the reaction is initiated by photochemical formation of transient $CpZrCl_2$ (**2a**) which starts the observed very efficient radical chain reaction being consumed by molecular chlorine to form **3** and a chain carrying Cl radical. $CpZrCl_3$ and 1,2,3,4,5-pentachlorocyclopentane (**4**) are the only reaction products observed. After separation from the organic component, $CpZrCl_3$ is obtained in an almost quantitative yield practically free from Cp_2ZrCl_2 and $ZrCl_4$.

$$\underset{\mathbf{1}}{Cp_2ZrCl_2} \xrightarrow{Cl\cdot} \underset{\mathbf{2}}{[CpZrCl_2(\eta^4\text{-}C_5H_5Cl)]} \xrightarrow{3Cl_2} \underset{\mathbf{3}}{CpZrCl_3} + \underset{\mathbf{4}}{C_5H_5Cl_5} + Cl\cdot$$

$CpZrCl_3$ thus obtained appears to be insoluble in common noncoordinating solvents. It becomes well dissolved, however, even in benzene or chloroform upon addition of donor agents ether, tetrahydrofuran, triethylamine, or pyridine in excess of 2 molar equiv. Variable-temperature ^1H NMR spectroscopy is of high diagnostic value to characterize the constitution of these adducts in solution. At room temperature in each case only one set of signals due to the added substrates is observed, indicating rapid equilibration between free and coordinated donor molecules. However, at low temperature even in the presence of an excess of the donor an adduct $CpZrCl_3(py)_2$ (py = pyridine) can be identified showing two chemically different coordinated pyridine moieties. In $CDCl_3$ solution at −45 °C we observe a sharp singlet (δ 6.65, 5 H) representing five equivalent Cp protons and two broad doublets (δ 9.0, 2 H, and δ 8.8, 2 H) resulting from orthohydrogens of coordinated pyridine ligands clearly separated from the corresponding resonance (δ 8.6, br d, 2 H) caused by free pyridine in the sample.[5] From these spectroscopic features a description of the $CpZrCl_3$ adduct with two monodentate donor ligands as (OC-6-33)-(η^5-cyclopentadienyl)bis(pyridine)zirconium(IV) trichloride[6] (**3a**) is implied. From our NMR observations it appears that such hexacoordinate zirconium(IV) complexes prefer to adopt similar structures in solution as has been disclosed by X-ray diffraction methods for the example $CpZrCl_3$(dme) (dme = 1,2-dimethoxyethane) (**3b**) in the solid state.[3a]

There is evidence, however, that the energy separation between geometrical $CpZrCl_3L_2$ isomers may not be very large in solution. In contrast to the reaction of **3** with pyridine, treatment with excess 3,5-lutidine results in the formation of three different 1:2 addition products. By its low-temperature ^1H NMR spectrum,[7] **3c**, the major component of this mixture, can be identified as being structurally equivalent to **3a** and **3b**. Both minor congeners, formed in 30% and 10% relative yield, respectively, exhibit similar NMR spectra but appear to lack the characteristic differentiation of lutidiene ligands. Above room temperature rapid equilibration of all these isomers on the NMR time scale is observed.

An etheral suspension of $CpZrCl_3$ rapidly reacts with aryllithium reagents (aryl = phenyl and *p*- and *m*-tolyl) forming tris(aryl)(η^5-cyclopentadienyl)zirconium(IV) complexes **5a–c**. Like $CpZrCl_3$, the isolated pure compounds **5b,c** are only slightly soluble in aromatic hydrocarbon solvents. They too readily form highly soluble adducts with the monodentate donor substrates mentioned above. Thus, the complex triphenylcyclopentadienylzirconium (**5a**) could only be isolated as a monoetherate. Nevertheless, rapid equilibration of free and coordinated diethyl ether can be observed with all these complexes in solution at ambient temperature by ^1H NMR spectroscopy.[8]

Experimental Section

Reactions with zirconium compounds were performed in an argon atmosphere with standard Schlenk techniques. Solvents were distilled from $P_4O_{10}(CCl_4)$ or $LiAlH_4$ prior to use. Cl_2 was dried by passing through H_2SO_4. Microanalyses were performed by Dornis und Kolbe, mikroanalytisches Laboratorium, Mülheim a. d. Ruhr.

$CpZrCl_3$. In a 500-mL two-necked Schlenk tube, equipped with a thermometer, a gas inlet tube, and a magnetic stirrer, a suspension of 30 g (0.106 mol) of Cp_2ZrCl_2 in CCl_4 (300 mL) is saturated with chlorine gas. The reaction is initiated by short irradiation (1–2 min) with a 200-W Osram sunlight lamp. Chlorine is introduced at such a rate to maintain the exothermic reaction. Occasional external cooling may be necessary to keep the temperature of the reaction mixture within the optimal range of 20–23 °C. Chlorination is complete after about 2 h. A stream of argon is passed through the resulting white suspension to remove excess chlorine. The precipitate of pure $CpZrCl_3$ is separated and washed successively with chloroform (50 mL), CCl_4 (100 mL), and pentane (100 mL). After the precipitate is dried in vacuo, $CpZrCl_3$ is obtained as a white powder; yield 26 g (96%). Anal. Calcd for $C_5H_5ZrCl_3$: C, 22.83; H, 1.92. Found: C, 22.63; H, 1.93. Evaporation of the CCl_4 filtrate yields 24 g (95%) of pentachlorocyclopentane.

$CpZrPh_3$. A 60-mL sample of a 1.1 M etheral solution of phenyllithium is added to a suspension of 4.6 g (17 mmol) of $CpZrCl_3$ in 300 mL of ether at −30 °C over a period of 30 min. The reaction mixture is allowed to warm up and is then stirred at 0 °C for 1 h. After removal of the ether in vacuo, the resulting dark residue is washed twice with cold pentane. The reaction product is dissolved in toluene (50 mL) at +5 °C and filtered cold from lithium chloride. Addition of the resulting clear solution to 300 mL of pentane at −10 °C precipitates $CpZrPh_3 \cdot Et_2O$, obtained as a pale yellow solid after filtration and drying in vacuo; yield 4.6 g (58%). Anal. Calcd for $C_{27}H_{30}OZr$: C, 70.23; H, 6.55; Found: C, 70.27, H, 6.51. Tris(*p*- and *m*-tolyl)cyclopentadienylzirconium complexes have been obtained by analogous procedures. Anal. Calcd for $C_{26}H_{26}Zr$: C, 72.67; H, 6.1; Found (**5b**): C, 72.69; H, 6.6. Found (**5c**): C, 73.18; H, 6.16.

Registry No. **1**, 1291-32-3; **3**, 34767-44-7; **3a**, 80327-21-5; **3c**, 80327-20-4; **5a**·Et_2O, 80327-19-1; **5b**, 80327-18-0; **5c**, 80327-17-9.

(5) Pyridine meta and para hydrogens are not well resolved under these conditions and appear as one broad multiplet (δ 8.1–6.8); warming the sample results in line broadening and a pairwise coalescence of ortho hydrogen resonances of the differently coordinated pyridine molecules with free ones. Only one set of sharp pyridine ^1H NMR signals is observed in the limiting high-temperature spectrum at +57 °C.

(6) Nomenclature: Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1975**, *14*, 1273.

(7) ^1H NMR for **3c** ($CDCl_3$, −47 °C): δ 6.60 (s, 5H), Cp group; 8.60 (s, 2 H), 7.55 (br s, 1 H), 2.40 (s, 3 H), 8.30 (s, 2 H), 7.25 (br. s, 1 H), 2.20 (s, 3 H), 3,5-lutidine ligands.

(8) ^1H NMR (toluene-D_8, 250 MHz): for **5a**, δ 7.62 (d, 6 H), 7.04 (t, 6 H), 6.84 (t, 3 H, phenyl), 6.02 (s, 5 H, Cp); for **5b**, δ 7.58, 6.88 (AA′BB′, 12 H), 2.07 (s, 9 H, *p*-tolyl), 6.08 (s, 5 H, Cp); for **5c**, δ 7.54 (s, 3 H), 7.52 (d, 3 H), 7.02 (t, 3 H), 6.69 (d, 3 H), 2.13 (s, 9 H, *m*-tolyl), 6.08 (s, 5 H, Cp). Resonances due to 1 molar equiv of coordinated diethyl ether are observed at δ 2.17 (q, 4 H) and 0.23 (t, 6 H) for **5a–c**.

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Reactions of Coordinated Molecules. 31. Rhena β-Keto Imine Derivatives of Several Biologically Important Molecules Containing 2-Ethylamino Groups

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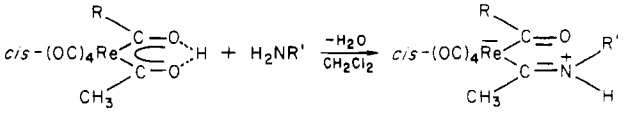
We reported recently that the rhena β-diketones **1** and **2**



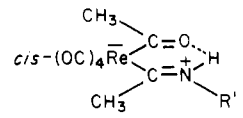
1, R = CH_3
2, R = $(CH_3)_2CH$

3, R′ = H, alkyl, or aryl

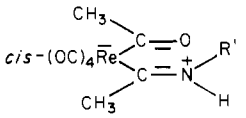
condense with NH_3 and primary alkyl- or arylamines to afford

0020-1669/82/1321-1278$01.25/0

rhena β-keto imine molecules, **3**, as shown.[1,2] The zwitterionic structure and geometrical or structural isomerism exhibited by the complexes **3** have been established by X-ray crystallographic or spectroscopic analyses.[1-3] For example, when R is methyl, the complexes **3** can exist as *intra* or *inter* geometrical isomers, **4** and **5**, respectively, depending on whether the molecule exhibits intramolecular or intermolecular hydrogen bonding.



4, *intra* isomer



5, *inter* isomer

Very recently, we reported that complex **1** condenses with ethyl glycinate and ethyl L-alaninate to afford the corresponding rhena β-keto imine derivatives of these amino acid esters.[4] The rhena moiety acts as an N-terminal end protecting group in subsequent peptide synthesis and as a heavy-atom label. The X-ray structure of the ethyl L-rhenaalaninate complex was solved by using the heavy-atom method due to the presence of the rhenium atom.

Upon realizing the considerable interest generated by our report of rhena β-keto imine derivatives of amino acids and peptides, we decided to prepare rhena Schiff-base derivatives of *selected* biologically important primary amines in order to demonstrate the synthesis and characterization of such rhena derivatives over a wide range of compounds. We now report the preparation of several rhena β-keto imine derivatives of biologically important primary amines which contain a 2-ethylamino group. These primary amines include 2-chloroethylamine (a DNA-alkylating reagent), cystamine (an heparin antagonist), histamine (a potent vasodilator), tryptamine and *O*-methylserotonin (two indole alkaloids), and *O,O*-dimethyldopamine (an adrenergic drug).

Interest in these rhena derivatives centers on the strong covalent bonding between the rhena moiety and the amino group. These compounds should have different distribution and transport properties than the free amines, and they may act as latent or prodrug forms of the biologically active amines. Use of the Re atom as a heavy-atom label, or the analogous Tc complexes as radiolabels, may be of some interest, also.

Experimental Section

All reactions were performed under dry, prepurified nitrogen at 25 °C. Diethyl ether was dried over Na-K alloy with added benzophenone, methylene chloride was dried over P_2O_5, and hexane was dried over active alumina.

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. All frequencies are reported in cm^{-1}. Proton NMR spectra were obtained on a JEOL MH-100 NMR spectrometer as $CDCl_3$ solutions using Me_4Si as an internal reference. Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

Complexes **1** and **2** were prepared by literature methods.[5,6] All amines were purchased from either Aldrich Chemical Co. or Sigma Chemical Co. as either the free base or the HCl salt. Free base was generated from an HCl salt by deprotonation with KOH, as described previously.[4]

General Preparation of the Rhena β-Keto Imine Derivatives. To 0.2–0.5 g of **1** or **2** in 5–20 mL of CH_2Cl_2 was added a slight excess (ca. 5–95%) of the amine as the free base. The reaction solution was stirred under N_2 for ca. 1–24 h. In some instances, excess base was removed by adding a small amount of HCl/Et_2O. The products were isolated by precipitation from CH_2Cl_2/hexane solution at −20 °C. Specific data for each product are provided below.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2CH_2Cl)(H)]$ (6). The reaction solution containing 2-chloroethylamine was stirred for 1 h. From 0.30 g of **1**, 0.15 g (43%) of **6** was isolated as greenish yellow needles: mp 128–130 °C; IR (CH_2Cl_2) ν(CO) 2075 (m), 1975 (sh, vs), 1960 (vs), 1945 (sh, vs), ν(C=O, C=N) 1580 (br, m); ^1H NMR (intra isomer) δ 2.65 (CH_3CO), 2.76 (CH_3CN); ^1H NMR (inter isomer) δ 2.52 (s, 3, CH_3CO), 2.91 (s, 3, CH_3CN), 3.86 (t, 2, CH_2Cl, J = 8 Hz), 4.10 (quartet, 2, CH_2N, J = 8 Hz), 9.53 (br s, 1, NH). Anal. ($C_{10}H_{11}NO_5ClRe$) C, H, N, Cl.

Preparation of $\{$*cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2CH_2S)(H)]\}_2$ (7). The reaction time with cystamine with 15 h. From 0.40 g of **1** was isolated 0.15 g (31%) of **7** as a yellow oil: IR (CH_2Cl_2) ν(CO) 2075 (m), 1980 (br, vs), 1940 (s), ν(C=O, C=N) 1560 (br, m); ^1H NMR (intra isomer) δ 2.64 (s, 3, CH_3CO), 2.76 (s, 3, CH_3CN), 3.16 (t, 2, CH_2S, J = 8 Hz), 3.89 (quartet, 2, CH_2N, J = 8 Hz), 13.12 (br s, 1, NH); ^1H NMR (inter isomer) δ 2.55 (s, 3, CH_3CO), 2.88 (s, 3, CH_3CN), 3.24 (t, 2, CH_2S, J = 8 Hz), 4.19 (quartet, 2, CH_2N, J = 8 Hz), 10.02 (br s, 1, NH). Anal. ($C_{20}H_{22}N_2S_2O_{10}Re_2$) C, H, N.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2CH_2C_3H_3N_2)(H)]$ (8). The reaction time with histamine was 1 h. From 0.5 g of **1** was isolated 0.20 g (32%) of **8** as a very hygroscopic yellow oil: IR (CH_2Cl_2) ν(CO) 2075 (m), 1980 (br, vs), 1940 (s), ν(C=O, C=N) 1560 (br, m); ^1H NMR (intra isomer) δ 2.60 (s, 3, CH_3CN), 2.63 (s, 3, CH_3CO), 3.13 (t, 2, CH_2Ar, J = 8 Hz), 3.83 (quartet, 2, CH_2N, J = 8 Hz), 7.00 (s, 1, CCHN), 7.62 (s, 1, NCHN), 9.90 (br s, 1, NH of Ar), 12.69 (br s, 1, NH). Anal. ($C_{13}H_{14}N_3O_5Re$) H, N; C: calcd, 32.61; found, 32.01.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2CH_2C_8H_6N)(H)]$ (9). The reaction time with tryptamine was 24 h. From 0.30 g of **1** was isolated 0.045 g (11%) of **9** as pale yellow crystals: mp 151–153 °C; IR (CH_2Cl_2) ν(CO) 2075 (m), 1980 (br, vs), 1940 (s), ν(C=O, C=N) 1560 (br, m); ^1H NMR (intra isomer) δ 2.29 (s, 3, CH_3CN), 2.66 (s, 3, CH_3CO), 3.27 (t, 2, CCH_2, J = 8 Hz), 3.79 (quartet, 2, CH_2N, J = 7 Hz), 7.12–7.67 (m, 5, Ar), 8.50 (br s, 1, NH of Ar), 13.09 (br s, 1, NH). Anal. ($C_{18}H_{17}N_2O_5Re$) H, N; C: calcd, 40.96; found, 41.48.

Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2CH_2C_8H_5N\text{-}5\text{-}OCH_3)(H)]$ (10). The reaction time with *O*-methylserotonin was 24 h. From 0.20 g of **1** was isolated 0.04 g (14%) of **10** as pale yellow crystals: mp 160–162 °C; IR (CH_2Cl_2) ν(CO) 2075 (m), 1980 (br, vs), 1940 (s), ν(C=O, C=N) 1560 (br, m); ^1H NMR (intra isomer) δ 2.46 (s, 3, CH_3CN), 2.64 (s, 3, CH_3CO), 3.22 (t, 2, CCH_2, J = 8 Hz), 3.82 (quartet, 2, CH_2N, J = 7 Hz), 3.92 (s, 3, OCH_3), 6.93–7.36 (m, 4, Ar), 8.60 (br s, 1, NH of Ar), 13.07 (br s, 1, NH). Anal. ($C_{19}H_{19}N_2O_6Re$) C, H, N.

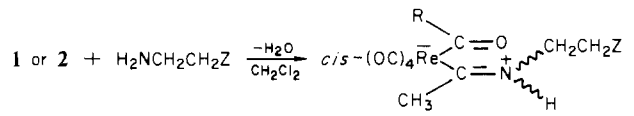
Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN[CH_2CH_2C_6H_3\text{-}3,4\text{-}(OCH_3)_2][H]]$ (11). The reaction time with *O,O*-dimethyldopamine was 24 h. From 0.50 g of **1** was isolated 0.20 g (28%) of **11** as a yellow oil: IR (hexane) ν(CO) 2070 (m), 1985 (vs), 1980 (vs), 1940 (s), ν(C=O, C=N) 1560 (br, m); ^1H NMR (intra isomer) δ 2.51 (s, 3, CH_3CN), 2.63 (s, 3, CH_3CO), 3.07 (t, 2, CCH_2, J = 8 Hz), 3.76 (quartet, 2, CH_2N, J = 6 Hz), 3.85 (s, 3, OCH_3), 3.91 (s, 3, OCH_3), 6.80 (s, 3, CH), 12.92 (br s, 1, NH). Anal. ($C_{18}H_{20}NO_7Re$) C, H, N.

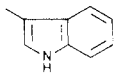
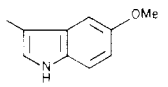
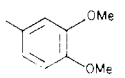
Preparation of *cis*-$(OC)_4Re[CH_3C(O)][CH_3CN(CH_2CH_2C_6H_5)(H)]$ (12). The reaction time with 2-phenethylamine was 70 min. From 0.40 g of **1** was isolated 0.12 g (23%) of **12** as a yellow oil: IR (hexane) ν(CO) 2070 (m), 1980 (br, vs), 1940 (s), ν(C=O, C=N) 1550 (br, m); ^1H NMR (intra isomer) δ 2.43 (s, 3, CH_3CN), 2.64 (s, 3, CH_3CO), 3.09 (t, 2, CH_2Ph, J = 8 Hz), 3.86 (quartet, 2, CH_2N, J = 8 Hz), 7.43 ("s", 5, C_6H_5), 13.03 (br s, 1, NH). Anal. ($C_{16}H_{16}NO_5Re$) C, H, N.

Preparation of *cis*-$(OC)_4Re[(CH_3)_2HCCO][CH_3CN(CH_2CH_2C_6H_5)(H)]$ (13). The reaction time with 2-phenethylamine was 45 min. From 0.40 g of **2** was isolated 0.21 g (39%) of **13** as a yellow oil: IR (hexane) ν(CO) 2075 (m), 1980 (br, vs), 1940 (s), ν(C=O, C=N) 1560 (br, m); ^1H NMR (intra isomer) δ 0.90 (d, 6, CH_3CH, J = 8 Hz), 2.40 (s, 3, CH_3CN), 3.09 (t, 2, CH_2Ph, J = 8

(1) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2774.
(2) Lukehart, C. M.; Zeile, J. V. *Inorg. Chem.* **1978**, *17*, 2369.
(3) Darst, K. P.; Lukehart, C. M. *Inorg. Chim. Acta* **1980**, *41*, 239.
(4) Baskar, A. J.; Lukehart, C. M.; Srinivasan, K. *J. Am. Chem. Soc.* **1981**, *103*, 1467.
(5) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1977**, *99*, 4368.
(6) Darst, K. P.; Lukehart, C. M.; Warfield, L. T.; Zeile, J. V. *Inorg. Synth.* **1980**, *20*, 200.

Chart I



R	Z	isomer	compd
CH_3	-Cl	intra + inter	6
CH_3	$(-S)_2$ (dimer)	intra + inter	7
CH_3		intra	8
CH_3		intra	9
CH_3		intra	10
CH_3		intra	11
CH_3	Ph	intra	12
i-Pr	Ph	intra	13

Hz), 3.24 (m, 1, CH, J = 8 Hz), 3.77 (quartet, 2, CH_2N, J = 8 Hz), 7.25 ("s", 5, C_6H_5), 13.27 (br s, 1, NH). Anal. ($C_{18}H_{20}NO_5Re$) C, H, N.

Results and Discussion

Complex **1** or **2** condenses with 2-chloroethylamine, cystamine, histamine, tryptamine, *O*-methylserotonin, *O,O*-dimethyldopamine, and 2-phenethylamine to afford, respectively, the corresponding rhena β-keto imine complexes **6–13** as shown in Chart I.

Proton NMR spectra of crude reaction residues indicate that these condensation reactions proceed in high yield. The low yields reported reflect material loss when separating the products from unreacted amine and solvent. These products are yellow oils except for complexes **6**, **9**, and **10**, which are pale yellow solids. Complexes **9** and **10** are the first intra isomers known to exist as solids at room temperature. IR spectra of these complexes are consistent with rhena β-keto imine formation.[1,2,4]

Complexes **8–11** exhibited an unusual pattern of relative chemical shifts for the two methyl groups within the rhena moiety. For rhena β-keto imine derivatives of *N*-alkyl primary amines, the ^{1}H NMR spectra of the intra isomers show a sharp singlet at ca. δ 2.62 for the acetyl methyl group and a broader singlet at ca. δ 2.73 ppm for the iminium methyl group.[2] This pattern is observed for complexes **6** and **7**, also. However, complexes **8–11** exhibit a reversed pattern for these two singlets. In these intra isomers, the sharp acetyl methyl resonance appears at the normal chemical shift of δ 2.64 ± 0.02, but the more broad iminium methyl resonance now appears, *in each case*, at *higher* field than the acetyl methyl resonance. These iminium methyl resonances appear in the range of δ 2.29–2.60 and represent an upfield shift of from 13 to 44 Hz relative to the "normal" chemical shift of an iminium methyl group in *N*-alkyl rhena β-keto imines.

This upfield shift of the iminium methyl resonance is attributed to a through-space interaction between this methyl group and the π system of an aromatic substituent attached to the carbon atom which is β to N. Crude molecular models confirm the proximity of these moieties in several of the various conformations of intra isomers containing such *N*-alkyl substituents. Complexes **12** and **13** were prepared as the most simple *N*-alkyl derivative containing a phenyl group β to N. For both complexes, the iminium methyl resonance appears at high field (δ 2.42 ± 0.02). In complex **12**, this resonance is 21 Hz to higher field than the acetyl methyl resonance. Thus, the position of the iminium methyl resonance is greatly affected by the presence of an aromatic substituent on the β-carbon atom of the *N*-alkyl group.[7,8]

The preparation of rhena derivatives of other biologically important amines which are representative members of important classes of pharmaceutical drugs is being pursued with appropriate selectivity.

Acknowledgment. C.M.L. thanks the National Science Foundation (Grant Nos. CHE-7907557 and CHE-8106140) and the University Research Council of Vanderbilt University for support of this research. C.M.L. acknowledges support from the Alfred P. Sloan Foundation as a Research Fellow.

Registry No. **1**, 59299-78-4; **2**, 66808-98-8; **6** (intra isomer), 80374-42-1; **6** (inter isomer), 80327-16-8; **7** (intra isomer), 80374-41-0; **7** (inter isomer), 80327-15-7; **8** (intra isomer), 80327-14-6; **9** (intra isomer), 80327-13-5; **10** (intra isomer), 80327-32-8; **11** (intra isomer), 80327-31-7; **12** (intra isomer), 80327-30-6; **13** (intra isomer), 80339-93-1; 2-chloroethylamine, 689-98-5; cystamine, 51-85-4; histamine, 51-45-6; tryptamine, 61-54-1; *O*-methylserotonin, 608-07-1; *O,O*-dimethyldopamine, 120-20-7; 2-phenethylamine, 64-04-0.

(7) The ^{1}H NMR spectrum of the rhena β-keto imine derivatives of ethyl L-phenylalaninate shows the same "reversed" pattern of rhena–methyl group resonances for the intra isomer. However, the inter isomer exhibits a "normal" pattern for the two methyl resonances. Molecular models reveal that an iminium methyl–aromatic interaction is not possible for the inter isomer, which is consistent with these spectral data reported here: Lukehart, C. M.; Afzal, D., unpublished results.[9]

(8) Note that the *N*-benzylrhenaacetylacetonimine complex reported in ref 2 does *not* exhibit this "reversed" order of the two rhena–methyl resonances in the intra isomer. In this complex, the aromatic group is a substituent on the carbon atom α to N.

(9) When **9** or **10** are prepared at 1:1 stoichiometry with a reaction time of 16 h, both intra and inter isomers are observed. The chemical shifts of the acetyl- and iminium-methyl resonances of the inter isomers *also* follow the "normal" pattern.

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High-Performance Liquid Chromatography Studies on Platinum Thymine Blue

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Platinum pyrimidine blues (PPBs) are currently of great interest because of their unusual color and their antitumor properties.[1] Apart from an extended X-ray absorption fine structure study on platinum uridine blue[2] and a powder X-ray diffraction study on platinum acetamide blue,[3] the majority of our knowledge of these species is based upon comparison with platinum α-pyridone blue, whose structure has been solved by single-crystal X-ray studies.[4] PPBs have proved to be very difficult to prepare reproducibly; for example, the EPR spectra vary considerably from batch to batch.[5] Their visible spectra do not obey Beer's law, with the absorptions also showing a

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