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Reactions of Coordinated Molecules. 19. Metalla-β-diketonate Complexes of Copper(II), Iron(III), Chromium(III), Zinc(II), and Magnesium(II)

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The reaction of the metalla-β-diketone molecules, $[cis\text{-}(OC)_4Re(CH_3CO)(RCO)]H$, where R is methyl or isopropyl, with $Cu(OCH_3)_2$, $Fe(OCH_2CH_3)_3$, $Cr[N(i\text{-}Pr)_2]_3$, $Zn(CH_2CH_3)_2$, and $Mg(C_6H_5)_2$ affords the neutral metalla-β-diketonate complex of the metal ion, $[cis\text{-}(OC)_4Re(CH_3CO)(RCO)]_nM$, with the elimination of methanol, ethanol, diisopropylamine, ethane, and benzene, respectively. These complexes are isolated and characterized by normal methods. A green, mixed-ligand copper complex, $\{[cis\text{-}(CO)_4Re(CH_3CO)_2]Cu(OCH_3)\}_2$, is isolated also from the $Cu(OCH_3)_2$ reaction. This complex can be prepared independently from the reaction of the bis(metallaacetylacetonate)copper complex with sodium methoxide.

The discovery of the first metalla-β-diketonate complex[2] of a metal ion has developed into an extensive area of research.[3-6] These complexes are unique in that discrete, noncluster molecules containing up to four metal atoms can be synthesized. Also, since the metal atoms are connected via unsaturated carbon–oxygen bridges, these complexes may be catalytically important where various substrate fragments need to be protected or activated through coordination or where some degree of metal–metal interaction is required.[7]

At present, the metalla-β-diketonate ligands possess either a rhenium, manganese, or iron moiety,[3,8] and the central, coordinating metal ion is either aluminum(III) or gallium(III). The incorporation of a transition-metal atom as the central coordinating metal ion has been a particularly elusive goal.

In this paper we wish to report the successful synthesis of several transition-metal complexes from the very reactive metalla-β-diketone molecules[8] via an elimination reaction rather than a halide displacement reaction. A preliminary report of this procedure appeared recently.[9] This synthetic method may become a general preparative route to the formation of metalla-β-diketonate complexes, especially of those metal ions which exhibit pronounced catalytic reactivity.

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25 °C. Diethyl ketone and methylene chloride were dried over P_2O_5. Freshly opened methanol was distilled over magnesium turnings and spectrograde chloroform was dried over 4A molecular sieves. All other organic solvents were distilled over Na/K alloy under a nitrogen atmosphere. Diethylzinc and diphenylmagnesium were purchased from Alfa Products and Orgmet (Hampstead, N.H.), respectively.

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as hexane or diethyl ether solutions in 0.10-mm sodium chloride cavity cells by using the solvent as a reference and a polystyrene film as a calibration standard. Band frequencies are reported in cm^{-1}. Proton NMR spectra were measured on a JOEL MH-100 NMR spectrometer using Me_4Si as an internal reference. Magnetic measurements were obtained by the Faraday method by using $Hg[Co(SCN)_4]$ as a calibrating standard. Corrections for the diamagnetic contributions to the magnetic moments were determined from the magnetic susceptibility of the diamagnetic diacetyltetracarbonylrhenium hydrogen molecule and from Pascal's constants available in the literature. Ultraviolet and visible spectra were measured on a Cary Model 14 spectrophotometer and a Coleman Model EPS-3T Hitachi spectrophotometer as chloroform solutions in 0.1-mm glass cells with the solvent as a reference. Solutions of ca. 1×10^{-3} M were prepared quantitatively by using a microbalance for visible spectra and diluted volumetrically to ca. 1×10^{-4}–1×10^{-5} M for ultraviolet spectra. EPR spectra were recorded on a Varian E-3 EPR spectrometer. The X-band microwave frequency was used between 9.125 and 9.110 GHz at a field strength between 3100 and 2100 G.

Microanalysis was performed by Galbraith Laboratories, Inc. (Knoxville, Tenn.).

$Cu(OCH_3)_2$,[11] $Fe(OCH_2CH_3)_3$,[12] $Cr[N(i\text{-}Pr)_2]_3$,[13] and $[cis\text{-}(OC)_4Re(CH_3CO)(RCO)]H$, where R is methyl or isopropyl,[8] were prepared by literature procedures.

Preparation of $[cis\text{-}(OC)_4Re(CH_3CO)_2]_2Cu$ (1). To a stirred solution of 0.30 g (0.78 mmol) of $[cis\text{-}(OC)_4Re(CH_3CO)_2]H$ in 4 mL of diethyl ketone at 25 °C was added 0.06 g (0.47 mmol) of $Cu(OCH_3)_2$. The pale yellow solution turned black immediately after addition of the $Cu(OCH_3)_2$ and a brown precipitate formed within 5 min. The reaction solution was stirred for 0.5 h followed by the removal of the solvent under reduced pressure giving a black semisolid as the crude product. The impure product was crystallized from toluene solution at −20 °C affording 70 mg (18%) of **1** as deep red needles which are air stable: mp 120–121 °C; IR (hexane) $\nu(CO)$ 2087 (m), 1991 (s), 1975 (vs), 1965 (s), $\nu(C\overline{\cdots}O)$ 1506 (m) cm^{-1}; $\mu_{eff} = 1.8\ \mu_B$. Anal. Calcd for $C_{16}H_{12}O_{12}Re_2Cu_1$: C, 23.09; H, 1.46; Cu, 7.46. Found: C, 23.29; H, 1.48; Cu, 7.48.

Preparation of $[cis\text{-}(OC)_4Re(CH_3CO)(i\text{-}PrCO)]_2Cu$ (2). Complex **2** was prepared from 0.120 g (0.31 mmol) of $[cis\text{-}(OC)_4Re(CH_3CO)(i\text{-}PrCO)]H$ and 0.20 g (0.16 mmol) of $Cu(OCH_3)_2$ following the same general method described for the synthesis of complex **1**. The reaction afforded 24 mg (19%) of **2** as deep red needles which are air stable: mp 93.5–94 °C; IR (hexane) same as for complex **1**; $\mu_{eff} = 2.2\ \mu_B$. Anal. Calcd for $C_{20}H_{20}O_{12}Re_2Cu$: C, 27.04; H, 2.27; Cu, 7.15. Found: C, 26.91; H, 2.37; Cu, 7.31.

Preparation of $[cis\text{-}(OC)_4Re(CH_3CO)_2]_3Fe$ (3). To a stirred solution of 0.250 g (0.64 mmol) of $[cis\text{-}(OC)_4Re(CH_3CO)_2]H$ in 5 mL of benzene at 25 °C was added dropwise over a 1-min period 3 mL of (0.86 M) of a benzene solution of $Fe(OCH_2CH_3)_3$ (0.26 mmol). During the addition of $Fe(OCH_2CH_3)_3$ the pale yellow solution gradually turned black and a brown precipitate formed within 10 min. The reaction solution was stirred for 0.5 h followed by the removal of solvent at reduced pressure. The black residue was extracted with 1.5 mL of toluene and the toluene solution was filtered. The filtrate was cooled to −20 °C for 18 h affording 40 mg (15%) of the product as air-stable, deep red needles: mp 125–127 °C; IR (hexane) $\nu(CO)$ 2089 (m), 1989 (s), 1981 (vs), 1957 (s), $\nu(C\overline{\cdots}O)$ 1494 (m) cm^{-1}; $\mu_{eff} = 5.8\ \mu_B$. Anal. Calcd for $C_{24}H_{18}O_{18}Re_3Fe_1$: C, 23.84; H, 1.50; Fe, 4.62. Found: C, 23.89; H, 1.60; Fe, 4.37.

Preparation of $[cis\text{-}(OC)_4Re(CH_3CO)_2]_3Cr$ (4). To a stirred solution of 0.140 g (0.36 mmol) of $[cis\text{-}(OC)_4Re(CH_3CO)_2]H$ in 10 mL of hexane at 25 °C was added dropwise 2 mL (0.061 M) of a pentane solution of $Cr[N(i\text{-}Pr)_2]_3$ (0.12 mmol) over a 3-min period. During the addition of $Cr[N(i\text{-}Pr)_2]_3$ the pale yellow solution gradually turned brown. A brown precipitate formed within 5 min and 0.5 h later the reaction solution was olive green. The solution was stirred for an additional 0.5 h followed by the removal of the solvent at reduced pressure to give a green solid as the impure product. The product was crystallized from 3 mL of 5% ether/95% hexane at −20 °C for 18 h affording 30 mg (21%) of **4** as an air stable, green powder: mp 90–180 °C dec; IR (hexane) $\nu(CO)$ 2098 (m), 1993 (s, sh), 1987 (vs), 1958 (s), $\nu(C\overline{\cdots}O)$ 1502 (m) cm^{-1}; $\mu_{eff} = 3.9\ \mu_B$. Anal. Calcd for $C_{24}H_{18}O_{18}Re_3Cr_1$: C, 23.92; H, 1.51; Cr, 4.32. Found: C, 24.72; H, 1.80; Cr, 4.24.

Preparation of $[cis\text{-}(OC)_4Re(CH_3CO)_2]_2Zn$ (5). To a stirred solution of 0.214 g (0.56 mmol) of $[cis\text{-}(OC)_4Re(CH_3CO)_2]H$ in 15 mL of hexane at 25 °C was added dropwise over a 1-min period 0.20 mL (0.31 mmol) of $Zn(CH_2CH_3)_2$ (25% in hexane by weight). The pale yellow solution was stirred for 4 h followed by the removal of the solvent at reduced pressure. The semisolid residue was extracted twice with 30 mL of hexane, and the hexane solution was then filtered. The

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hexane was removed at reduced pressure, and the product was crystallized from a methylene chloride–hexane (1:4) solution affording 93 mg (20%) of **5** as an air-stable white solid: mp 132–135 °C; IR (hexane) ν(CO) 2095 (m), 1995 (s), 1985 (vs), 1963 (s), $\nu(\mathrm{C\overset{-}{\cdot\cdot}O})$ 1492 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) τ 7.22 (s, CH$_3$). Anal. Calcd for $C_{16}H_{12}O_{12}Re_2Zn$: C, 23.04; H, 1.45; Zn, 7.84. Found: C, 23.25; H, 1.69; Zn, 7.59.

Preparation of [*cis*-(OC)$_4$Re(CH$_3$CO)$_2$]$_2$Mg (6). To a stirred solution of 0.220 g (0.57 mmol) of [*cis*-(OC)$_4$Re(CH$_3$CO)$_2$]H in 4 mL of diethyl ether at 25 °C was added dropwise over a 5-min period 2 mL (0.140 M) of a diethyl ether solution of Mg(C$_6$H$_5$)$_2$ (0.28 mmol). A cloudy white precipitate formed within 0.5 h. The reaction solution was stirred for an additional 0.5 h followed by the removal of the solvent under reduced pressure. The yellow residue was extracted for 15 min with 2 mL of a hexane–toluene (1:1) solution. The extracted solution was then filtered and cooled to –20 °C for 3 days affording 32 mg (14%) of the product as air-stable, white crystals: 120–169 °C dec; IR (diethyl ether) ν(CO), 2078 (m), 1968 (s, sh), 1953 (vs), 1930 (s), $\nu(\mathrm{C\overset{-}{\cdot\cdot}O})$ 1563 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) τ 7.37 (s, CH$_3$). This representative-metal complex was prepared only as a Zn(II) analogue, and microanalysis was not performed.

Preparation of {[*cis*-(OC)$_4$Re(CH$_3$CO)$_2$]Cu(OCH$_3$)}$_2$ (7) with Cu(OCH$_3$)$_2$. To a mixture of 0.30 g (0.78 mmol) of [*cis*-(OC)$_4$Re(CH$_3$CO)$_2$]H in 15 mL of diethyl ether was added 0.08 g (0.63 mmol) of anhydrous Cu(OCH$_3$)$_2$ as a fine powder. The pale yellow reaction solution turned brown immediately upon the addition of the Cu(OCH$_3$)$_2$. The reaction solution was stirred for 30 min during which time a pale blue-green solid precipitated. This solid was isolated by filtration and was crystallized from diethyl ether solution at –20 °C affording 20 mg (5%) of the product as air-stable, green crystals: 105–190 °C dec; IR (hexane) ν(CO) 2090 (m), 1997 (m), 1980 (vs), 1972 (s), $\nu(\mathrm{C\overset{-}{\cdot\cdot}O})$ 1510 (w) cm^{-1}; $\mu_{\mathrm{eff}} = 1.2\ \mu_B$. Anal. Calcd for $C_{18}H_{18}O_{14}Re_2Cu_2$: C, 22.56; H, 1.88; Cu, 13.27. Found: C, 21.66; H, 1.85; Cu, 13.35.

Preparation of 7 by Using Sodium Methoxide. To a mixture of 0.010 g of **1** in 2 mL of hexane was added dropwise over a 1-min period 0.10 mL (1.14×10^{-7} M) of a methanol solution of NaOCH$_3$ (0.012 mmol). During this addition the brown reaction solution turned green. The reaction solution was stirred for 15 min, and then the solvent was removed at reduced pressure affording a green powder. The infrared spectrum of this solid was identical with that of **7** reported above.

Results and Discussion

The displacement of an anionic ligand of a transition metal ion by a metalla-β-diketonate anion did not afford the corresponding metalla-β-diketonate complex. Specifically, the lithium salt of the *cis*-diacetyltetracarbonylrhenate anion did not react with anhydrous salts such as Co(BF$_4$)$_2$, NiBr$_2$, CuCl$_2$, or (PPN)$_2$NiCl$_4$, where PPN is the bis(triphenylphosphin)iminium cation, to form the transition-metal metallaacetylacetonate complexes. Since the O–O "bite" distance of the rhenium metalla-β-diketonate anions should be large enough to permit coordination to the transition-metal ions, an alternative synthetic route was attempted.

This synthesis is based on the elimination of a neutral molecule rather than a halide or anion displacement reaction. The reactants are a neutral metalla-β-diketone molecule and an anhydrous metal complex where the ligands are good Brönsted bases. The transition-metal complexes are formed, presumably, as the enolic hydrogen atom is removed by the basic ligands as shown in Scheme I.

The reactions forming the complexes **1**–**7** are performed in organic solvents and the eliminated molecule is methanol, ethanol, diisopropylamine, ethane, or benzene. This reaction is analogous to the method used for the synthesis of several nonmetalla-β-diketonate complexes of the transition metals.[13]

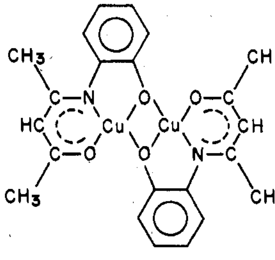
The complexes **1**–**7** have excellent air stability, and decompose thermally between 90 and 190 °C. These complexes are soluble in aliphatic hydrocarbon solvents except for the magnesium complex, **6**, which is soluble only in aromatic or polar organic solvents. The zinc and magnesium complexes, **5** and **6**, are white solids, as expected, while the copper, iron, and chromium complexes, **1**–**4**, exhibit unusual colors. The copper and iron complexes are black solids which are deep red under intense light. The chromium complex is a dark green solid.

Scheme I

$$n[cis\text{-}(OC)_4Re(CH_3CO)(RCO)]H + ML_n \rightarrow [cis\text{-}(OC)_4Re(CH_3CO)(RCO)]_nM + nLH$$

n	R	M	L	no.
2	CH$_3$	Cu	OCH$_3$	1
2	*i*-Pr	Cu	OCH$_3$	2
3	CH$_3$	Fe	OCH$_2$CH$_3$	3
3	CH$_3$	Cr	N(*i*-Pr)$_2$	4
2	CH$_3$	Zn	CH$_2$CH$_3$	5
2	CH$_3$	Mg	C$_6$H$_5$	6
1	CH$_3$	Cu(OCH$_3$)	OCH$_3$	7

The copper methoxide metallaacetylacetonate complex, **7**, is a green solid like the mixed salt, Cu(OCH$_3$)Cl,[11] and the Cu(II) β-ketoimine complex, **8**.[15] Since the IR spectrum of **7** indicates that the metallaacetylacetonate is acting as a bidentate ligand, it presumably has the dimeric bridging structure **9**.



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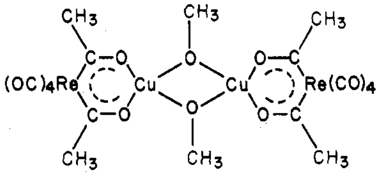

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When the reaction with diethyl zinc was performed in diethyl ether solution at 25 °C, an ionic solid was isolated. The infrared spectrum of this solid was essentially identical with that of the lithium salt, Li[*cis*-(OC)$_4$Re(CH$_3$CO)$_2$], in the terminal carbonyl stretching region. Presumably this solid is the zinc salt of the zincate anionic complex Zn[*cis*-(OC)$_4$Re(CH$_3$CO)$_2$]$_3^-$. The nonmetalla analogue of this complex is known also.[16]

A similar anionic complex is known for magnesium; however, the only magnesium complex isolated was the neutral bis complex **6**, as indicated by its solubility in toluene. The lower solubility of this complex suggests some ionic or polymeric character, and the carbonyl stretching frequencies are ca. 20 cm^{-1} lower than those of the other metal complexes. This shift is characteristic of an increase in the negative charge on the rhenium atom.

Infrared and Proton NMR Spectra. Complexes **1**–**7** exhibit the expected carbonyl stretching pattern for the *cis*-(OC)$_4$Re moiety.[3,5] The most intense carbonyl bands of **1**–**5** and **7** appear at 1981 ± 6 cm^{-1} which is consistent with a covalent complex having a neutral charge. This band for the magnesium complex **6** appears at much lower frequency, 1953 cm^{-1}, which indicates considerable ionic character with a larger negative charge residing on the rhenium atom. Complex **6** has a carbonyl stretching pattern identical with that of the corresponding lithium complex.

The $\mathrm{C\overset{-}{\cdot\cdot}O}$ stretching bands of the acyl groups within the metalla-β-diketonate ligands of **1**–**5** and **7** appear at 1502 ±

6 cm^{-1} which is a diagnostic indication for the formation of a covalent coordination complex.[3] For complex **6**, the acyl band appears at much higher frequency, 1563 cm^{-1}. This shift apparently reflects the partial ionic character of **6** since the corresponding band in the lithium complex appears at 1578 cm^{-1}. A similar trend is observed for the nonmetalla-acetylacetonate complexes.[17,18]

Of the complexes prepared, only the zinc and magnesium compounds, **5** and **6**, are diamagnetic. Both complexes exhibit a single resonance for the methyl substituents as expected for tetrahedral coordination. These resonances appear in $CDCl_3$ solution at δ 2.78 and 2.63 for **5** and **6**, respectively. The frequency of the methyl resonance of **5** is typical of that for neutral metalla-β-diketonate complexes of metal ions;[3,8] however, the methyl resonance of **6** appears at slightly higher field than for any other such metal complex. This shift reflects the partial ionic character of the magnesium complex, and this resonance is only 90 Hz to lower field than the methyl resonance of the PPN salt of the *cis*-diacetyltetracarbonylrhenate anion.[6]

Magnetic Moments and Electronic Spectra. The magnetic moments of the complexes **1**–**4** and **7** were determined at 22 °C by the Faraday method. Complexes **1**, **2**, **3**, and **4** exhibit magnetic moments of 1.8, 2.2, 5.8, and 3.9 μ_B, respectively, which are within the usual range of values for Cu(II)–d^9, high-spin octahedral Fe(III)–d^5, and octahedral Cr(III)–d^3 complexes. Presumably, the complexes **1** and **2** are monomeric like $Cu(acac)_2$ since no Cu–Cu interaction is observed. The magnetic moment of the iron complex, **3**, is very close to the spin-only value of 5.9 μ_B since the ^6S ground state of the Fe(III) ion lacks orbital angular momentum.

The dimeric Cu(II) complex **7** has a subnormal magnetic moment of 1.2 μ_B. This feature is very common to dimeric Cu(II) complexes having monatomic, bridging oxygen atoms.[19] Complex **8** is one such example. This complex is also a green solid, and it has a subnormal magnetic moment of 1.37 μ_B.[20] Similar complexes have magnetic moments of from 1.02 to 1.2 μ_B.[19] These complexes have magnetic properties like that of copper(II) acetate without possessing a similar structure. The magnetic moment of complex **7** strongly supports the bridged structure **9**. The energy separation of the singlet and triplet states of **7** has not been determined. Also, the mechanism of this interaction has not been elucidated.

The electronic spectra of the three transition-metal complexes having only metallaacetylacetonate ligands, **1**, **3**, and **4**, were obtained as chloroform solutions in the region of 240–900 nm along with a reference spectrum of the colorless metallaacetylacetone molecule, $[cis\text{-}(OC)_4Re(CH_3CO)_2]H$. The absorption bands may be assigned qualitatively by comparison to the electronic spectra of the nonmetalla analogues and other reference compounds.

A rhenium metal to carbonyl carbon atom band is present in all four complexes. This band, which usually occcurs between 220 and 380 nm,[21] appears at 288 (4.31), 274 (4.44), and 273 (4.48) nm for the complexes **1**, **3**, and **4**, respectively. The numbers in parentheses are the values of log ϵ for each band. The metallaacetylacetone molecule has a similar absorption at 275 nm.

The deep red color of the copper complex **1** results from the extension of three intense absorption bands at 313 (4.13), 415 (3.94), and 440 (3.98) nm into the visible region. Presumably these bands result from metal to ligand and ligand to ligand charge-transfer transitions. For $Cu(acac)_2$ the only band of this intensity between 270 and 450 nm is a ligand to ligand ($\pi_3 \rightarrow \pi_4{}^*$) transition of 296 nm.[22]

Similarly, the deep red color of the iron complex **3** arises from the tailing of an intense band at 505 (3.57) nm. The origin of this band is uncertain because it appears at such a low energy. Charge-transfer bands of most nonmetalla-β-diketonate complexes appear at ca. 300–400 nm.[23] The $d_\epsilon \rightarrow \pi_4$ transition of $Fe(acac)_3$ occurs at 353 (3.52) nm; however, $Fe(acac)_3$ has a band at 437 nm (3.51) which has yet to be assigned, also. Unfortunately the tailing edge of these intense bands at 440 and 505 nm for complexes **1** and **3**, respectively, mask the expected d–d transitions.[22,23]

A corresponding low-energy charge-transfer band for the chromium complex, **4**, is not observed, and the d–d transitions can be assigned. The $^4A_{2g} \rightarrow {}^4T_{2g(F)}$ and $^4A_{2g} \rightarrow {}^4T_{1g(F)}$ transitions occur at 430 (2.40) and 575 (1.86) nm, respectively, and these bands agree quite closely with the same transitions of $Cr(acac)_3$ which appear at 435 (1.70) and 560 (1.82) nm.[23] The band for the $^4A_{1g} \rightarrow {}^4T_{1g(P)}$ transition is not observed due to the tailing of the intense rhenium to carbonyl carbon band at 273 nm.

From the energy of the $^4A_{2g} \rightarrow {}^4T_{2g(F)}$ band the value of the ligand field splitting parameter, Δ_0, is calculated to be 17 390 cm^{-1}. This value places the diacetyltetracarbonylrhenate ligand significantly below the acac ligand (for $Cr(acac)_3$, $\Delta_0 = 17\,860$ cm^{-1}) and close to the aquo ligand (for $Cr(H_2O)_6{}^{3+}$, $\Delta_0 = 17\,400$ cm^{-1}) in the spectrochemical series. Apparently, the π-bonding interaction between the t_{2g} orbitals of the Cr(III) ion and the π orbitals of the metallaacetylacetonate ligands is considerably weaker than the corresponding interaction in $Cr(acac)_3$. This trend is consistent with the formal substitution of the methine group of an acac ligand by the more electronegative *cis*-$(OC)_4Re$ moiety.

EPR Spectra. The EPR spectra of complexes **1**, **3**, and **4** were recorded as solutions or glasses under an argon atmosphere. Powder EPR spectra were so severely broadened by intermolecular coupling interactions that detailed interpretation was abandoned.

A solution of 6.8 mg of the iron(III) complex **3** in 0.75 mL of toluene was converted to a glass at −166 °C. The EPR spectrum of this glass showed an essentially isotropic transition (width at half-height of 250 G) centered at a *g* value of 4.259. A very weak and broad resonance was observed at a *g* value of 10.025. This spectrum is interpreted best as a case where the zero-field splitting parameters *D* and *E* are not zero such as found with the iron(III) complex, $Na[Fe(EDTA)]\cdot 4H_2O$, which has a nearly isotropic transition at a *g* value of 4.27 and two very anisotropic transitions at *g* values of 9.64 and 1.10.[24] The high-field transition of complex **3** was not observed. A spectrum of $Fe(acac)_3$ in a toluene glass at −166 °C showed the principal transition at a *g* value of 4.572.

A solution of the chromium(III) complex **4** in $CHCl_3$ gave a poor quality EPR spectrum having an unsymmetrical single transition at a *g* value of 2.004. The calculated *g* value using the spin–orbit coupling energy of $Cr(acac)_3$, 40 cm^{-1}, and the value of Δ_0 for **4**, 17 390 cm^{-1}, was 1.984. The *g* value of the very intense $-{}^1/_2 \rightarrow +{}^1/_2$ transition of $Cr(acac)_3$ is 1.982.[25] The *g* value of **4** is in close agreement with that of $Cr(acac)_3$ considering the poor quality of the spectrum. Presumably, trace paramagnetic impurities caused the observed resonance broadening.

The magnetic moment and powder EPR data of the copper complex **1** were reported previously and indicated a copper(II)–d^9 configuration having essentially square coordination about the copper ion. Unfortunately, the intermolecular electron spin interactions of the solid prevent the detection of any copper or rhenium hyperfine coupling.[9] However, the dissolution of complex **1** in an organic solvent circumvented this difficulty.

The EPR spectrum of **1** as an ca. 0.03 M solution in chloroform/toluene (40:60) at 25 °C is shown in Figure 1 and indicates a typical "isotropic" copper(II) EPR pattern of four resonances (for $^{63,65}Cu$, $I = {}^3/_2$). The value of "g_{iso}" is 2.118,

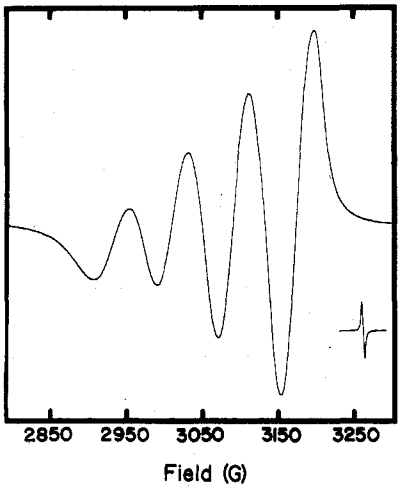

Figure 1. The X-band EPR spectrum of $[cis\text{-}(CO)_4Re(CH_3CO)_2]_2Cu$ (**1**) as a 0.03 M solution in chloroform/toluene (40:60) solution at 25 °C. The reference is DPPH, and the microwave power and frequency are 6.3 mW and 9.123 GHz, respectively.

and the copper hyperfine coupling constant, A_{iso}^{Cu}, is 80.7 × 10^{-4} cm^{-1}. Presumably, the molecular correlation time is sufficiently short that rhenium superhyperfine coupling is not observed. The EPR spectrum of $Cu(acac)_2$ in the same solvent and at the same temperature is nearly superimposable on this spectrum of **1** giving values of "g_{iso}" and A_{iso}^{Cu} of 2.112 and 67.8 × 10^{-4} cm^{-1}, respectively.[26]

Figure 2 shows the EPR spectrum of the above sample solution of **1** at −166 °C. This glass affords the expected anisotropic spectrum for the frozen solution. The four low-field resonances represent the copper hyperfine peaks defining $g_{\parallel}$. The values of $g_{\parallel}$ and $A_{\parallel}^{Cu}$ are, respectively, 2.252 and 194.5 × 10^{-4} cm^{-1}. Furthermore, each $g_{\parallel}$ resonance exhibits rhenium superhyperfine coupling, $A_{\parallel}^{Re}$, of 22.1 × 10^{-4} cm^{-1}. This rhenium coupling (for $^{185,187}Re$, $I = {}^5/_2$) is shown in expanded scale as inserts. For the two equivalent rhenium nuclei, 11 peaks are expected. The experimental spectra clearly show nine of these peaks along with a reproducible shoulder for the remaining two peaks of lowest intensity. The calculated relative intensities of these rhenium superhyperfine peaks are 1:2:3:4:5:6:5:4:3:2:1. Unfortunately, the relaxation broadening of the copper $g_{\parallel}$ resonances which are split by the rhenium nuclei prevents a clean separation of the peaks and distorts the relative intensities, also. The overlapping of adjacent copper $g_{\parallel}$ resonances and the presence of both isotopes of copper further complicate the analysis of peak intensities. However, assuming that the three most intense peaks would be proportionately less affected by such distortions, the experimental relative intensities were measured to be 3.9:6.0:4.4 by using the "peak-to-trough" method. These values are resonably close to the calculated values when considering the above complications.

The more intense peaks centered about 3188 G represent the $g_{\perp}$ portion of the spectrum. An estimated value of $g_{\perp}$ is 2.044. The values of $g_{\parallel}$ and $g_{\perp}$ give an average g value of 2.113 which is very close to that of g_{iso}, 2.118. The value of $A_{\perp}^{Cu}$ is not determined directly due to peak superposition, but it is estimated from A_{iso}^{Cu} and $A_{\parallel}^{Cu}$ to be ca. 23.8 × 10^{-4} cm^{-1}. The corresponding values for $Cu(acac)_2$ are very similar ($g_{\parallel} = 2.286$, $g_{\perp} = 2.0611$, $A_{\parallel}^{Cu} = -0.0173$ cm^{-1}, $A_{\perp}^{Cu} = -0.00130$ cm^{-1}).[27]

The $g_{\perp}$ region of **1** is nearly identical with that observed for $Cu(acac)_2$.[27] The separation and intensity of the three negative absorptions at 3120, 3153 and 3195 G are determined by the amount of quadrupole coupling. This coupling appears to be near 6.8 × 10^{-4} cm^{-1} or less for **1**. The one unique feature of the $g_{\perp}$ region of **1** is the obvious splitting of the two intense resonances at 3171 and 3218 G. These peaks appear as sharp singlets in the $Cu(acac)_2$ spectrum, and we tentatively assign this splitting to the rhenium superhyperfine coupling, $A_{\perp}^{Re}$, of 21.0 × 10^{-4} cm^{-1}.

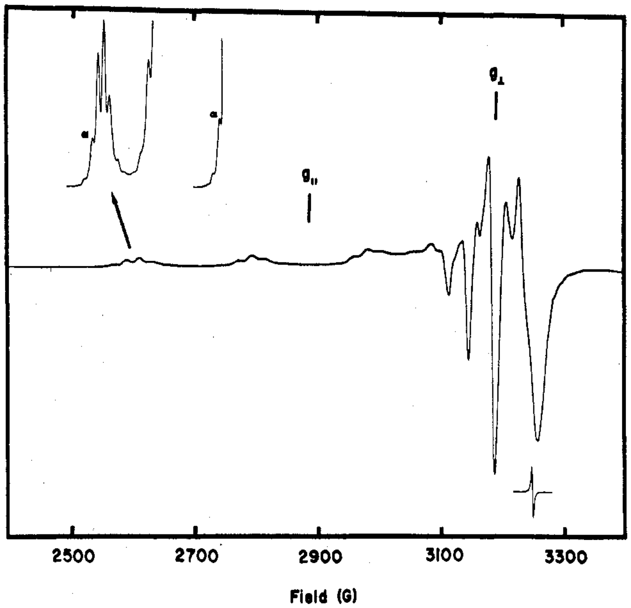

Figure 2. The X-band EPR spectrum of $[cis\text{-}(CO)_4Re(CH_3CO)_2]_2Cu$ (**1**) as a 0.03 M solution in chloroform/toluene (40:60) solution at −166 °C. Expanded scale regions are shown as inserts. The reference is DPPH, and the microwave power and frequency are 160 mW and 9.120 GHz, respectively.

The observation of rhenium superhyperfine coupling of the copper-centered electron spin is the first direct evidence for a metal–metal interaction in these polymetallic complexes. The detailed analysis of the mechanism responsible for this magnetic interaction must await the elucidation of the crystal and molecular structure and the results of a single-crystal EPR study. At present, a suitable diamagnetic host is not available. Also, intense charge-transfer bands prevent the detection of any d–d electronic transitions.

Since the rhenium and copper atoms are separated by carbon–oxygen bridges, the major contributions to the superhyperfine coupling probably arise from an isotropic Fermi contact interaction due to electron delocalization within the metalla-β-diketonate ligand and from dipolar coupling of the rhenium nucleus to unpaired spin density on the copper or other ligand atoms. Using the point-dipole approximation[28] and a minimum copper–rhenium distance of 3.60 Å and noting that the magnetic moments of ^{185}Re and ^{187}Re differ by only 1%, we calculated the dipolar superhyperfine coupling from the copper atom to be 0.29 × 10^{-4} cm^{-1} for $A_{\parallel}^{Re}$. This value is only 1.3% of the observed $A_{\parallel}^{Re}$. Although the carbon and oxygen atoms are closer to the rhenium atom, dipolar coupling from these atoms will be attenuated by the much smaller fractional electron spin density residing on these atoms.[29]

The degree of Fermi contact interaction is not known since A_{iso}^{Re} is not observed in the solution spectrum due to relaxation broadening. However, the similar values for $A_{\parallel}^{Re}$ and $A_{\perp}^{Re}$ indicate that some Fermi contact coupling is quite probable. Also, the g values of **1** are slightly lower than those of $Cu(acac)_2$ which may indicate a greater covalency in **1**.[28] By use of the average value of A_{iso} calculated for a 6s electron in Re(I) and Re(0),[28] the observed superhyperine coupling of **1**, $A_{\parallel}^{Re}$, corresponds to a maximum spin density of 0.005 electrons at the rhenium nucleus. On the assumption of a B_{1g} ground state for the copper ion (D_{2h} symmetry), this spin density would be transferred through inplane ligand molecular orbitals.[29]

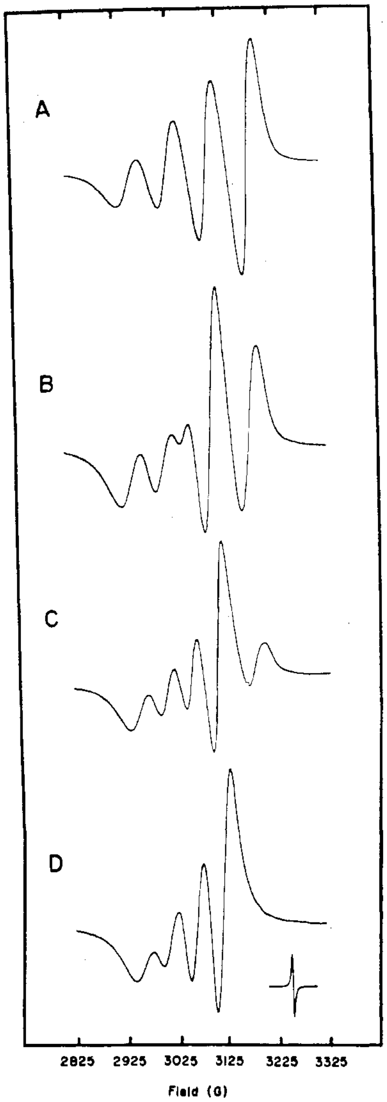

Figure 3. Ambient-temperature EPR spectra of **1** with added pyridine (molar ratio Cu/py): A (no pyridine), B (1:1), C (1:2), D (1:34). The reference is DPPH.

Detailed structural, spectroscopic, and theoretical studies are needed to verify this coupling mechanism.

The formation of Lewis base adducts by bis Cu(II) complexes is well-known.[30-32] Recently, the EPR spectra of these adducts have been used to determine the solution structure of these molecules with particular interest in the location of the Lewis base.

Figure 3 shows the EPR spectra of **1** at ambient temperature as an ca. 0.0217 M solution in chloroform/toluene solvent (40:60). Each spectrum was recorded also as a glass at −166 °C. Spectrum A is that of the pure solution of complex **1** while spectra B, C, and D have 1, 2, and 34 molar equiv of pyridine added to the sample solution of **1**.

When adducts of Cu(II) chelates are formed with donor bases, such as pyridine, an increase in the isotropic g value occurs along with a large reduction in the ^{63,65}Cu isotropic coupling constant.[32] These trends are followed by complex **1**. In spectrum A (no adduct) the value of g_{iso} is 2.118, and the copper hyperfine coupling constant, $A_{iso}{}^{Cu}$, is 80.7×10^{-4} cm^{-1}. In spectrum D (presumably a 1:1 adduct of **1** with pyridine) the corresponding values of g_{iso} and $A_{iso}{}^{Cu}$ are 2.154 and 55.3×10^{-4} cm^{-1}, respectively. Also, when pyridine is added to a solution of **1** the initial red-brown color changes to a lime-yellow color. An IR spectrum of the sample used for spectrum D showed no trace of any uncoordinated *cis*-diacetyltetracarbonylrhenium anion in the metal carbonyl region of the spectrum. However, after this solution was exposed to air for 15 min, the IR spectrum indicated that ca. 50% of the anionic rhenium ligand was uncoordinated. The greenish color and air instability of adducts to nonmetalla chelates of Cu(II) are observed frequently.[30]

The solution structure of the 1:1 adducts may be trigonal bipyramidal (TBP) or square pyramidal (SP). The TBP adduct is expected to have a d_{z^2} ground state and a $g_{x,y}$ value of ca. 2.2, while the SP adduct is expected to have a $d_{x^2-y^2}$ ground state and g values of g_z ca. 2.3 and $g_{x,y}$ ca. 2.07. The g values obtained from the glass spectrum of sample D, $g_{\parallel} = 2.263$ and $g_{\perp} = 2.048$, agree well with a square-pyramidal structure.

The location of the pyridine molecule in an axial or basal site of the SP is usually determined from the magnitude of the nitrogen superhyperfine coupling constant as observed on the copper $g_{\parallel}$ resonances.[33] The pyridine molecule of Cu(acac)$_2$·py probably occupies an axial site since nitrogen superhyperfine coupling is not observed ($A_N = 0.7$ G as determined by NMR), while in the hexafluoro analogue Cu(hfac)$_2$·py, the pyridine is probably in a basal site because of the large nitrogen superhyperfine coupling (A_N is ca. 9 G).[33]

For complex **1**, all of the pyridine adduct spectra at −166 °C show no resolvable nitrogen superhyperfine coupling on the copper $g_{\parallel}$ resonances. However, the $g_{\perp}$ region of the glass spectrum of sample D did show nitrogen coupling of 13.38×10^{-4} cm^{-1}. This spectrum is very similar to the published spectrum of CuCl$_2$ in 0.01 M pyridine/CHCl$_3$ solution at 77 K.[26] The interpretation of this result is difficult because both the color and the IR spectrum of the sample are not consistent with the formation of an ionic pyridine complex such as Cu(py)$_6{}^{2+}$ or with the liberation of any *cis*-diacetyltetracarbonylrhenate anion. At present, we believe that complex **1** forms a 1:1 pyridine adduct when using nearly stoichiometric amounts of pyridine although the structure of this adduct remains uncertain.

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Registry No. **1**, 67634-87-1; **2**, 71486-11-8; **3**, 71486-13-0; **4**, 71486-12-9; **5**, 71393-27-6; **6**, 71393-28-7; **7**, 71486-10-7; [*cis*-(OC)$_4$Re(CH$_3$CO)$_2$]H, 59299-78-4; [*cis*-(OC)$_4$Re(CH$_3$CO)(*i*-PrCO)]H, 66808-98-8; Cu(OCH$_3$)$_2$, 1184-54-9; Fe(OCH$_2$CH$_3$)$_3$, 5058-42-4; Cr[N(*i*-Pr)$_2$]$_3$, 19851-68-4; Zn(CH$_2$CH$_3$)$_2$, 557-20-0; Mg(C$_6$H$_5$)$_2$, 555-54-4.

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Preparation of Cationic η^2-Alkene and η^2-Alkyne Complexes of the $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]$ System and Reduction of These Complexes to σ-Alkyl and Vinyl Derivatives

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New π-alkene and π-alkyne complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3](\eta^2\text{-un})]BF_4$ (un = unsaturated hydrocarbon) have been prepared in high yield from the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ and $AgBF_4$ in CH_2Cl_2, followed by addition of 3 equiv of the alkene or alkyne. These complexes are much more stable in solution that the triphenylphosphine analogues reported previously. These new complexes can be reduced by hydride reagents to the corresponding alkyl and vinyl derivatives. The alkyl complexes in this system are very stable and do not thermally decompose by a β-elimination pathway. The *sec*-butyl complex formed from the hydride reduction of the *cis*-2-butene complex also shows no tendency to undergo alkyl isomerization on the metal to yield the *n*-butyl derivative. Thermal decomposition studies of the *sec*-butyl complex indicate that the diastereomer which forms preferentially is actually the less stable isomer.

Introduction

The synthesis and reaction of complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-olefin})]BF_4$ have recently become well developed. Rosenblum has shown that these complexes may be useful intermediates in organic synthesis.[1] We have recently reported a convenient synthesis of η^2-olefin and η^2-alkyne complexes in this system by the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $AgBF_4$ in methylene chloride solution, generating the highly reactive intermediate $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$, which is then treated with 2 or 3 equiv of the olefin or alkyne to produce the complexes in ca. 70% yield.[2] This procedure may also be used in an analogous manner with $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ to synthesize compounds of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-olefin})]BF_4$.[2] In contrast to the dicarbonyl system, almost no η^2-olefin complexes had been reported in the phosphine system. These complexes were of particular interest to us because of the chirality of the iron atom and the potential for modifying selectivity of nucleophilic additions to the olefin because of the considerable steric and electronic differences between a phosphine and a carbonyl ligand. This potential was diminished, unfortunately, by the relative instability of many of these complexes in solution. The propene and *cis*-2-butene adducts, for example, are thermally unstable and rapidly decompose above −20 °C.

In order to prepare a series of chiral η^2-olefin complexes of greater stability, we chose to use triphenyl phosphite as the phosphorus donor ligand rather than triphenylphosphine. This ligand had been used successfully to prepare the bis(phosphite) complex $[(\eta^5\text{-}C_5H_5)Fe[P(OPh)_3]_2(\eta^2\text{-}C_2H_4)]BF_4$,[3] but no mixed carbonyl–triphenyl phosphite salts had been reported. Also, only a few neutral compounds had been reported. Those of interest here are the methyl, ethyl, and propyl derivatives prepared by Su and Wojcicki[4] and alkyl and silyl derivatives prepared by Stanley and Baird.[5]

In this paper, we report a facile and high-yield preparation of η^2-olefin and η^2-alkyne complexes and the hydride reduction of these complexes to the respective alkyl and vinyl complexes. In addition, we report our observations concerning the thermal stability of the new alkyliron species.

Experimental Section

General Procedure. All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen by using solvents that were purified and degassed before use. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer. Proton NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer and chemical shifts are reported in δ vs. Me_4Si. Carbon-13 NMR spectra were recorded on a Varian CFT-20 spectrometer using CH_2Cl_2, $CHCl_3$, or dichloroethane as the solvent and internal standard. Chemical shifts are reported in δ vs. Me_4Si assigning the CH_2Cl_2 resonance to be at 54.00 ppm, the $CHCl_3$ resonance to be at 77.20 ppm, and the dichloroethane resonance to be at 44.19 ppm. All carbon-13 spectra were run with ^1H decoupling and all resonances may be assumed to be singlets unless multiplicity is specified. The carbonyl resonance was usually not observed because data were collected under conditions (0.5 s acquisition time, 41° flip angle pulse, and no pulse delay) which tended to saturate this carbon atom. The triphenyl phosphite carbon resonances were assigned following Stewart et al.[6] The $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ was prepared and recrystallized by the method of Brown et al.[7] The $AgBF_4$ was purchased from Ozark-Mahoning. The L-Selectride (lithium tri-*sec*-butylborohydride) was purchased from Aldrich as a 1.0 M solution in THF. Product mixtures containing silver salts were filtered through a bed of filter aid to ensure a fast flow rate. This bed was washed with fresh reaction solvent, ca. 15 mL, until the washings were colorless. Melting and decomposition points were determined in sealed evacuated capillaries and are uncorrected.

(Carbonyl)(η^5-cyclopentadienyl)(η^2-ethylene)(triphenyl phosphite)iron(II) Tetrafluoroborate. A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OPh)_3]I$ (1.0 g, 1.7 mmol) and $AgBF_4$ (0.38 g, 1.9 mmol) was stirred in CH_2Cl_2 (30 mL) for 30 min. This mixture was then filtered to yield a dark green filtrate. Ethylene was passed through the filtrate until the color changed to yellow-brown, ca. 4 min. This solution was first concentrated to 25 mL and then diluted with diethyl ether (75 mL). This precipitated yellow, air-stable crystals, which were collected, dried, and recrystallized from CH_2Cl_2–diethyl ether (1:3, v/v, 60 mL) (0.73 g, 75%); mp 135–136 °C. Anal. Calcd for $C_{26}H_{24}BF_4FeO_4P$: C, 54.42; H, 4.18. Found: C, 54.15; H, 4.39. ^1H NMR spectrum (acetone-d_6): 7.44 (15, mult, $P(OPh)_3$), 5.21 (5, d, J = 1.0 Hz, $\eta^5\text{-}C_5H_5$), 3.75, 3.38 (2, 2, mult, $CH_2{=}$). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CO) 2025. ^{13}C NMR spectrum (CH_2Cl_2): 150.31 (d, J = 10.3 Hz, O-bound phenyl carbons), 130.81 (meta phenyl carbons), 126.92 (para phenyl carbons), 120.90 (d, J = 4.3 Hz, ortho phenyl

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