Reactions of Coordinated Molecules. 10. The Preparation and Characterization of Several Metallo-β-Diketone Molecules as Enol Tautomers and as Complexes of the Enolate Anions

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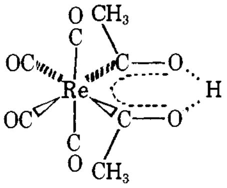
Abstract: The preparation of five metallo-β-diketone molecules as the enol tautomers, $M[C(CH_3)O\cdots H\cdots OC(R)]$, is reported. The metallo moiety, M, is either *cis*-$(OC)_4Re$ or η^5-$C_5H_5(OC)Fe$, and the substituent, R, is either methyl, isopropyl, benzyl, or diphenylmethyl. The preparation of the tris-chelate complexes obtained by coordinating the corresponding enolate anions to Al(III) ion is reported also. The ^1H NMR spectra of several of these aluminum complexes are discussed in detail. When R is not methyl and M is the iron moiety, the unsymmetrical tris-chelate aluminum complexes exhibit cis-trans isomerism of both the chelate-ring substituents and the iron-cyclopentadienyl ligands.

We recently reported the preparation of the first example of a metallo-β-diketone molecule, *cis*-$(OC)_4Re[C(CH_3)O\cdots H\cdots OC(CH_3)]$, **1**. This complex was structurally characterized as the enol tautomer of a metallo-acetylacetone molecule where the methine group of acetylacetone is replaced formally by the *cis*-$(OC)_4Re$ moiety.[1]



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In this paper we report the synthesis and characterization of five new metallo-β-diketone molecules as the enol tautomers as well as the tris-chelate aluminum complexes which are formed via the coordination of the corresponding enolate anions. These metallo-β-diketone complexes extend this unique class of compounds to include two different metallo moieties which can be incorporated directly into the σ- and π-electronic systems of β-diketone molecules. The preparation of such complexes is accomplished by a straight forward and general procedure. These complexes are intriguing because of the fundamentally novel interaction of a hydrogen atom with such relatively simple transition metal-organometallic complexes, especially when an interaction of this type may be relevant to the study of homogeneous catalytic processes.

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25 °C unless otherwise stated. Diethyl ether, tetrahydrofuran, benzene, and pentane were dried over Na/K alloy (with benzophenone added) under a nitrogen atmosphere and were freshly distilled before use. All other solvents were dried over 4Å molecular sieves and were purged with nitrogen before use. The reagents $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and $Re_2(CO)_{10}$ were purchased from Pressure Chemical Co. (Pittsburgh, Pa.).

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. Band frequencies are reported in reciprocal centimeters (cm^{-1}). ^1H NMR spectra were obtained on a Joel MH-100 NMR spectrometer using Me_4Si as an internal reference.

The complexes, $(CH_3)_2CHC(O)Re(CO)_5$[2] and η^5-C_5H_5-$(OC)_2FeC(O)CH_3$,[3] were prepared by slight modifications of known procedures using the corresponding metal anion and the appropriate acid chloride.

Preparation of Phenylacetylpentacarbonylrhenium. To a stirred solution of 2.14 g (6.13 mmol) of $Na[Re(CO)_5]$ in 25 mL of tetrahydrofuran at −78 °C was added dropwise 0.82 mL (6.13 mmol) of phenylacetyl chloride over a 5-min period. After being stirred at −78 °C for an additional 15 min, the reaction solution was allowed to warm to 25 °C. The solvent was then removed at reduced pressure affording a yellow residue. The residue was extracted with 15 mL of methylene chloride and was filtered. Hexane was added slowly to the filtrate until the solution became cloudy. Cooling this suspension at −20 °C for 20 h yielded 1.2 g (48%) of the product as bright yellow crystals: mp 139.5–149.5 °C; IR (CH_2Cl_2) ν(CO) 2028 (m), 2019 (m, sh), 2004 (vs), 1992 (s), 1989 (m, sh), ν(acyl) 1610 (m); ^1H NMR ($CDCl_3$) τ 6.10 (singlet, 2, CH_2), 2.85–1.64 (multiplet, 5, C_6H_5). Anal. ($C_{13}H_7O_6Re$) C, H.

Preparation of η^5-$C_5H_5(OC)_2FeC(O)CH(CH_3)_2$. A solution of 4.65 g (23 mmol) of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ in 50 mL of tetrahydrofuran at −78 °C was treated dropwise with 2.32 g (25 mmol) of isobutyryl chloride over a 5-min period. The reaction solution was then allowed to warm to 25 °C and was stirred for an additional 90 min after which time the solvent was removed at reduced pressure. The residue was extracted with 2 × 100 mL of petroleum ether and was filtered. The solvent was removed from the filtrate at reduced pressure. The residue was dissolved in 5 mL of benzene and chromatographed through a 30 × 2.5 cm silica gel (60–200 mesh) column using benzene as the eluent. A golden brown band was eluted which contained 3.19 g (56%) of a golden brown liquid after removing the benzene at reduced pressure. Crystallization at −20 °C from pentane solution afforded orange needles: mp 13–14 °C; IR (C_6H_{12}) ν(CO) 2003 (s), 1950 (vs), ν(acyl) 1662 (m); ^1H NMR (CS_2) τ 9.09 (doublet, 6, $2CH_3$, $J_{H\text{-}H}$ = 6.9 Hz), 7.06 (septet, 1, CH, $J_{H\text{-}H}$ = 6.9 Hz), 5.17 (singlet, 5, C_5H_5). Anal. ($C_{11}H_{12}O_3Fe$) C, H.

Preparation of η^5-$C_5H_5(OC)_2FeC(O)CH(C_6H_5)_2$. To a stirred solution of 3.4 g (17 mmol) of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ in 50 mL of tetrahydrofuran at −78 °C was added 3.83 g (17 mmol) of diphenylacetyl chloride. The reaction solution was stirred for an additional 15 min and was then allowed to warm to 25 °C. After stirring for another 30 min the solvent was removed at reduced pressure. The residue was extracted with 100 mL of hexane–methylene chloride (1:1) and was filtered and placed at −20 °C for 48 h affording 3.6 g (57%) of a golden brown solid: mp 115–116 °C; IR (C_6H_{12}) ν(CO) 2005 (s), 1958 (vs), ν(acyl) 1655 (m); ^1H NMR (CS_2) τ 5.39 (singlet, 5, C_5H_5), 4.46 (singlet, 1, CH), 2.89 (multiplet, 10, $2C_6H_5$). Anal. ($C_{21}H_{16}O_3Fe$) H, C: calcd, 67.71; found, 67.21.

Preparation of *cis*-$(OC)_4Re\{C(CH_3)O\cdots H\cdots OC[CH(CH_3)_2]\}$, 2. To a stirred solution of 0.25 g (0.63 mmol) of isobutyrylpentacarbonylrhenium in 15 mL of ether at 0 °C was added dropwise 0.33 mL of a 2.06 M solution of methyllithium in ether over a 5-min period. During this addition the initially bright yellow reaction solution became a more pale yellow color. The solution was stirred for an additional 30 min and then cooled at −78 °C and was treated with 0.022 g (0.61 mmol) of HCl in ether. A white precipitate formed within 15 min. The reaction solution was permitted to warm to 0 °C and then the solvent was removed at reduced pressure. The yellow residue was extracted with 25 mL of hexane and was filtered. The filtrate was evaporated to dryness under reduced pressure affording 0.056 g (20%) of the crude product which was crystallized from hexane at −78 °C as white needles: mp 42.5–43.5 °C; IR (C_6H_{12}) ν(CO) 2105 (m), 2003 (s), 1997 (vs), 1964 (s), ν(acyl) 1513 (m); ^{1}H NMR (CS_2) τ 9.00 (doublet, 6, $2CH_3$, J_{H-H} = 6.9 Hz), 7.20 (singlet, 3, CH_3), 6.73 (septet, 1, CH, J_{H-H} = 6.9 Hz), −11.70 (broad singlet, 1, enol H). Anal. ($C_{10}H_{11}O_6Re$) C, H.

Preparation of *cis*-$(OC)_4Re[C(CH_3)O\cdots H\cdots OC(CH_2C_6H_5)]$, 3. To a stirred suspension of 0.30 g (0.67 mmol) of phenylacetylpentacarbonylrhenium in 40 mL of ether at 0 °C was added dropwise 0.47 mL of a 1.45 M solution of methyllithium in ether. Within 30 min all of the solid had dissolved and the reaction solution was cooled to −78 °C and was treated with 0.024 g (0.67 mmol) of HCl dissolved in ether. A white precipitate formed during this addition and the mixture was warmed to 0 °C and was stirred for an additional 10 min. The solvent was removed at reduced pressure and the residue was extracted with 2 × 30 mL of hexane and was filtered. Removal of the solvent from the filtrate afforded 0.20 g (65%) of the crude product which was crystallized from pentane solution at −20 °C as a white solid: mp 77.5–79 °C; IR (C_6H_{12}) ν(CO) 2080 (m), 1995 (s), 1980 (vs), 1953 (s), ν(acyl) 1508 (m); ^{1}H NMR (CS_2) τ 7.28 (singlet, 3, CH_3), 5.87 (singlet, 2, CH_2), 2.91 (multiplet, 5, C_6H_5), −12.57 (broad singlet, 1, enol H). Anal. ($C_{14}H_{11}O_6Re$) C, H.

Preparation of η^5-$C_5H_5(OC)Fe[C(CH_3)O\cdots H\cdots OC(CH_3)]$, 4. All glassware was flame-dried, and all manipulations were conducted in an argon atmosphere. A solution of 0.50 g (2.3 mmol) of η^5-$C_5H_5(OC)_2FeC(O)CH_3$ in 40 mL of freshly distilled ether at −55 °C was treated with 1.00 mL of a 1.56 M solution of methyllithium in ether. The reaction solution was stirred for 30 min and then was cooled to −78 °C and was treated with 0.082 g (2.3 mmol) of HCl in ether. The reaction solution was stirred for an additional 10 min and then permitted to warm to 0 °C during which time a light colored precipitate formed. After stirring for an additional 15 min the solvent was removed at reduced pressure and the resulting residue was extracted quickly with freshly distilled pentane at 0 °C. The mixture was filtered into a cooled flask and the solvent was removed at reduced pressure affording 0.12 g (22%) of a gold solid: mp (argon) 87–89 °C dec; IR (C_5H_{12}) ν(CO) 1968; ^{1}H NMR (CS_2) τ 7.40 (singlet, 6, $2CH_3$), 5.19 (singlet, 5, C_5H_5), −9.45 (broad singlet, 1, enol H). Anal. ($C_{10}H_{12}O_3Fe$) H, C: calcd, 50.89; found, 50.38.

Preparation of η^5-$C_5H_5(OC)Fe\{C(CH_3)O\cdots H\cdots OC[CH(CH_3)_2]\}$, 5. All glassware was flame-dried, and all manipulations were conducted in an argon atmosphere. To a stirred solution of 0.50 g (2.0 mmol) of η^5-$C_5H_5(OC)_2FeC(O)C(H)(CH_3)_2$ in freshly distilled ether at −50 °C was added 1.41 mL of a 1.45 M solution of methyllithium in ether. After stirring for 10 min the reaction solution was cooled to −78 °C and treated with 0.07 g (2.0 mmol) of HCl dissolved in ether. A light colored precipitate formed as the reaction solution was warmed to 0 °C. The solvent was removed at reduced pressure and the resulting gold residue melted upon warming to 25 °C. This residue was extracted with freshly distilled pentane (2 × 30 mL) and was filtered. Removal of the pentane from the filtrate at reduced pressure afforded 0.07 g (13%) of a golden brown liquid: mp > −78 °C; IR (C_5H_{12}) ν(CO) 1930; ^{1}H NMR (CS_2) τ 9.00 (doublet, 6, $2CH_3$), 7.31 (broad singlet, 3, CH_3), 6.62 (broad multiplet, 1, CH), 5.27 (singlet, 5, C_5H_5), −10.08 (broad singlet, 1, enol H). This complex was too unstable for microanalysis.

Preparation of η^5-$C_5H_5(OC)Fe\{C(CH_3)O\cdots H\cdots OC[C(H)(C_6H_5)_2]\}$, 6. To a solution of 0.30 g (0.80 mmol) of η^5-$C_5H_5(OC)_2FeC(O)C(H)(C_6H_5)_2$ in 40 mL of ether at −40 °C was added 0.56 mL of a 1.45 M solution of methyllithium in ether. After stirring for 15 min the reaction solution was cooled to −78 °C and was treated with 0.03 g (0.83 mmol) of HCl dissolved in ether. After 10 min of additional stirring the solution was warmed to 0 °C and was stirred for 20 min. The solvent was removed at reduced pressure and the residue was extracted with 20 mL of benzene and was filtered. The solvent was removed at reduced pressure and crystallization of the residue from pentane solution at −45 °C afforded 5 mg (3%, based upon recovered starting material) of a golden solid: mp 27–28 °C; IR (C_6H_6) ν(CO) 1940; ^{1}H NMR (CS_2) τ 7.42 (singlet, 3, CH_3), 5.23 (singlet, 5, C_5H_5), 4.10 (singlet, 1, CH), 2.88 (multiplet, 10, $2C_6H_5$), −9.11 (broad, 1 enol H). Anal. ($C_{22}H_{20}O_3Fe$) C, H.

Preparation of [*cis*-$(OC)_4Re(CH_3CO)(C_6H_5CH_2CO)]_3Al$, 7. To a stirred solution of 0.40 g (0.90 mmol) of phenylacetylpentacarbonylrhenium in 20 mL of ether at 0 °C was added 0.63 mL of a 1.45 M solution of methyllithium in ether. After stirring for 20 min, 0.04 g (0.30 mmol) of anhydrous aluminum chloride dissolved in ether was added dropwise and stirring was continued for 90 min. The solvent was removed at reduced pressure and the yellow residue was extracted with 10 mL of methylene chloride and was filtered. The solvent was removed from the filtrate and the solid residue was washed with pentane (2 × 10 mL) and was dried affording 0.17 g (34%) of the product as a yellow solid: mp 245–246 °C rapid dec; IR (CH_2Cl_2) ν(CO) 2070 (m), 1988 (vs, broad), 1950 (s), $\nu(C\overset{\cdots}{=}O)$ 1512 (m); ^{1}H NMR (CS_2) τ 6.46–7.33 (four singlets, 3, CH_3), 5.88 (complex multiplet, 2, CH_2), 2.93 (complex multiplet, 5, C_6H_5). Anal. ($C_{42}H_{30}O_{18}AlRe_3$) C, H, Al.

Preparation of $[\eta^5$-$C_5H_5(OC)Fe(CH_3CO)_2]_3Al$, 8. All glassware was flame-dried, and all manipulations were conducted in an argon atmosphere. To 0.50 g (2.3 mmol) of η^5-$C_5H_5(OC)_2FeC(O)CH_3$ in 30 mL of ether at −45 °C was added 1.5 mL of a 1.56 M solution of methyllithium in ether and the mixture was stirred for an additional 15 min. An ether solution of 0.10 g (0.75 mmol) of anhydrous aluminum chloride was added dropwise to the reaction solution. After stirring for 45 min, the reaction solution was permitted to warm to 0 °C during which time a light colored precipitate formed. The solvent was removed at reduced pressure and the solid residue was extracted with 20 mL of benzene. The mixture was filtered and removal of the solvent from the filtrate afforded 0.11 g (20%) of a gold solid: mp >250 °C; IR (C_5H_{12}) ν(CO) 1939; ^{1}H NMR (CS_2) τ 7.47 (broad singlet, 6, $2CH_3$), 5.51 (3 singlets, 5, C_5H_5). This complex was too unstable for microanalysis.

Preparation of $\{\eta^5$-$C_5H_5(OC)Fe(CH_3CO)[C(H)(CH_3)_2CO]\}_3Al$, 9. To a stirred solution of 0.50 g (2.0 mmol) of η^5-$C_5H_5(OC)_2FeC(O)C(H)(CH_3)_2$ in ether at −40 °C was added 1.42 mL of a 1.45 M solution of methyllithium in ether over a 5-min period. The reaction solution was stirred for 30 min and then warmed to 0 °C and then 0.09 g (0.7 mmol) of anhydrous aluminum chloride as an ether solution was added. After stirring for 45 min the solvent was removed at reduced pressure and the residue was extracted rapidly with 20 mL of pentane at 0 °C. The mixture was filtered into a flask at 0 °C, and the solvent was removed at reduced pressure affording 0.24 g (44%) of a gold solid: mp 53–54 °C dec; IR (C_5H_{12}) ν(CO) 1930 (vs), $\nu(C\overset{\cdots}{=}O)$ 1506 (m); ^{1}H NMR (CS_2) τ 9.66–9.02 (complex multiplet, 6, $2CH_3$), 7.51 (4 singlets, 3, CH_3), 6.98–6.35 (broad multiplet, 1, CH), 5.61–5.41 (4 singlets, 5, C_5H_5). Anal. ($C_{36}H_{45}O_9AlFe_3$) C, H, Al.

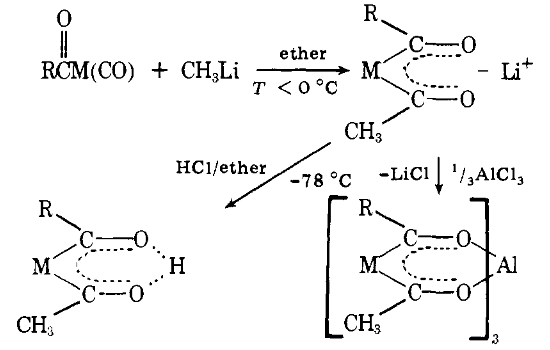
Preparation of $\{\eta^5$-$C_5H_5(OC)Fe(CH_3CO)[C(H)(C_6H_5)_2CO]\}_3Al$, 10. To a stirred solution of 0.50 g (1.3 mmol) of η^5-$C_5H_5(OC)_2FeC(O)CH(C_6H_5)_2$ in 35 mL of ether at −40 °C was added 0.94 mL of a 1.45 M solution of methyllithium in ether. After stirring for 45 min, the reaction solution was warmed to 0 °C and was treated with 0.06 (0.45 mmol) of anhydrous aluminum chloride as an ether solution. The reaction solution was stirred for 45 min and the solvent was removed at reduced pressure. The residue was extracted with 10 mL of methylene chloride and was filtered. The solvent was removed from the filtrate at reduced pressure, and the residue was washed with pentane (2 × 20 mL) and then dried under vacuum affording 0.31 g (59%) of a golden brown solid: mp 120–190 °C dec; IR (C_6H_{12}) ν(CO) 1945 (s), $\nu(C\overset{\cdots}{=}O)$ 1499 (m); ^{1}H NMR (CS_2) τ 7.46, 7.38 (2 singlets, 3, CH_3), 5.94–5.54 (4 singlets, 5, C_5H_5), 3.80 (singlet, 1, CH), 3.10–2.82 (complex multiplet, 10, $2C_6H_5$). Anal. ($C_{66}H_{57}O_9AlFe_3$) C, H, Al.

Results and Discussion

The metallo-β-diketone molecules and the complexes of the metalloenolate anions are prepared by the nucleophilic addition of methyllithium to a carbonyl ligand which is adjacent to the acyl ligand of an acylmetal carbonyl complex. The resulting metallo-β-diketonate anion is then either protonated with HCl/ether or coordinated to the aluminum ion as shown in Scheme I. The preparation of the aluminum complex of the enolate anion of **1** and the tris-chelate gallium(III) complexes of the enolate anions of **1** and **2** were reported previously.[2] A similar tris-chelate complex of aluminum having metalloacetylacetonate ligands has been structurally characterized recently.[4]

The rhenium-enol complexes, **1**-**3**, are white solids having good air stability while the iron-enols, **4**-**6**, are lower melting

Scheme I



M	R		M	R	
cis-$(OC)_4Re$	CH_3	1	*cis*-$(OC)_4Re$	$C_6H_5CH_2$	7
cis-$(OC)_4Re$	$(CH_3)_2CH$	2	η^5-$C_5H_5(OC)Fe$	CH_3	8
cis-$(OC)_4Re$	$C_6H_5CH_2$	3	η^5-$C_5H_5(OC)Fe$	$(CH_3)_2CH$	9
η^5-$C_5H_5(OC)Fe$	CH_3	4	η^5-$C_5H_5(OC)Fe$	$(C_6H_5)_2CH$	10
η^5-$C_5H_5(OC)Fe$	$(CH_3)_2CH$	5			
η^5-$C_5H_5(OC)Fe$	$(C_6H_5)_2CH$	6			

complexes which decompose rapidly when exposed to air. These iron complexes undergo significant decomposition over a 2-day period even when stored at −20 °C under an argon atmosphere.

The rhenium–aluminum tris-chelate complex, **7**, decomposes rapidly when heated in the air to 245–246 °C, and it possesses excellent stability toward air oxidation. Although the iron–aluminum tris-chelate complexes, **8**–**10**, have slightly better thermal and air stability than the corresponding iron–enol complexes, these aluminum complexes are still very sensitive to air oxidation. Solutions of these complexes are particularly reactive with the air.

Infrared Spectra. The rhenium–enol complexes **2** and **3** exhibit solution phase infrared spectra which are nearly identical with that of complex **1**.[1] The terminal carbonyl region confirms the *cis*-$(OC)_4Re$ stereochemistry[2,5] and the $C \overset{...}{=} O$ stretching mode assigned to the acyl groups within the metallo-β-diketonate ligand occurs at 1513 and 1508 cm^{-1} for **2** and **3**, respectively. The corresponding band of complex **1** occurs at 1520 cm^{-1}. The solution phase infrared spectra of the iron–enol complexes, **4**–**6**, show one absorption for the terminal carbonyl ligand. The ligand $C \overset{...}{=} O$ stretching vibration probably occurs below 1500 cm^{-1} and is not observed due to solvent interference. Neither thin film nor mull spectra were attempted because of the extreme air sensitivity of these complexes.

The rhenium–aluminum tris-chelate complex, **7**, exhibits an essentially identical solution phase infrared spectrum in the 1500–2200-cm^{-1} region to the analogous complexes of the enolate anions of **1** and **2**.[2] The local-oscillator approximation holds since no dipolar coupling is observed between the three $Re(CO)_4$ groups. The ligand $C \overset{...}{=} O$ stretch occurs at 1512 cm^{-1}. The iron–aluminum tris-chelate complexes, **8**–**10**, show only one terminal carbonyl stretching band. This band occurs at a frequency of 10–20 cm^{-1} lower than the antisymmetric stretching mode of the terminal carbonyl ligands in the corresponding acyl complex. The ligand $C \overset{...}{=} O$ stretch is observed at 1506 and 1499 cm^{-1} for complexes **9** and **10**, respectively. This band appears at ca. 6–13 cm^{-1} lower in frequency than the corresponding band of the rhenium complexes.

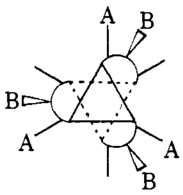
^1H NMR Spectra. A unique feature of the ^1H NMR spectra of the enol complexes, **1**–**6**, is the resonance assigned to the enol proton. This resonance always appears as a broad singlet at very low field. The enol proton resonances of the three rhenium complexes, **1**–**3**, occur at τ −11.79, −11.70, and −12.57, respectively, while the enol protons of the iron complexes, **4**–**6**, resonate at slightly higher field, τ −9.45, −10.08, and −9.11, respectively. As discussed earlier,[1] the very low frequency of this resonance does not reflect an extremely high acidity of this proton. In fact, the acidity of complex **1** is qualitatively very similar to the acidity of acetylacetone. Presumably, this low field chemical shift is very dependent upon the metallo group which is incorporated directly into the σ- and π-electronic systems of the metallo-β-diketone molecule. The rhenium enol protons resonate in a different region of the spectrum than the iron enol protons which is consistent with this assumption. The slightly higher value of the chemical shift of the iron enol protons may reflect a more electron-rich metal atom in the η^5-$C_5H_5(OC)Fe$ group than in the *cis*-$(OC)_4Re$ group.

The broadening of the enol proton resonance probably indicates both intra- and intermolecular exchange processes. The width of this resonance, measured at half-height, for the complexes **1**–**6** is 24, 54, 97, 45, 51, and 48 Hz, respectively, at solution concentrations of ca. 50 mg/0.5 mL in carbon disulfide.

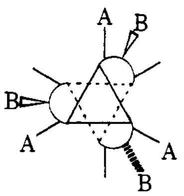
The ^1H NMR spectra of the tris-chelate aluminum complexes, **7**–**10**, reveal extensive intramolecular geometrical isomerism. The rhenium complex, **7**, exists in carbon disulfide solution as a mixture of both cis (or fac) and trans (or mer) isomers. The methyl substituent of the chelate ring acts as an effective probe to this geometrical isomerism as was demonstrated previously. The set of resonances assigned to this methyl group of complex **7** is nearly identical with the pattern of resonances observed for this substituent in the manganese analogue.[2] A set of four singlets is observed for these methyl groups. The set of three resonances of nearly equal intensity which are centered at δ 2.57 is assigned to the three nonequivalent methyl groups of the trans isomer. The singlet of weaker intensity which is located at 10 Hz to lower field is assigned to the methyl substituents of the cis isomer. Of the several known unsymmetrical tris-chelate complexes having metallo-β-diketonate ligands, complex **7** and its manganese analogue are the only compounds where the methyl resonance of the cis isomer appears completely outside of the set of resonances for the methyl substituents of the trans isomer. For complex **7**, 27% of the molecules exist as the cis isomer in carbon disulfide solution at 36 °C, while 16% of the molecules of the manganese analogue exist as the cis isomer at 36 °C in carbon tetrachloride solution. The statistical proportion of the cis isomer is 25%.

The ^1H NMR spectra of the iron–aluminum complexes, **8**–**10**, reveal even more stereochemical information because both the chelate ring substituents (for **9** and **10** only) and the η^5-C_5H_5 rings may define cis and trans isomers. Since the orientation of the ligands about the iron atom is approximately tetrahedral, the three η^5-C_5H_5 rings may be either all on the same side of an imaginary σ_h plane of symmetry (cis isomer) or only two of the three rings will be on the same side of this plane (trans isomer). This isomerism may produce ^1H NMR spectra which are quite complex.

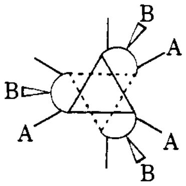
Ideally, the trans orientation of the chelate-ring methyl groups would afford a set of three resonances (1:1:1) because of the low symmetry of this isomer (C_1). Frequently the local asymmetry only produces two resonances having a 2:1 relative intensity.[2] The methyl groups of the cis isomer are equivalent (C_3 symmetry) and would appear as a singlet. The same analysis applies to the cis and trans isomers of the η^5-C_5H_5 rings. The possible complexity arises when either of these groups which are acting as probes to the geometrical isomerism at the iron and aluminum centers can magnetically sense the orientation or symmetry of the other probe. For example, there are ten geometrical isomers possible for a molecule having this isomerism at *both* the iron and aluminum atoms. These ten geometrical isomers belong to one of four distinct classes of isomers. The four *classes* of isomers are defined by the various combinations of cis and trans orientations of the methyl and η^5-C_5H_5 groups and are shown below (where A is the methyl group and B is the η^5-C_5H_5 ligand):



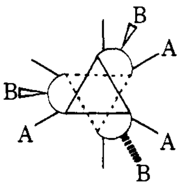
cis A–cis B



cis A–trans B



trans A–cis B



trans A–trans B

Within each of these classes of isomers, the specific geometrical isomers are defined by the *relative* orientation of the methyl and η^5-C_5H_5 groups with respect to the imaginary σ_h plane. The cis–cis, cis–trans, and trans–cis classes each define two distinctly different geometrical isomers while the trans–trans class defines four geometrical isomers. For example, the two geometrical isomers of the cis–cis type are constructed readily using the figure above. The first isomer is the one shown where the three η^5-C_5H_5 ligands and the three methyl groups are on the same side of the imaginary σ_h plane. The second isomer has the two sets of equivalent groups on opposite sides of this imaginary plane. The remaining eight isomers are generated similarly.

The possible spectral complexity due to this isomerism can now be examined in detail. Only two possibilities are considered for brevity. When considering the methyl region of the spectrum, if only the two cis–cis isomers are present in solution, then there would be two singlets for the methyl groups. However, if all ten isomers were present in solution, a total of 26 singlets could be observed for the methyl substituents. The same analysis would apply to the η^5-C_5H_5 region of the spectrum, also. A further complication arises from statistical considerations. The statistical abundance of each isomer is not equal for all ten isomers. The 32 statistically distinct isomers are apportioned among the ten geometrical isomers as follows: the two cis–cis isomers are weighted 1:1 (6.25%), the two cis–trans isomers are weighted 3:3 (18.75%), and the four trans–trans isomers are weighted 3:6:3:6 (56.25%). On a statistical basis, then, the trans–trans class of isomer would exhibit the most complex spectrum and would be in the largest relative concentration. The intensity of the ^{1}H NMR resonances would reflect these statistical weights if the ten isomers have nearly equal free energy.[6]

Fortunately, the pattern of resonances observed for each experimental probe apparently reflects only the relative orientation of like-groups. The asymmetry generated by one probe is not experimentally resolved in the resonances of the other probe. Although this prevents the identification of the specific geometrical isomers, it does permit a reasonable assignment as to which *class* of isomer is present. We need not consider the various possibilities for optical isomerism at this time. Also, due to the air sensitivity of these complexes we did not attempt to separate or isolate the isomers observed.

The ^{1}H NMR spectrum of complex **8** exemplifies this analysis. In this complex, both chelate-ring substituents are methyl groups so the only possible geometrical isomerism is at the iron atom. The spectrum shows a slightly broadened singlet (width of 6 Hz at half-height) at δ 2.68 for the methyl groups and a set of three singlets at δ 4.56, 4.59, and 4.62 which are assigned to the η^5-C_5H_5 ligands. Upon scale-expansion, the two peaks at δ 4.62 and 4.56 are of ca. 1.8:1 relative intensity while the peak at δ 4.59 is ca. 44% as intense as these two peaks. Our interpretation is that the η^5-C_5H_5 ligands are present in both cis and trans orientations. The two peaks of ca. 2:1 relative intensity are assigned to the trans isomer, and the third singlet is assigned to the cis isomer. With this assignment, approximately 30% of the molecules have a cis orientation of the η^5-C_5H_5 ligands. Apparently, the η^5-C_5H_5 ligands establish a nearly statistical distribution of cis and trans isomers, and the asymmetry caused by the trans orientation of these ligands is not significantly sensed by the methyl groups.

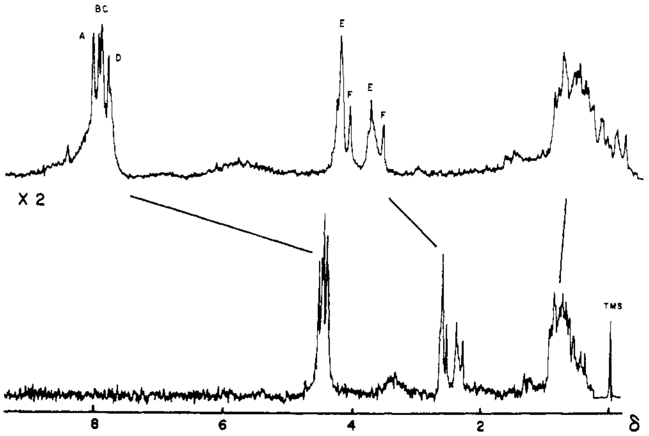


Figure 1. The 100-MHz ^{1}H NMR spectrum of $\{\eta^5$-$C_5H_5(OC)Fe(CH_3CO)[C(H)(CH_3)_2CO]\}_3Al$, **9**, in carbon disulfide solution at 36 °C under an argon atmosphere recorded at 1080 and 540 Hz spectral widths.

The ^{1}H NMR spectrum of complex **9** is shown in Figure 1. The four prominent peaks, A–D, are assigned to the η^5-C_5H_5 ligands. Three of these peaks probably belong to the trans isomer while one of them, perhaps A or C, belongs to the cis orientation of these ligands. With this assignment, the majority of the molecules have a trans orientation of the η^5-C_5H_5 ligands. The methyl substituent of the chelate ring gives two sets of resonances, E and F, where each set is two peaks of ca. 2:1 relative intensity. Both of these sets are assigned to a trans orientation of the methyl groups. Based upon relative intensities, the E set presumably belongs to the trans-η^5-C_5H_5 isomer and the F set belongs to the cis-η^5-C_5H_5 isomer. It is reasonable to expect the resonances of the trans–trans isomer to exhibit more complexity than those of the cis–trans isomer as discussed above. Even the most idealized analysis of the spectrum of the methyl groups of the isopropyl substituent would predict a superposition of two 12-line patterns of unequal relative intensity. At least 16 peaks are observed for these methyl groups.

The ^{1}H NMR spectrum of complex **10** shows four singlets for the η^5-C_5H_5 ligands. This pattern is very similar to that observed for complex **9** except that the peak corresponding to A is more separated from the other three peaks (16 Hz to lower field). This resonance is assigned to those molecules which have a cis orientation of the η^5-C_5H_5 ligands while the other three resonances are assigned to a trans-η^5-C_5H_5 isomer. The trans isomer is preferred with this complex, also. The chelate-ring methyl substituents give two singlets at δ 2.54 and 2.62 of ca. 3:1 relative intensity. Two explanations seem reasonable.

One possibility is that each peak represents a molecule having a cis orientation of the methyl groups about the aluminum atom. The smaller peak would belong to the cis-η^5-C_5H_5 isomer, and the larger peak would belong to the trans-η^5-C_5H_5 isomer. A second possibility is that the smaller peak represents a trans orientation of the methyl substituents where the smaller component peak of a 2:1 set of resonances happens to appear directly under the larger singlet. This possibility presumes that 36% of the molecules have cis-η^5-C_5H_5

ligands and trans methyl groups and that 64% have trans-η^5-C_5H_5 ligands and cis methyl groups. A distinction between these explanations is not possible. However, with either assignment complex **10** is unique in that the cis orientation of the methyl groups is the preferred isomer.

The apparent reversal of isomer stability at the aluminum atom of complex **10** may be related to a known trend in isomer stability of non-metallo-β-diketonate complexes and may indicate that electronic effects determine the preferred geometrical isomer.[7,8] As the ring substituents of tris-chelate β-diketonate complexes of aluminum become less electronegative, the trans isomer becomes less stable until the cis isomer finally becomes the more stable isomer. Even though the influence of steric effects on this trend has not been determined, it is tempting to speculate that the ligand of complex **10** might be more basic or electron-rich than the ligand of complex **9** and, therefore, rationalize the enhanced stability of the cis isomer of complex **10**. It is interesting, though perhaps fortuitous, that the enolate proton of complex **6** has the highest field chemical shift observed for any metallo-β-diketone molecule yet prepared.

Acknowledgment. We thank the Research Corporation, the University Research Council of Vanderbilt University, and the generous support of the National Science Foundation (Grant No. CHE-76-14304) for support of this research. We gratefully acknowledge the support of a DuPont fellowship to Jane V. Zeile.

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Ruthenium(II) Catalysis in Redox Fragmentation of Allyl Ethers

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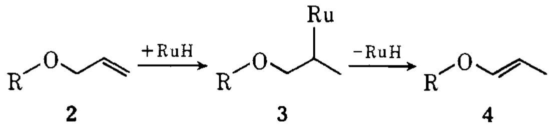
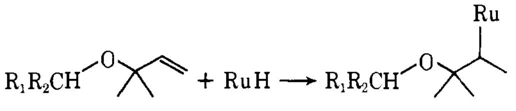
Abstract: A new type of homogeneous transition metal catalyzed process, redox fragmentation of allyl ethers in the presence of tris(triphenylphosphine)ruthenium(II) dichloride (**1**), is reported. α,α-Dimethylallyl benzyl ethers give benzaldehyde and 2-methyl-2-butene. Thus, redox fragmentation is accompanied by allylic transposition of the carbon-carbon double bond. Cleavage of the allylic carbon-oxygen bond is inferred to be rate determining since para substituents on the aryl ring and benzylic deuterium substitution in benzyl ethers have no appreciable effect on the rate of catalyzed fragmentation. Thus, a rate determining elimination of ruthenium(II) alkoxide from a β-alkoxyruthenium(II) intermediate is proposed. Subsequent facile decomposition to carbonyl compound and ruthenium(II) hydride, the actual catalyst of redox fragmentation, is shown to be feasible since sodium benzyl oxide gives benzaldehyde upon reaction with 1 equiv of **1**.

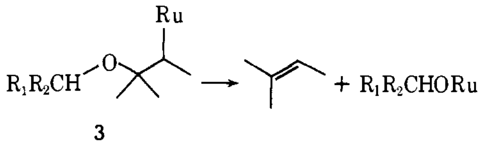
A hydride addition–elimination sequence is considered to account for allylic isomerization of olefins catalyzed by tris(triphenylphosphine)ruthenium(II) dichloride (**1**).[1-3] Thus, allylic ethers **2** yield vinyl ethers **4** via putative intermediate β-alkoxyruthenium alkyls **3**.[4] We speculated that these intermediates might undergo β-elimination of ruthenium alkoxide if β-hydride elimination is precluded by the absence of allylic hydrogen (eq 2). The alkoxides could then eliminate ruthenium hydride[5] to give aldehydes and regenerate the catalyst (eq 3). The overall process (eq 1–3) would be a ruthenium catalyzed redox fragmentation of allylic ethers, and might occur under milder conditions of thermal activation than required for the corresponding retro-ene fragmentation (eq 4).[6] Catalysis would enhance the utility in organic synthesis of such fragmentations since many substrates cannot withstand the thermally harsh conditions (400–500 °C) required for the corresponding uncatalyzed reaction. The reduction of the allyloxy portion and concomitant oxidation of the alkoxy portion of the substrates may both find synthetic applications.



2 **3** **4**

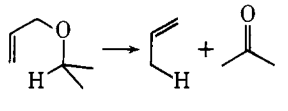


2 **3** (1)



3 (2)

$$R_1R_2CHORu \longrightarrow R_1R_2C{=}O + RuH \qquad (3)$$



(4)

We now report that α,α-dimethylallyl benzyl ethers give benzaldehydes by a new type of homogeneous transition metal catalyzed process, redox fragmentation, in the presence of **1** as catalyst. Furthermore, allyl ethers which have allylic hy-