **2**, which is consistent with the greater localization of negative charge on the rhenium atom in the metalla-β-ketoimine molecules. A diagnostic indication of the formation of these complexes is the appearance of a band at 1550–1585 cm^{-1}. This band represents the C–O and C–N symmetric stretching vibration within the metalla-β-ketoimine ligand.

The ^{1}H NMR spectra provide the most detailed information. Table I summarizes the chemical shift data for the methyl substituents on the ligand backbone and for the NH protons. The various types of isomers can be assigned from the positions of these resonances.

The two *N*-arylmetallaacetylacetonimine complexes, **3** and **5**, are included in Table I, also.[1] For complex **3** both geometrical isomers have been isolated as pure solids. The X-ray structure of **3** characterizes the A isomer unambiguously as the molecule having the enolic NH hydrogen atom anti to the acyl oxygen atom or in a nonchelating site. This isomer has a large separation (81 Hz) of the two methyl resonances, and a high-field NH resonance (δ 11.56). In contrast, isomer B, **4**, is characterized by having the enolic NH hydrogen atom syn to the acyl oxygen atom or in a chelating site. This structure apparently facilitates electron delocalization as evidenced by the deeper yellow color of the complex and the smaller separation (8 Hz) of the two methyl resonances. Also, the enolic NH proton resonance appears now at a much lower field (δ 15.26) apparently due to its increased acidity.

The *N*-*p*-tolyl complex, **5**, was isolated as the A isomer only. Using the above criteria the isomers of the remaining complexes can be assigned. The methyl resonance of the iminium ligand always appears at lower field than the resonance of the methyl group of the acetyl ligand. This lower field methyl resonance is always slightly broader and has little or no ringing due, apparently, to the closer proximity of the nitrogen atom.

The *N*-alkylmetallaacetylacetonimine complexes, **6**–**11**, exhibit the geometrical isomerism mentioned above. Isomer A is the predominant isomer of these ketamine tautomers. It is the higher melting isomer which is isolated directly via crystallization. The average values of the chemical shifts of the iminium methyl and acetyl methyl resonances are δ 2.85 and 2.55, respectively, giving an average anisochronism[6] of 30 Hz for these methyl substituents. The average value of the chemical shift of the NH resonance for these A isomers is δ 9.34. Isomer B is the low melting isomer which is usually isolated from the supernatant solution by vacuum distillation. As for the *N*-aryl complexes, this isomer seems to have a more symmetric electronic distribution due to its chelating geometry. The average values of the chemical shifts of the iminium methyl and acetyl methyl resonances are δ 2.73 and 2.62, respectively, giving an average anisochronism of only 11 Hz. Also, the average value of the chemical shift of the NH resonance for these B isomers is δ 13.27 which is at much lower field than observed for the A isomers. In many cases isomers A and B could not be separated, and the relative percent abundance of each isomer is shown. However, for the *N*-methyl, **6**, and *N*-benzyl, **11**, complexes both isomers could be isolated essentially pure.

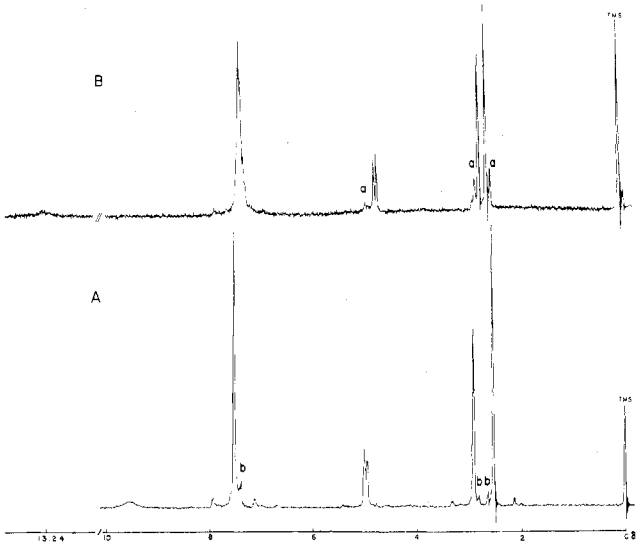


Figure 1. ^{1}H NMR spectra of both isomers of *cis*-$(OC)_4Re[CH_3C(O)][CH_3N(CH_2C_6H_5)(H)]$, **11**, in $CDCl_3$ solution at 34 °C. The lower spectrum, A, is that of isomer A, while the upper spectrum, B, is that of isomer B. The a and b notations indicate residual quantities of the other isomer.

Figure 1 shows the complete ^{1}H NMR spectrum of each isomer for the *N*-benzyl complex, **11**. The lower spectrum is that of isomer A showing both the wide separation of the methyl resonances and the high-field NH resonance. The upper spectrum is that of isomer B. This isomer is characterized by the narrower separation of the two methyl resonances and by the lower field NH resonance. Trace amounts

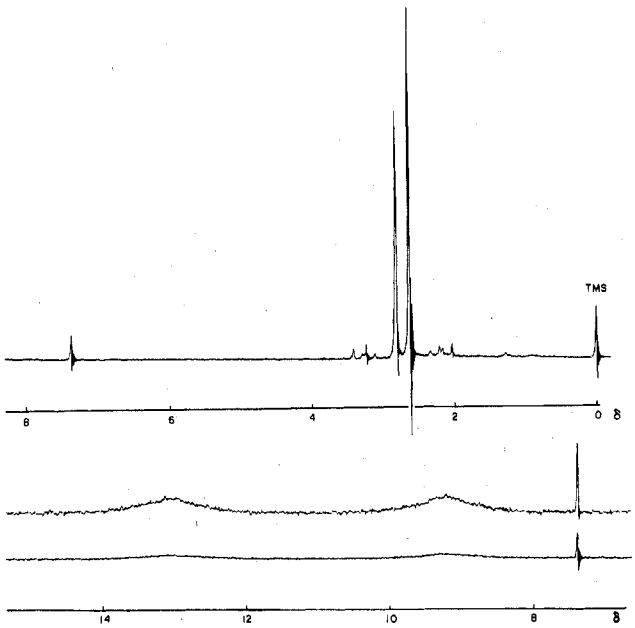


Figure 2. ^{1}H NMR spectrum of the metallaacetylacetonimine complex *cis*-$(OC)_4Re[CH_3C(O)][CH_3CNH_2]$, **19**, in $CDCl_3$ solution at 34 °C. The low-field region is shown at higher amplitude.

of the other isomer are present in each spectrum. The two sets of methyl resonances have the same midpoint. The benzylic methylene resonance appears as a doublet due to coupling to the enolic NH proton. This coupling will be discussed below.

The *N*-alkylmetallaisobutyrylacetonimine complexes, **12–16**, exhibit both structural and geometrical isomerism. For all of these ketamine tautomers the structural isomer resulting from the condensation on the acetyl ligand is the predominant product. The geometrical isomers, A and B, of this structural isomer are assigned readily from the positions of the iminium methyl and the NH resonances. The A isomers have the iminium methyl and enolic NH resonances in the ranges δ 2.83 ± 0.05 and 9.36 ± 0.21, respectively. The ranges for these resonances of the B isomers are δ 2.73 ± 0.04 and 13.38 ± 0.12, respectively.

The identification of the C and D geometrical isomers, which are derived from the other structural isomer, is less certain since the highest relative abundance for any of these isomers is only 11% (for complex **16**). For the complexes **13**, **14**, **15**, and **16** a sharp acetyl methyl resonance is observed in the range δ 2.63 ± 0.04. This resonance in **15** is accompanied by an NH resonance of δ 8.28, and, therefore, these isomers are assigned to structure C. Isomer D may be present in the complexes **13** and **15**. For these complexes an acetyl methyl resonance is observed at δ 2.54 and 2.56, respectively, although a distinct low-field NH resonance is not observed since each isomer has a relative abundance of only ca. 5%. The large preference for condensation on the acetyl ligand parallels the synthetic results of the organic β-ketoimines and may reflect a steric influence on the site of condensation.[7]

There are three isomers possible for the two metallaacetylacetonediimine complexes **17** and **18**. Two of these isomers are symmetrical isomers of the AA or BB type while the third isomer would be the unsymmetrical AB or BA type (indicating a 50% probability of formation). Using the ^{1}H NMR criteria demonstrated above, the relative intensities of the various resonances and the separation of the isomers of the ethylenediimine complex **17**, it is clear that only the symmetrical isomers are observed. The relative abundance of the AA and BB isomers is nearly 40:60. The preferential formation of the symmetrical isomer of nonmetalla-β-ketodiimines has been noted, recently.[8]

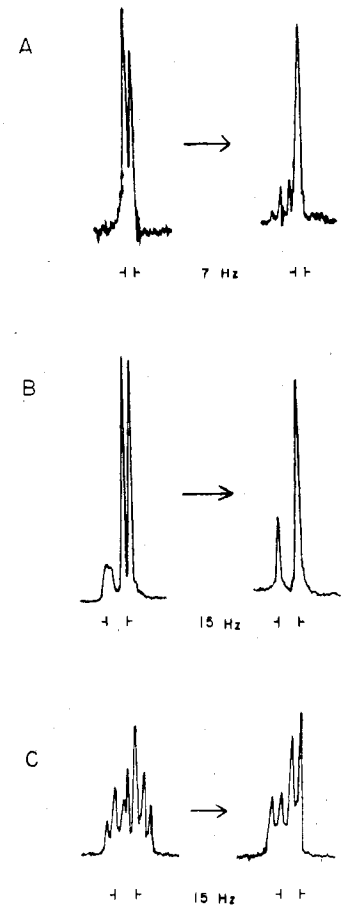


Figure 3. ^{1}H NMR spectra of the protons on the α-carbon atoms of the nitrogen atom substituent R′ for the *N*-methyl (A), *N*-benzyl (B), and *N*-isobutyl (C) metallaacetylacetonimine complexes. The spectra on the right show the loss of NH coupling due to deuterium exchange upon adding methanol-d_4 to the sample.

A confirmation of the above assignment of the syn and anti enolic NH resonances is provided from the ^{1}H NMR spectra of the parent metalla-β-ketoimine complexes, **19** and **20**. Figure 2 is the ^{1}H NMR spectrum of the metallaacetylacetonimine complex, **19**. This molecule should possess both a syn and an anti NH proton. The spectrum shows these two NH resonances at δ 13.43 and 9.11, respectively. The corresponding resonances of the isobutyryl analogue, **20**, appear at δ 13.58 and 9.05. The NH resonances of the metalla-β-ketoimine molecules **3–20** always appear as broad singlets. The average value of the peak widths at half-height is 42 Hz. These resonances disappear either by adding methanol-d_4 to the ^{1}H NMR sample or by recording the spectrum in neat methanol-d_4.

Although the NH resonances never show coupling to the proton nuclei of the R′ group, the protons on the α-carbon atoms of the R′ substituents do show coupling to the NH proton. This coupling constant is ca. 6 Hz. Also, the X-ray structure of **3** confirmed the presence of the N–H bond. Figure 3 shows the α-proton resonances of the *N*-methyl- (A), *N*-benzyl- (B), and *N*-isobutylacetylacetonimine (C) complexes, **6**, **11**, and **9**, respectively. The *N*-benzyl and *N*-isobutyl spectra show both geometrical isomers. The spectra on the left show the coupling to the NH proton. Upon adding methanol-d_4 to the sample solution, the deuterium exchange of the NH proton causes the loss of this coupling to the methyl, benzyl, and methylene protons as expected. The methylene protons of the isobutyl group are still coupled to the methine proton.

A brief comparison of these ^1H NMR data to those spectral data of several nonmetalla-β-ketoimine analogues is warranted.[9,10] For the *N*-phenyl, *N*-methyl, *N*-benzyl, and the unsubstituted acetylacetonimine molecules the NH resonances appear at δ 12.6 (CCl_4), 10.7 ($CDCl_3$), 11.2 ($CDCl_3$), and 9.7 (CCl_4), respectively. The average values of the syn and anti NH resonances in $CDCl_3$ for the analogous metalla molecules **3**, **6**, **11**, and **19** are δ 13.41, 11.44, 11.44, and 11.27, respectively. This lowering of the NH resonance along with the observation of benzylic coupling to the *NH* proton in *N*-benzylacetylacetonimine may indicate a greater acidity (or localized positive charge) of the NH protons of the metalla-β-ketoimine molecules than for the organic analogues. This conclusion is consistent with the zwitterionic structures **3** and **4**. However, the NH proton of the nonmetalla molecules (e.g., *N*-benzylacetylacetonimine) also undergoes relatively facile deuterium exchange,[9] and the electronic and magnetic influence of incorporating the rhenium atom directly into the β-ketoimine molecule is not well defined.

It is also evident from the structure of complex **3** and the above ^1H NMR data that the metalla-β-ketoimine molecules are quite different from the amino carbenoid complexes. The NH resonances of $(OC)_5Cr[C(CH_3)(NHCH_2C_6H_5)]$ and $(OC)_5Cr[C(CH_3)(NHC_6H_5)]$[11] in $CDCl_3$ are δ 9.67 and 10.43, respectively. These values are 1.77 and 2.98 ppm to higher field than the average enolic NH resonances of the *N*-benzyl- and *N*-phenylmetallaacetylacetonimine complexes. Also, the NH proton of the *N*-benzyl carbenoid complex does not undergo deuterium exchange with methanol-d_4.[1]

Complex **1** did not react with *p*-nitroaniline, (±)-α-phenylethylamine, or (±)-α-*tert*-butylethylamine. Although the mechanism of the condensation reaction was not examined, if the condensation reaction is stopped prematurely, then a monoamine adduct of the metalla-β-diketone molecule can be isolated. The cyclohexylamine and isobutylamine adducts, **21** and **22**, of complex **1** are crystalline solids which melt at slightly lower temperatures than the corresponding metalla-β-ketoimine molecules (ΔT = 8 and 14 °C, respectively). Although the structures of these adducts, which appear to be nonionic solids, are not known, they may be related structurally to the hydrogen-bonded adducts between amines and alcohols.[12]

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.

Registry No. **1**, 59299-78-4; **2**, 66808-98-8; **3**, 66841-15-4; **4**, 66808-97-7; **5** (isomer A), 66808-96-6; **6** (isomer A), 66841-14-3; **6** (isomer B), 66808-95-5; **7** (isomer A), 66841-13-2; **7** (isomer B), 66808-94-4; **8** (isomer A), 66808-93-3; **9** (isomer A), 66841-12-1; **9** (isomer B), 66808-89-7; **10** (isomer A), 66808-88-6; **11** (isomer A), 66841-09-6; **11** (isomer B), 66808-87-5; **12** (isomer A), 66841-11-0; **12** (isomer B), 66808-92-2; **13** (isomer A), 66841-10-9; **13** (isomer B), 66808-91-1; **13** (isomer C), 66808-90-0; **13** (isomer D), 66900-42-3; **14** (isomer A), 66841-08-5; **14** (isomer B), 66808-86-4; **14** (isomer C), 66808-85-3; **15** (isomer A), 66841-07-4; **15** (isomer B), 66808-84-2; **15** (isomer C), 66841-06-3; **15** (isomer D), 66808-83-1; **16** (isomer A), 66808-82-0; **16** (isomer C), 66808-81-9; **17** (isomer AA), 66841-05-2; **17** (isomer BB), 66808-80-8; **18** (isomer AA), 66841-04-1; **18** (isomer BB), 66808-79-5; **19**, 66808-78-4; **20**, 66808-77-3; $NH_2C_6H_5$, 62-53-3; $NH_2C_6H_4$-*p*-CH_3, 106-49-0; NH_2CH_3, 74-89-5; $NH_2CH_2CH_2CH_3$, 107-10-8; $NH_2CH_2CH_2CH_2CH_3$, 109-73-9; $NH_2CH_2C(H)(CH_3)_2$, 78-81-9; $NH_2C_6H_{11}$, 108-91-8; $NH_2CH_2C_6H_5$, 100-46-9; NH_3, 7664-41-7; $NH_2CH_2CH_2NH_2$, 107-15-3; $NH_2CH_2CH_2CH_2NH_2$, 109-76-2.

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Preparation, Structure, and Reactions of Triphenyl Phosphite Complexes of Iron, Ruthenium, and Osmium

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The iron complex $Fe[P(OC_6H_5)_3]_2[(C_6H_4O)P(OC_6H_5)_2]_2$ has been synthesized by metal atom evaporation techniques. The complex, formally the result of two ortho oxidative C–H additions accompanied by loss of a molecule of hydrogen, is compared with its previously known Ru and Os analogues. Structural aspects of these complexes and their reaction products with phosphorus ligands, CO, H_2, and HCN are reported.

Introduction

There has been considerable interest recently in iron complexes containing only phosphorus ligands. The complexes FeL_5 [L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr)_3$, or $P(OCH_2)_3CEt$][1] and $Fe[P(CH_3)_3]_3H[CH_2P(CH_3)_2]$[2] have recently been prepared by both metal atom evaporation and chemical reduction methods. In an attempt to synthesize a zerovalent iron compound with triphenyl phosphite ligands using metal atom evaporation techniques, $Fe[P(OC_6H_5)_3]_2[C_6H_4OP(OC_6H_5)_2]_2$ (**1a**), a complex in which CH bonds of two ligands have reacted with the metal center with the elimination of H_2, was obtained. The reactions of this unusual compound with small ligands imply a single reactive coordination site.

The osmium analogue **3a** has been reported[3] as a product of the reaction of $OsH_4[P(C_6H_5)_3]_3$ with $P(OC_6H_5)_3$ in boiling decane. More recently the ruthenium analogue **2a** was

