in heme and inversely proportional to oxygen concentration as required by eq 13 when Hm–O_2 is the dominant species.[64] Spectroscopic evidence for the Fe–O–O–Fe species was recently reported by La Mar et al.[65]

Mercaptide Chelated Heme

Although mixtures of mercaptide ion with hemes[66-68] mimic many of the properties of cytochrome P-450 and give evidence for the RS̄–Fe structure in this enzyme, there remains the possibility of the excess RS⁻ interfering with the dynamic behavior of the P-450 model system. We have prepared a chelated heme having an internally bound mercaptide[69] (Figure 6) which shows strikingly similar behavior, in aqueous micelles, to that of cytochrome P-450. The low CO affinity of this model compound is in agreement with the anion data presented above and with the mercaptide heme–CO kinetic data of Chang and Dolphin.[68b]

We have also discovered diagnostic NMR resonances in this model compound which afford definitive probes in the enzyme.[70] (See Figure 6.) Both the ^{13}CO NMR

and the NMR of the protons α and β to the –S–Fe are definitive for this structure. The model RS–Fe–^{13}CO is the only such system (including Im⁻–Fe–CO) in which the chemical shift for ^{13}CO is less than 200 ppm. In P-450$_{cam}$ this resonance is at 200 ppm, compared to 197 ppm in the model. The α- and β-CH_2 proton resonances, being at higher field than Me_4Si, should be clearly visible in the protein. The ^{13}C and proton NMR of various P-450 enzymes, their P-420 forms, and chloroperoxidase should reveal a great deal about the structure around the heme.

Conclusions

Model compounds have been designed to probe structure–reactivity relationships in the ligation of hemes with O_2, CO, and isonitriles. The heme affinity for dioxygen was shown to be sensitive to electronic effects, proximal basicity, and solvent polarity, none of which greatly affect CO affinities. Both CO and O_2 affinities are lowered by proximal base tension. Distal side steric effects in model compounds approximating those in myoglobin have been achieved, and a kinetic method for distinguishing distal from proximal side effects has been discovered.

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Metalla-β-diketones and Their Derivatives

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β-Diketones are versatile reagents in both inorganic and organic chemistry. Coordination of the enolate anions of β-diketones to metal ions affords a large class of thermally stable metal complexes. Complexes of macrocyclic ligands can be prepared by reacting β-diketones with metal amine complexes via template synthesis. β-Diketones also condense with trigonal boron molecules and other nonmetallic compounds to give coordination complexes of these representative elements. In most of these complexes, a β-diketonate anion acts as a bidentate, chelating ligand.

Condensation reactions of β-diketones or β-keto esters provide a convenient synthetic route to several different classes of molecules. For example, condensation with amines affords β-keto imines, while condensation with

hydrazines gives pyrazole derivatives. Ureas and amidines afford pyrimidine condensation products, including uracil derivatives, and pyridine ring systems are formed by condensation of β-diketones with cyanacetamide. Self-condensation of poly-β-ketide anions affords aromatic molecules, e.g., resorcinol, orcinol, or orsellinic acid.

Recently, a class of organometallic complexes has been prepared in which the methine group of either a β-diketonate anion or the enol tautomer of a neutral β-diketone has been substituted by a transition-metal organometallic moiety. These transition metal fragments are isovalent to a methine group, and such complexes are referred to as metalla-β-diketones because the metal moieties are directly incorporated into the σ- and π-bonding network of the β-diketonate functionality. When using these metalla-β-diketones as reagents, it is possible to prepare metalla analogues of many of the compounds prepared via β-diketone chemistry. These new classes of compounds include the metalla-

β-diketones and their enolate anions, polynuclear (but noncluster) complexes containing up to four metal atoms, (metalla-β-diketonato)boron complexes, and metalla-β-keto imine molecules. Triacylmetalate complexes have also been prepared.

This Account is a brief review of metalla-β-diketone chemistry which attempts to demonstrate the unusual opportunity provided by these molecules in extending organometallic chemistry into research areas normally considered to be solely organic or inorganic. Several condensation reactions are presented, including the formation of metalla derivatives of amino acids and peptides, and an intriguing recent discovery of a transannular C–C coupling between the acyl carbon atoms within a metalla-β-diketonate ring is included.

Background

We have discovered that when acylmetal carbonyl complexes, 1, are treated with strong bases that can also react as nucleophiles, such as organolithium reagents, nucleophilic addition to a carbonyl ligand occurs rather than reaction at the acyl ligand as shown in eq 1.

$$RC(O)M(CO)_xL_y + R'Li \rightarrow$$
$$\mathbf{1}$$

$$Li[M(RCO)(R'CO)(CO)_{x-1}L_y] \quad (1)$$
$$\mathbf{2}$$
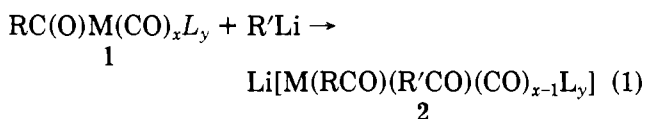
Attack at a carbonyl ligand is easily recognized by IR changes in the carbonyl ligand C–O stretching bands, and it occurs with a variety of acyl complexes and organolithium (or LiNR$_2$) reagents. The IR spectra of the diacylmetalate anions **2** indicate a cis relative orientation of the acyl ligands. Because of M–CO synergistic bonding, the cis isomer is preferred electronically.
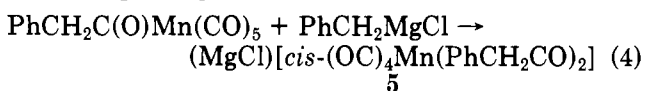
Nucleophilic attack at carbonyl ligands is well established, and the formation of cis-diacylmetalate complexes via such addition reactions has been reported by others. L'Eplattenier found that CH$_3$MgBr added to two carbonyl ligands of OsBr$_2$(CO)$_4$ to afford the all-cis diacetylosmate complex **3**, as shown in eq 2.[1]

$$OsBr_2(CO)_4 + 2CH_3MgBr \xrightarrow{THF}$$
$$cis,cis\text{-}[MgBr]_2[Os(CH_3CO)_2Br_2(CO)_2]\cdot 5THF \quad (2)$$
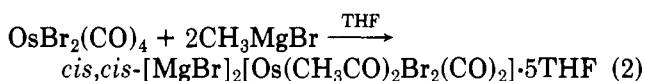
Casey and Bunnell confirmed the addition of methyllithium to a cis-carbonyl ligand of benzoylpentacarbonylmanganese, as shown in eq 3, by determining

$$PhC(O)Mn(CO)_5 + CH_3Li \xrightarrow{Me_4NCl}$$
$$(Me_4N)[cis\text{-}(OC)_4Mn(PhCO)(CH_3CO)] \quad (3)$$
$$\mathbf{4}$$
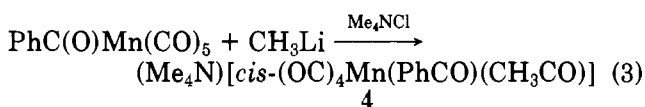
the X-ray structure of the cis-acetylbenzoyltetracarbonylmanganate complex **4**.[2-4] In an independent study, Darensbourg et al. observed formation of the Cis-bis(phenylacetyl)manganate complex **5** when treating phenylacetylpentacarbonylmanganese with PhCH$_2$MgCl (eq 4).[5]

$$PhCH_2C(O)Mn(CO)_5 + PhCH_2MgCl \rightarrow$$
$$(MgCl)[cis\text{-}(OC)_4Mn(PhCH_2CO)_2] \quad (4)$$
$$\mathbf{5}$$
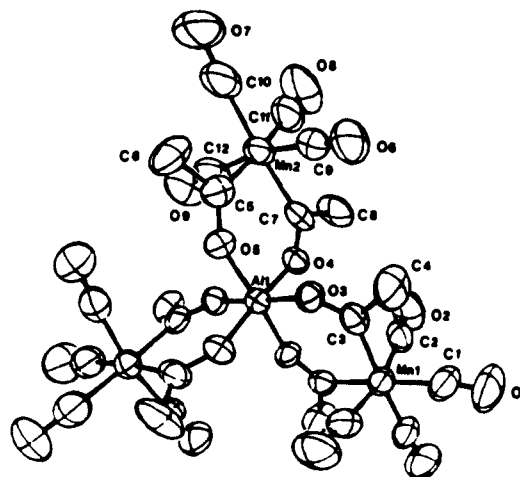
Figure 1. An ORTEP view of [cis-(OC)$_4$Mn(CH$_3$CO)$_2$]$_3$Al (**7**).

Since the formation of diacylmetalate complexes was both undesired and not particularly unique chemistry, we decided to abandon our study of acyl–ligand chemical reactivity. However, we recognized a close similarity between diacylmetalate complexes and organic β-diketonate anions. When the effective atomic number rule was applied to the most simple diacyltetracarbonylmanganate complexes, it became obvious that these metalate species were isovalent to the well-known β-diketonate anions. Since the methine group of the corresponding β-diketonate anion has been substituted formally by the organometallic moiety, cis-(OC)$_4$Mn, these organometallic complexes are referred to as metalla-β-diketonate anions.
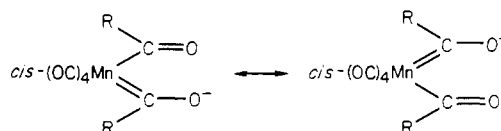
We immediately initiated a designed research effort to probe the chemistry exhibited by these metalla-β-diketonate anions. These anions were expected to act as chelating coordination ligands and to undergo organic condensation reactions as well. However, since the relatively electronegative metalla moiety is incorporated directly into the σ- and π-bonding networks of the β-diketonate skeleton, a general study of the chemical reactivity and bonding of these complexes was undertaken.

The synthesis of a manganaacetylacetonate anion (**6**) and its coordination to Al(III) ion affording the neutral, tris-chelate complex **7** was successful (eq 5[6,7]) and the molecular structure of **7** is shown in Figure 1. The Mn and Al atoms have slightly distorted octahedral coordination geometries, and, although the molecule has crystallographically imposed C_2 symmetry, the idealized molecular symmetry is D_3. The manganaacetylacetonate chelate ring is symmetrical and essentially planar (maximum atomic deviation from planarity is 0.096 Å). Within this chelate ring, the Mn–C(acyl) distances indicate a bond order of ca. 1.18, which supports at least partial π-electron delocalization. The

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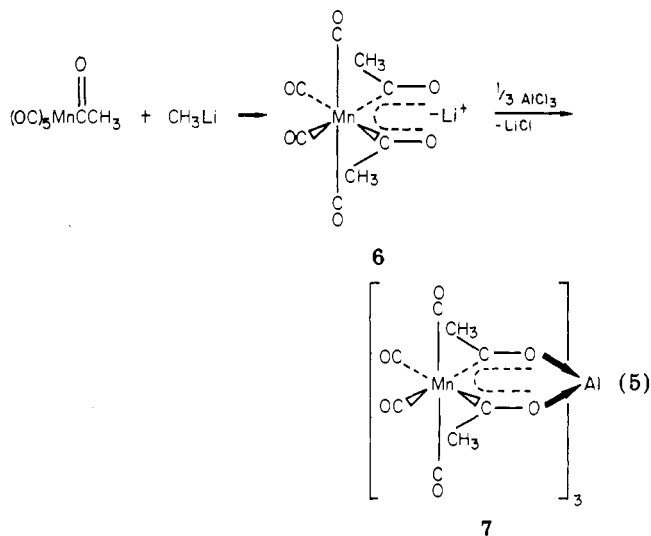(4) Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2728.

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6

7

C(acyl)–O and Al–O distances and the O–Al–O angles are not significantly different from the corresponding values observed in tris(acetylacetonato)aluminum, Al-(acac)$_3$. Complex **7** and Al(acac)$_3$ also have the same ligand O···O "bite" distance of 2.73 Å.

Protonation of a rhenaacetylacetonate anion, **8**, afforded the first example of a neutral metalla-β-diketone, **9**, as shown in eq 6.[8,9] This molecule exists as the enol

8

9
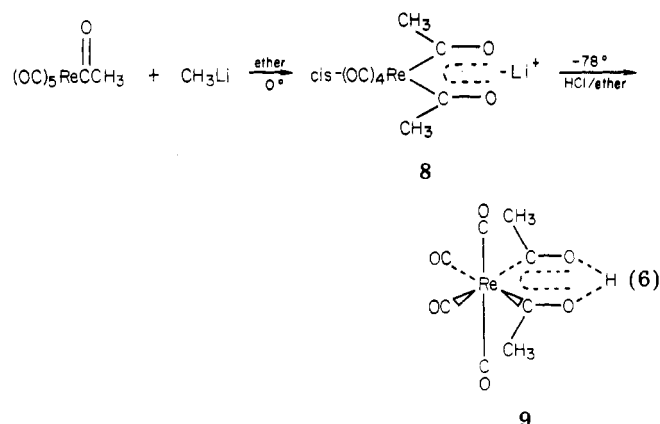
tautomer, and the molecular structure of **9** was confirmed by X-ray crystallography. The idealized molecular symmetry of **9** is C_{2v}, and the atoms comprising the rhenaacetylacetone ring are essentially coplanar (maximum atomic deviation is +0.08 Å). The Re–C-(acyl) distances indicate a bond order of ca. 1.21 and at least partial π-electron delocalization. Since the acetyl oxygen atoms are located at positions of closest proximity, the enolic hydrogen atom, which was not located in the X-ray study, is believed to be positioned between the two acetyl oxygen atoms. The O(1)···O(2) "bite" distance of 2.40 Å is not significantly different from the observed "bite" distance in the dienolic tautomer of tetraacetylethane. For such short O···O "bite" distances, a symmetrical, linear O···H···O hydrogen bond has been proposed, although a slightly bent and asymmetrical O···H···O hydrogen bond is also likely. Neutron diffraction analysis of **9** is anticipated.

The ^{1}H NMR resonance of the enolic hydrogen atom of **9** appears at very low field, δ 21.79 (in CS$_2$ solution),

and is a diagnostic indication of the formation of a metalla-β-diketone molecule. Corresponding resonances of (hydroxy)(methyl)carbenoid complexes, such as [(C-H$_3$)(HO)C]Cr(CO)$_5$, occur at ca. 9.5 ppm to higher field. The enolic proton of **9** is easily ionized, and it readily undergoes deuterium exchange with methanol-d_4. At present, the pK_a of **9** has not been measured.

Metal Complexes Containing Metalla-β-diketonate Ligands

Equation 7 shows the preparation of 18 neutral, tris-chelate metalla-β-diketonate complexes of Al or Ga.[10-12] Notice that unsymmetrically substituted

M	R	R'	M'	ref
cis-(OC)$_4$Mn	Me, Et, PhCH$_2$, *i*-Pr, EtO	Me	Al	10
cis-(OC)$_4$Mn	Me	Bu, Me$_2$N	Al	10
cis-(OC)$_4$Mn	*i*-Pr	Bu	Al	10
fac-(OC)$_3$(RNC)Mn (R = Me, C$_6$H$_{11}$, *t*-Bu)	Me	Me	Al	11
cis-(OC)$_4$Re	Me, PhCH$_2$	Me	Al	10
cis-(OC)$_4$Re	Me, *i*-Pr	Me	Ga	10
η-C$_5$H$_5$(OC)Fe	Me, *i*-Pr, Ph$_2$CH	Me	Al	12

metalla-β-diketonate ligands are prepared via a general route by choosing among a variety of acylmetal carbonyl complexes and organo- or amidolithium reagents. The metalla moieties include *cis*-(OC)$_4$Mn, *fac*-(OC)$_3$-(RNC)Mn, *cis*-(OC)$_4$Re, and η-C$_5$H$_5$(OC)Fe, all of which are isovalent to a methine group. The central coordinating ion is Al(III) or Ga(III). These tris-chelate complexes are discrete molecules containing four metal atoms which are connected by C···O bridges. Interest in organometallic complexes which contain acyl ligands bridging two different metal atoms has increased recently since such complexes have been isolated from reactions of acyl complexes with Lewis acids.[13]

In solution, metalla-β-diketonate complexes exhibit the expected geometrical isomerism resulting from the relative orientation of the chelating ligands about the central coordinating ion, M'. Unsymmetrical chelate ring substitution or the presence of an isocyanide ligand on the metalla moiety generates cis and trans isomers in these tris-chelate complexes. The two ferra-β-diketonate complexes containing unsymmetrical chelating ligands exhibit extensive geometrical isomerism because the relative orientations of both the η-C$_5$H$_5$ ligands and the chelate ring substituents can produce geometrical cis–trans isomers. The resulting ten possible geometrical isomers belong to one of four distinct classes of isomers. ^{1}H NMR spectra indicate that the two most statistically preferred isomer types are present in solution.
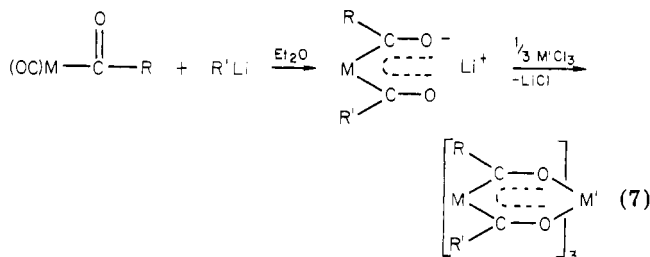
(8) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1976**, *98*, 2365. For a convenient preparation of complex **9**, see ref 9.

(9) Darst, K. P.; Lukehart, C. M.; Warfield, L. T.; Zeile, J. V. *Inorg. Synth.* **1980**, *20*, 200.

(10) Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *Inorg. Chem.* **1976**, *15*, 2393.

(11) Darst, K. P.; Lukehart, C. M. *Inorg. Chim. Acta* **1978**, *27*, 219.

(12) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1977**, *99*, 4368.

(13) Stinson, R. E.; Shriver, D. F. *Inorg. Chem.* **1980**, *19*, 1141.

A kinetic and equilibrium study of the cis–trans isomerization of $[cis\text{-}(OC)_4Mn(CH_3CO)(PhCH_2CO)]_3Al$, $Al(abtm)_3$, revealed that the rate of isomerization at 298 K of 0.76×10^{-3} s^{-1} is very similar to the value observed for $Al(pmhd)_3$, 0.40×10^{-3} s^{-1}.[14] $Al(pmhd)_3$ is a β-diketonate complex of Al(III) where the chelate ring substituents are benzyl and isopropyl groups. Furthermore, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the isomerization of $Al(abtm)_3$ closely agree with the calculated values of the activation parameters of $Al(pmhd)_3$ undergoing geometrical isomerization via various Al–O bond rupture mechanisms. However, the trans isomer of $Al(abtm)_3$ is more stable thermodynamically than the cis isomer, whereas alkyl- or aryl-substituted β-diketonate complexes of Al usually have a more stable cis isomer.

Transition-metal complexes containing metalla-β-diketonate ligands cannot be prepared from a metalla-β-diketonate anion and a transition-metal salt via an anion displacement reaction. Rather, an acid–base reaction must be used, as shown in eq 8.[15,16] By using
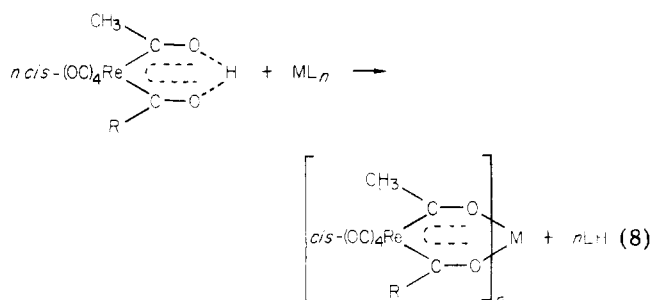
n	R	M	L
2	Me, i-Pr	Cu	MeO
3	Me	Fe	EtO
3	Me	Cr	(i-Pr$_2$)N
2	Me	Zn	Et

rhena-β-diketones and transition-metal complexes having basic ligands, rhena-β-diketonate complexes of Cu(II), Fe(III), Cr(III), and Zn(II) can be prepared by the elimination of methanol, ethanol, diisopropylamine, and ethane, respectively. A bis(rhenaacetylacetonato)magnesium complex is prepared similarly from 9 and Ph$_2$Mg with the elimination of benzene.

The Cu, Fe, and Cr complexes are paramagnetic solids which have different visible chromophores from the analogous acetylacetonate complexes. An EPR spectrum of $[cis\text{-}(OC)_4Re(CH_3CO)_2]_2Cu$ in a CHCl$_3$/toluene glass at -166 °C reveals symmetrical superhyperfine coupling of the unpaired Cu electron to the two Re nuclei ($I = {}^5/_2$, $A_{\perp}{}^{Re} = 21.0 \times 10^{-4}$ cm^{-1}. Although the nature of this coupling is not known, it may indicate partial π-electron delocalization throughout the rhenaacetylacetonato ligands. The molecular structure of this Cu complex has been determined by X-ray crystallography. Each chelate ring has a nonplanar boat shape affording an overall "chaise lounge" molecular structure. Bond distances and angles within the rhenaacetylacetonate ligands are not significantly different from those found in the rhenaacetylacetone molecule 9. Therefore, the nonplanarity of the rhena chelate ring does not appear to alter the ligand electronic structure

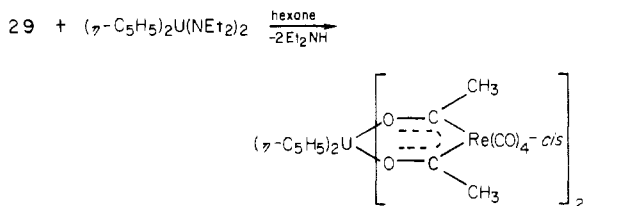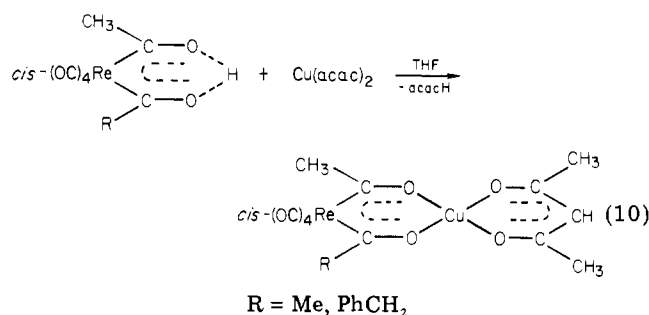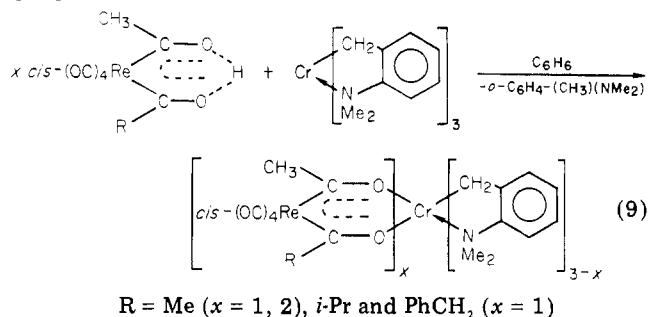substantially. The Cu coordination geometry, including the O···O "bite" distance of 2.783 (4) Å, is not significantly different from that observed in Cu(acac)$_2$.

By using the same acid–base reaction, several mixed-ligand rhena-β-diketonate complexes have been prepared, as shown in eq 9–11.[17] The paramagnetic

$$R = Me\ (x = 1, 2),\ i\text{-Pr and PhCH}_2\ (x = 1)$$

$$R = Me, PhCH_2$$

chromium complexes are particularly interesting because both the Re and Cr atoms are organometallic centers. These complexes are expected to be active catalysts for olefin polymerization. The uranium complex is the first metalla-β-diketonate complex of an actinide element.

Condensation Chemistry of the Metalla-β-diketones

For a demonstration of the general synthesis of metalla-β-diketone molecules, the following six complexes have been prepared and characterized: $[cis\text{-}(OC)_4Re(CH_3CO)_2]H$ (9), $[cis\text{-}(OC)_4Re(CH_3CO)(Me_2HCCO)]H$ (10), $[cis\text{-}(OC)_4Re(CH_3CO)(PhCH_2CO)]H$ (11), $[\eta\text{-}C_5H_5(OC)Fe(CH_3CO)_2]H$ (12), $[\eta\text{-}C_5H_5(OC)Fe(CH_3CO)(Me_2HCCO)]H$ (13), and $[\eta\text{-}C_5H_5(OC)Fe(CH_3CO)(Ph_2HCCO)]H$ (14).[8,12] Enolic proton resonances of the rhena- and ferra-β-diketones appear, respectively, in the ranges δ 21.79–22.57 and 19.11–20.08. The higher field chemical shift for the ferra–enolic resonances probably reflects the lower electronegativity of the $\eta\text{-}C_5H_5(OC)Fe$ moiety. Two phosphine-substituted rhena-β-diketones have been prepared to facilitate the characterization of the corresponding enolate anions.[18]

(14) Lukehart, C. M.; Torrence, G. P. *Inorg. Chem.* **1978**, *17*, 253.
(15) Lukehart, C. M.; Torrence, G. P. *J. Chem. Soc., Chem. Commun.* **1978**, 183.
(16) Lukehart, C. M.; Torrence, G. P. *Inorg. Chem.* **1979**, *18*, 3150.

(17) Darst, K. P.; Hobbs, D. T.; Lukehart, C. M. *J. Organometal. Chem.* **1979**, *179*, C9. For the uranium complex see: Arduini, A. L.; Takats, J.; Lukehart, C. M. *61st Can. Chem. Conf. Abstr.* **1978**, Winnipeg, Manitoba.
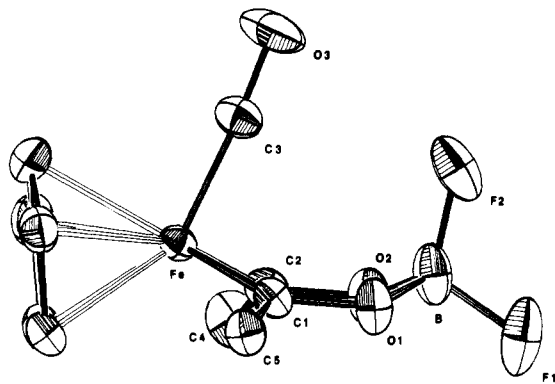(18) Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723.

Figure 2. An ORTEP view of $[\eta\text{-}C_5H_5(OC)Fe(CH_3CO)\text{-}(Me_2HCCO)]BF_2$ showing the boat-shaped structure of the ferrachelate ring. C(4) is the methyl carbon and C(5) is the methine carbon atom of the isopropyl group.

Metalla-β-diketones condense with trigonal boron compounds, BX_2Y, where $X = Y$ = halogen or $X = Cl$ and $Y = Ph$, to afford neutral metalla-β-diketonate complexes of boron, as shown in eq 12. Seventeen

$$|H[BX_3Y]| \quad (12)$$
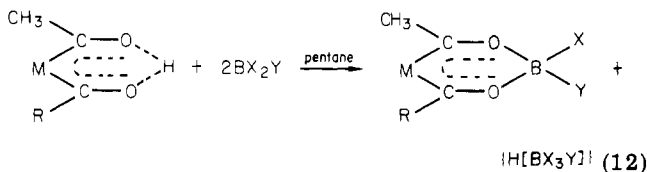
boron complexes have been isolated by using this procedure.[19,20] The rhena-β-diketones 9–11 condense with all four boron trihalides and dichlorophenylboron, and BF_2 complexes resulting from condensation of the ferra-β-diketones 13 and 14 with BF_3 have also been prepared. In comparison, acetylacetone condenses with BF_3 to form the neutral (acetylacetonato)BF_2 complex, but condensation with the remaining boron halides gives ionic boron complexes of the type $[(acac)_2B]X$. Boronium complex formation is not observed with the metalla-β-diketones, presumably due to the weaker Lewis basicity of these ligands. This observation is consistent with the inability of metalla-β-diketonate anions to displace halide ligands from anhydrous transition-metal halides.

The molecular structure of the (ferra-β-diketonato)-BF_2 complex $[\eta\text{-}C_5H_5(OC)Fe(CH_3CO)(Me_2HCCO)]BF_2$ is shown in Figure 2.[21] The geometry about the Fe atom resembles the normal "three-legged piano stool" structure, and the average Fe–C(acyl) distance of 1.863 Å indicates significant Fe–C multiple bonding. Within the ferra chelate ring, the C–O and B–O distances, the O(1)···O(2) "bite" distance of 2.422 (2) Å, and the O–B–O angle are very similar to the corresponding values found for (benzoylacetonato)BF_2. A slightly boat-shaped chelate ring conformation is observed where the carbonyl ligand is closer to the boron atom than is the $\eta\text{-}C_5H_5$ ligand. Another isomer is observed in solution, and it presumably has the other boat-shaped structure formed by flipping the chelate ring through a planar intermediate.

When the manganaacetylacetonate anion 6 is treated with BF_3 in CH_2Cl_2 solution, the (manganaacetyl-

acetonato)BF_2 complex is formed. This complex may be a valuable synthetic reagent since neutral mangana-β-diketones have not been isolated.

Condensation of 9 with hydrazine, methylhydrazine, or phenylhydrazine affords an acetyl amine complex, $cis\text{-}(OC)_4Re(CH_3CO)(NH_2R)$, acetonitrile and, presumably, the elimination of water, as shown in eq 13.[22]

$$[cis\text{-}(OC)_4Re(CH_3CO)_2]H \;+\; H_2NNHR \xrightarrow[-H_2O]{Et_2O}$$

     9

$$\qquad + \; CH_3CN \quad (13)$$

$$R = H,\, Me,\, Ph$$
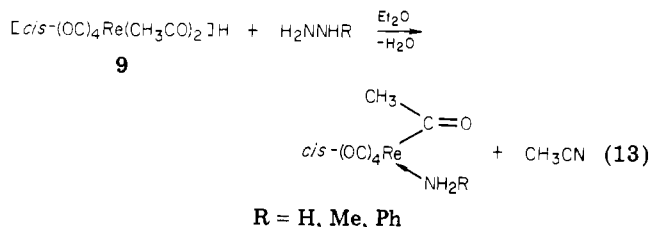
These reactions were followed by using ^1H NMR, and the reaction with phenylhydrazine, which is the slowest reaction, has a half-life of 8.67 min at 36 °C. The x-ray structure of the acetyl aniline product complex was determined also. Presumably, hydrazines attack the acyl carbon atoms of 9, forming hydrazone or aminocarbenoid ligand intermediates, followed by an intramolecular rearrangement and elimination of the products. Contrary to β-diketonate chemistry, ring closure to form rhenapyrazoles does not occur in these reactions because the long Re–C(acyl) bond distances generate too much strain in the expected five-membered ring.

Schiff-base condensation of the rhena-β-diketones 9 and 10 with ammonia or primary amines affords metalla-β-keto imine molecules which exist as the ketamine tautomers (eq 14).[23-25] As found with β-diketones,

$$cis\text{-}(OC)_4Re[(CH_3CO)(RCO)]H \;+\; H_2NR' \xrightarrow{-H_2O}$$

    9 or 10

$$\qquad (14)$$
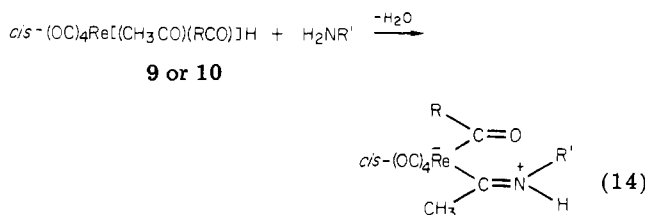
$R = CH_3;\, R' = H,\, CH_3,\, PhCH_2,\, C_6H_{11},\, n\text{-propyl},\, n\text{-butyl},$
                       isobutyl, Ph, p-tolyl
$R = i\text{-Pr};\, R' = H,\, CH_3,\, PhCH_2,\, n\text{-propyl},\, n\text{-butyl},\, isobutyl$

Schiff-base condensation occurs preferably on the carbonyl group bearing the least bulky substituent, although the other structural isomer is observed as a minor product for these rhena derivatives, also.

The molecular structure of the N-phenylrhenaacetylacetone imine complex is shown in Figure 3. Adjacent molecules are held together by a chain network of N—H···O intermolecular hydrogen bonds formed between the acetyl oxygen atoms and the imine N—H groups. Within the iminium ligand, the methyl and phenyl substituents are oriented anti with respect to the C(5)–N bond. The C(5)–N and C(13)–O(5) bond distances of 1.26 (2) and 1.19 (2) Å, respectively, indicate normal C–N and C–O double bonds while the Re–C(5) and Re–C(13) distances of 2.20 (2) and 2.22 (2)

(19) Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1978,** *17,* 201.
(20) Lukehart, C. M.; Warfield, L. T. *J. Organometal. Chem.* **1980,** *187,* 9.
(21) Lenhert, G. P.; Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1980,** *19,* 2343.

(22) Lukehart, C. M.; Zeile, J. V. *J. Organometal. Chem.* **1977,** *140,* 309.
(23) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1978,** *100,* 2774.
(24) Lukehart, C. M.; Zeile, J. V. *Inorg. Chem.* **1978,** *17,* 2369. For a convenient preparation of the rhenaacetylacetonimine complex, see ref 25.
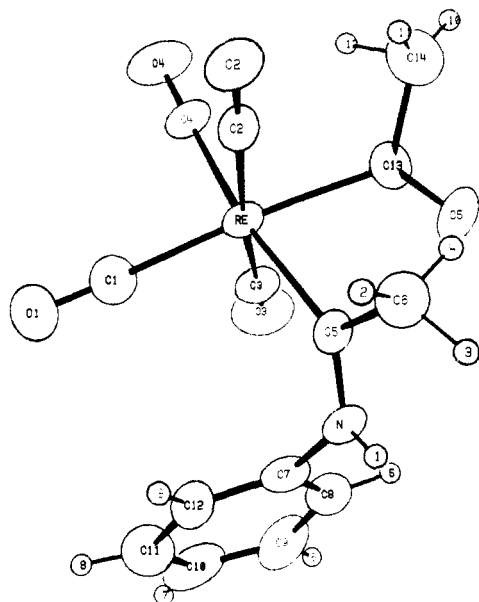(25) Hobbs, D. T.; Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *Inorg. Synth.* **1980,** *20,* 204.

Lukehart

Scheme I

Figure 3. An ORTEP view of cis-$(OC)_4Re[CH_3C(O)][CH_3CN-(Ph)(H)]$.

Å, respectively, represent nearly Re–C(sp²) single bond distances. These structural data support the zwitter-ionic formulation for the chemical bonding of rhena-β-keto imines rather than the enamine structure observed for β-keto imines. Furthermore, in solution, slow geometrical isomerization occurs about the C(5)–N multiple bond, as shown in eq 15. Isomer 15 isomerizes
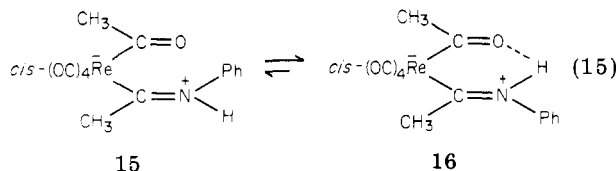

to 16 with an overall rate constant of $(4.97 \pm 0.17) \times 10^{-5}$ s^{-1} in CDCl$_3$ solution at 34 °C. The value of the equilibrium constant under these conditions is 15.9. Isomer 16 apparently possesses intramolecular N—H··O hydrogen bonding because its N—H ^{1}H NMR resonance occurs at much lower field (δ 15.26) than does the N—H resonance of isomer 15 (δ 11.56).

Condensation of 9 with ethylenediamine or 1,3-diaminopropane at a 2:1 molar ratio affords the corresponding rhena-β-keto diimine molecules. For example, the product obtained from the ethylenediamine condensation is the dirhena derivative of the well-known N,N'-ethylenebis(acetylacetone imine), acacen, ligand. Ethyl glycinate and ethyl L-alaninate condense with 9 to form rhena-β-keto imine derivatives of these amino acid esters.[26] Acidic or basic hydrolysis of the esters affords the free rhenaamino acids, and subsequent amino acid coupling gives a rhena dipeptide derivative as shown for the rhenaglycine complex in Scheme I. The X-ray structure of the ethyl L-rhenaalaninate complex, cis-$(OC)_4Re[CH_3C(O)][CH_3CN(L$-$CHCH_3CO_2CH_2$-$CH_3)(H)]$ (17), has been determined. A comparison of this structure to those of the N-phenylrhenaacetyl-acetone imine complex 15 (Figure 3) and L-alanine reveals the same relative ligand orientation and isomer type for the rhena moiety and no structural perturba-

(26) Baskar, A. J.; Lukehart, C. M.; Srinivasan, K. *J. Am. Chem. Soc.* **1981**, in press.
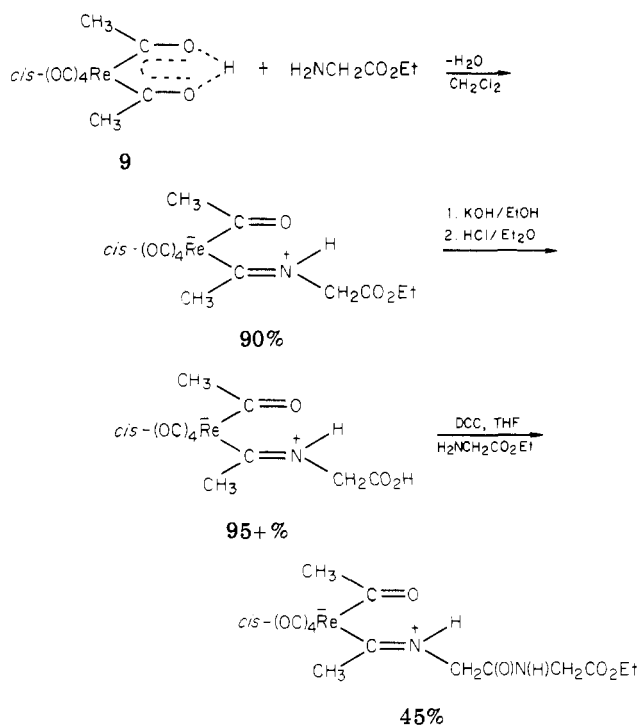
tion by the rhena moiety on the ethyl L-alaninate fragment. The N—H··O intermolecular hydrogen bonding between rhena moieties of adjacent molecules is still present. Cleavage of the rhena moiety from the amino acid fragment under various solvolytic reaction conditions is very difficult and occurs only in very low yield. However, oxidative cleavage of the rhena moiety of 17 with iodosobenzene affords ethyl N-acetyl-L-ala-ninate in an unoptimized yield of 67%. These synthetic and structural data demonstrate that rhena-β-keto imine derivatives of amino acids or peptides may be useful as N-terminal end protecting groups or as heavy atom labels. The latter function may be particularly interesting since the technetium derivatives could be prepared by using the same procedure.

Structure and Bonding

The X-ray structures of 7 and 9 revealed a 9 and 8° tilting, respectively, of the two axial carbonyl ligands on each metalla atom toward the metallaacetylacetonate chelate ring. When considering a variety of causes for this distortion, we were attracted most to the possibility of an intramolecular π-bonding interaction between the filled and empty π molecular orbitals of the axial carbonyl ligands and the filled and empty π molecular orbitals of the metallaacetylacetonate chelate ring. A symmetry analysis indicated that such interactions were possible and that they would tend to lower the C–O bond order of the axial carbonyl ligands.[27] An unrelated force constant analysis of the C–O stretching vibrations of 7, 9, and the Re analogue of 7 not only confirmed the assignment of the carbonyl bonds but also demonstrated that the force constant of the axial CO ligands is smaller for the complex having the greater tilting of these ligands toward the metalla chelate ring.[28] However, this apparent correspondence between axial

(27) Lukehart, C. M.; Torrence, G. P. *Inorg. Chim. Acta* **1977**, *22*, 131.
(28) Lukehart, C. M.; Torrence, G. P. *J. Chem. Soc., Dalton Trans.* **1978**, 93.

CO ligand force constant and the degree of axial CO tilting may be fortuitous.

X-ray structural data and IR, EPR, and ^{1}H NMR spectroscopic data are consistent with at least partial π-electron delocalization within the essentially symmetrical metalla-β-diketonate chelate rings in the metalla-β-diketones and metalla-β-diketonate complexes of boron or metal ions, whereas the metalla-β-keto imines have localized zwitterionic electronic structures. ^{13}C NMR data support these bonding descriptions and provide solution-phase structural information, also.[29,30] For example, the rhenaacetylacetone molecule **9** has only one acyl carbon ^{13}C resonance, δ 297.9, and this resonance appears at nearly the average frequency of the acyl carbon resonance in $CH_3C(O)$-$Re(CO)_5$, δ 244.7, and the carbenoid carbon resonance of $[(CH_3)(HO)C]W(CO)_5$, δ 334.4. These data support a delocalized C_{2v} structure for **9** rather than a localized structure having acetyl and (hydroxy)(methyl)carbenoid ligands. However, a rapid equilibration between localized structures due to proton transfer is possible also. Conversely, when one of the N–H hydrogen atoms of the rhenaacetylacetone imine complex is replaced by other substituents, very little electronic influence is transmitted to the acetyl ligand as expected for a predominately localized structure. Also, the iminium carbon resonance of the *N*-methylrhenaacetylacetone imine complex appears at much higher field than does the carbenoid carbon resonance of $[(CH_3)(MeHN)C]W$-$(CO)_5$. This unusual chemical shift may reflect the zwitterionic electronic structure of these rhena-β-keto imines.

A great amount of spectroscopic evidence and synthetic chemistry suggests that the rhena-β-diketonate ligands are more electronegative than the acetylacetonate ligand. Recent cyclic voltammetric data on the redox chemistry of the rhenaacetylacetonato complexes of Fe(III), Cr(III), and Cu(II) seem to support these observations.[31] The quasi-reversible iron reduction potential is 0.63 V more positive than that of $Fe(acac)_3$. A similar trend to more positive reduction potentials is observed for the Cr and Cu complexes, although these complexes exhibit considerable irreversibility in their redox reactions.

Derivatives of the Metalla-β-diketonate Anions

Acylpentacarbonylrhenium complexes react *stoichiometrically* with 2 mol of methyllithium to afford triacylrhenate dianions, as shown in eq 16. A similar

$$RC(O)Re(CO)_5 + 2CH_3Li \xrightarrow[0°C]{THF}$$
$$Li_2[fac\text{-}(OC)_3Re(RCO)(CH_3CO)_2] \quad (16)$$
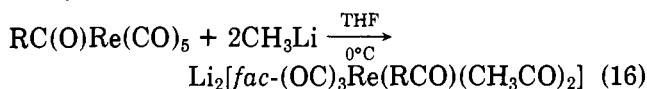
R =
   CH_3, *i*-Pr, $PhCH_2$, or bridging $(CH_2)_5$ and $(CH_2)_6$

manganese dianion, $fac\text{-}(OC)_3Mn(PhCH_2CO)_3^{2-}$, has been prepared earlier from $PhCH_2C(O)Mn(CO)_5$ in the presence of a 20-fold excess of $PhCH_2MgCl$.[5] These triacylrhenate dianions form bis-chelate complexes with Al(III), Ga(III), Hf(IV), and Zr(IV).[32,33] Reaction of

the triacetylrhenate dianion with the boron trihalides gives the neutral $[fac\text{-}(OC)_3Re(CH_3CO)_3]BX$ complexes, as shown in eq 17.[34] When the boron bromide complex

$$X = F, Cl, Br, I$$
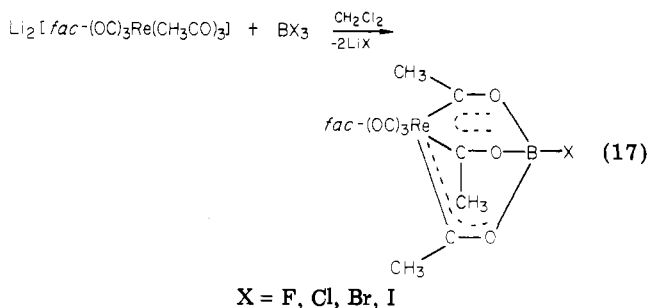
is treated with $AgBF_4$ in alcohol solution, the corresponding boron alkoxide complex, $[fac\text{-}(OC)_3Re$-$(CH_3CO)_3]B(OR)$, is formed.

The X-ray structure of $[fac\text{-}(OC)_3Re(CH_3CO)_3]BCl$ confirms the supposition that the triacetylrhenate ligand acts as a trioxygen, vicinal, bifurcated chelating ligand.[35] Unfortunately, crystal decomposition prevents a precise assessment of the chemical bonding within the three acetyl ligands. The molecule possesses a delocalized C_{3v} structure at the ±3σ limit but a localized C_{2v} structure at the ±2σ limit.

As shown in eq 18 and 19, one of the acetyl ligands in metalla-β-diketonate anions or triacetylmetalate dianions can be replaced by other one-electron donor ligands. Protonation of the halo(acetyl)metalate

$$M = Mn; X = Br$$
$$M = Re; X = Cl, Br, I, CH_3, H$$

$$M = Mn; X = Br$$
$$M = Re; X = Cl, Br, I$$

$$X = Cl, Br, I$$

species affords the corresponding mono- or bis(hydroxy)(methyl)carbenoid complexes.[36,37] Halo(acetyl)manganate anions have been prepared previously from $CH_3Mn(CO)_5$ and halide salts by alkyl migration reactions, and protonation of these anions led to the corresponding (hydroxy)(methyl)carbenoid complex-

(29) Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1978**, *161*, 1. See ref 30 for corrected chemical shifts for acetylpentacarbonylrhenium.
(30) Darst, K. P.; Lukehart, C. M. *Inorg. Chim. Acta* **1980**, *41*, 239.
(31) Beaver, B. D.; Hall, L. C.; Lukehart, C. M.; Preston, L. D. *Inorg. Chim. Acta* **1981**, *47*, 25.
(32) Hobbs, D. T.; Lukehart, C. M. *J. Am. Chem. Soc.* **1977**, *99*, 8357.
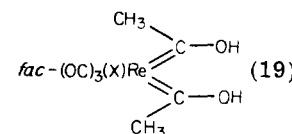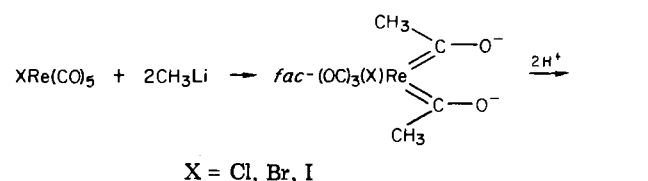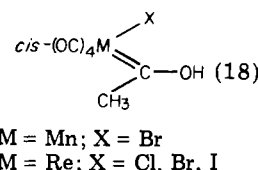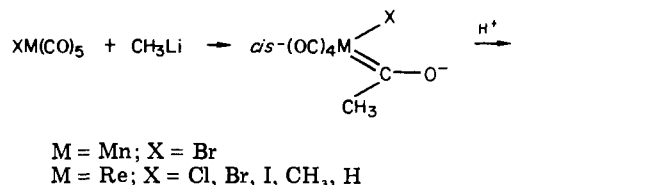
(33) Hobbs, D. T.; Lukehart, C. M. *Inorg. Chem.* **1979**, *18*, 1297.
(34) Hobbs, D. T.; Lukehart, C. M. *Inorg. Chem.* **1980**, *19*, 1811.
(35) Lukehart, C. M.; Warfield, L. T. *Inorg. Chim. Acta* **1980**, *41*, 105.
(36) Darst, K. P.; Lukehart, C. M. *J. Organometal. Chem.* **1979**, *171*, 65.
(37) Darst, K. P.; Lenhert, G. P.; Lukehart, C. M.; Warfield, L. T. *J. Organometal. Chem.* **1980**, *195*, 317.

es.[38,39] A phosphine derivative of one of the rhenate monoanions, Li[fac-(OC)$_3$(PPh$_3$)(Br)Re(CH$_3$CO)], was reported recently.[40] When Li[BEt$_3$H] is used in place of CH$_3$Li, the halorhenate formyl complexes, Li[cis-(OC)$_4$(X)Re(HCO)] (X = Cl, Br, I), are formed.[36,41,42]

It is interesting that the methyllithium adds to the carbonyl ligands rather than displace the halide ligand under these conditions. Also, the iodo biscarbenoid complex fac-(OC)$_3$(I)Re[C(CH$_3$)(OH)]$_2$ decomposes in solution at room temperature with elimination of acetaldehyde.[37]

Recent Results and Future Directions of Research

When the ferra-β-diketonate complex [η-C$_5$H$_5$(OC)-Fe(CH$_3$CO)(Me$_2$HCCO)]BF$_2$ (Figure 2) is treated with a stoichiometric amount of KH, a proton of the acetyl group is removed, affording an anionic complex in essentially quantitative yield.[43] This anion has the molecular formula {[η-C$_5$H$_5$(OC)Fe(CH$_2$CO)-(Me$_2$HCCO)]BF$_2$}$^-$, although an X-ray structure of the Me$_4$N$^+$ salt reveals that C–C bond formation has occurred between the original acyl carbon atoms. These two carbon atoms and the exo-methylene carbon atom coordinate to the η-C$_5$H$_5$(OC)Fe moiety as a substituted η-allyl ligand, as shown in eq 20.

This interligand C–C bond formation represents a transannular coupling across the six-membered metalla-β-diketonate ring and also demonstrates C–C bond formation between adjacent acyl ligands prior to a formal reductive elimination. Cleavage of the Fe and boron moieties may afford glycol or acyloin products. Such interligand coupling reactions are relevant to stoichiometric and catalytic reaction chemistry which occurs at metal atoms.

Future research goals include (1) effecting dicondensation reactions to give unsaturated metalla heterocyclic molecules, (2) preparing metalla derivatives of amino acids, peptides, and other biologically important amines, and (3) investigating the generality and synthetic utility of the transannular C–C bond formation in the α-enolate anions of metalla-β-diketonate molecules. We believe that additional new classes of organometallic compounds will be prepared from designed synthetic methods by utilizing metalla-β-diketone chemistry. The metalla-β-diketones provide an entry into areas of chemistry which are not easily accessible when using more classical transition metal organometallic synthetic methods.

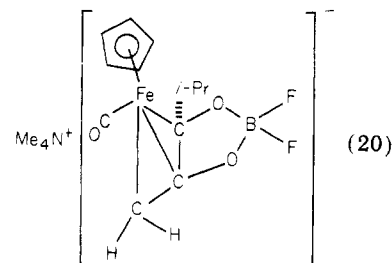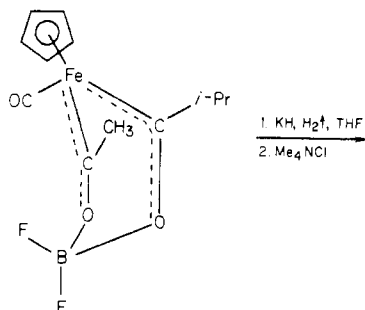(38) Noack, K.; Calderazzo, F. *J. Organometal. Chem.* **1967**, *10*, 101.
(39) Moss, J. R.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 975.
(40) Parker, D. W.; Marsi, M.; Gladysz, J. A. *J. Organometal. Chem.* **1980**, *194*, C1.
(41) The bromo analog has been prepared by others.[42]
(42) Gladysz, J. A. *Aldrichim. Acta* **1979**, *12*, 13.
(43) Lukehart, C. M.; Srinivasan, K. *J. Am. Chem. Soc.*, accepted for publication.

Laser Magnetic Resonance Spectroscopy and Its Application to Atmospheric Chemistry

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The paramagnetism of free radicals has always provided an attractive method for detecting them in the presence of molecules which lack unpaired electronic

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angular momentum. Historically, electron paramagnetic resonance (EPR) has been the favored technique, and for a simple free radical trapped in a solid, a steady magnetic field of strength H causes a level with net electron spin S to split into $(2S + 1)$ components with energy $g\beta M_s H$, where $g = 2.00232$ and β is the Bohr magneton ($=0.04669$ cm^{-1}/kG). Transitions between these components with $\Delta M_s = \pm 1$ are induced by the interaction between the magnetic dipole of the electron and the magnetic vector of the microwave radiation