Reactions of Coordinated Molecules. 38. Carbon–Carbon Bond Formation between Adjacent Acyl Ligands in Metalla-β-diketonate Anions of Iron and Manganese

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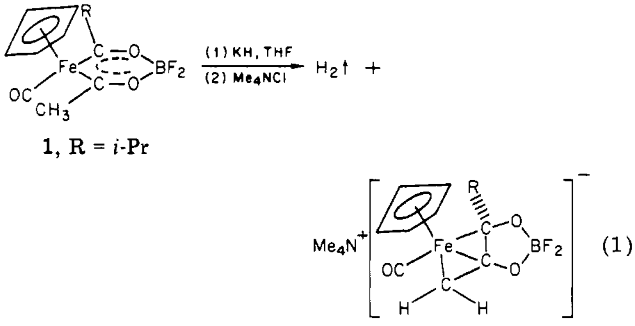
When $(\eta\text{-}C_5H_5)(OC)_2FeC(O)CH_3$ and $(OC)_5MnC(O)CH_3$ are treated sequentially with methyllithium and lithium tetramethylpiperidide, the corresponding η^3-allyl complexes $(\eta\text{-}C_5H_5)(OC)Fe[\eta^3\text{-}CH_2C(O^-)C(O^-)(CH_3)]$ and $(OC)_4Mn[\eta^3\text{-}CH_2C(O^-)C(O^-)(CH_3)]$ are formed by a metal-induced, interligand C–C bond formation. Diacylation of these dianionic complexes with acetyl or benzoyl chloride affords the neutral complexes $(\eta\text{-}C_5H_5)(OC)Fe\{\eta^3\text{-}CH_2C[OC(O)R]C[OC(O)R](CH_3)\}$ and $(OC)_3Mn\{\eta^3\text{-}CH_2C[OC(O)R]C[OC(O)R](CH_3)\}$, where R is methyl or phenyl. In the Mn complexes, one of the acyl oxygen atoms is coordinated to the metal atom. Silylation of the dianionic iron complex with Me_3SiCl gives an unstable neutral η^3-allyl complex. Effecting interligand C–C bond formation directly with metalla-β-diketonate anions should enhance the use of these organometallic reagents for organic synthesis.

Introduction

We reported recently an intramolecular, interligand C–C bond formation reaction that occurs between adjacent acyl ligands, as shown in eq 1.[1] When the (ferra-β-diketonato)BF_2 complex 1 is treated with KH, a proton is removed from the methyl substituent of the ferra chelate ring, and complex 2 forms in essentially quantitative yield with concomitant elimination of molecular hydrogen. Complex 2 is an η^3-allyl complex (written in an all representation) as determined by X-ray crystallography. We have extended this reaction to include other (metalla-β-diketonato)BF_2 complexes where the metalla moieties are *cis*-$(OC)_4Mn$ or *cis*-$(OC)_4Re$.[2]

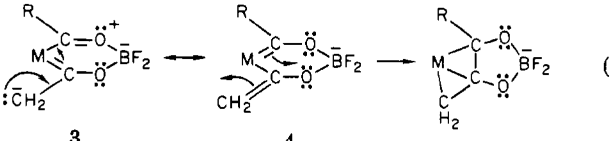


1, R = *i*-Pr

2

(1)

We can rationalize the apparent rearrangement of an α-enolate anion of a (metalla-β-diketonato)BF_2 complex to an η^3-allyl complex, as shown in eq. 2. The generated α-enolate anion is represented as 3. Structure 4 is presumably a better description of anion 3, because the negative charge on the α-carbon atom is stabilized by the metalla chelate ring. Structure 4 contains formally a Fischer carbenoid ligand and an η^1-alkenyl ligand bonded to the metal atom. Both of these ligand types are known to form stable complexes with ferra, magana, and rhena carbonyl moieties. Conversion of 4 to the observed product 5 occurs as a metal-mediated, transannular C–C bond formation.



3 4 5

(2)

As noted recently by us,[3] if the metalla moiety, M, in 4 is presumed to be isolobal[4,5] to an sp^2-CH group, then in structure 5, M is isolobal to an sp^3-CH group. Structure 4 is formally a *transoid*-2-metalla-1,3-butadiene, and 5 is formally a 1-metallabicyclo[1.1.0]butane. The conversion of 4 to 5 represents a *thermally* allowed, concerted $[{}_{\pi}2_a + {}_{\pi}2_s]$ ring closure, in analogy to the pericyclic ring opening of bicyclo[1.1.0] butanes to give *trans,trans*-1,3-butadienes.[6] The *transoid*-metalladiene structure of 4 is imposed on this "intermediate" by the BF_2 chelate ring.

Furthermore, because the acyl carbon donor atoms of 3 (or 4) undergo a formal reductive coupling (as M is oxidized by one electron and then subsequently reduced by one electron when the new M–C bond is formed), these reactions extend the known examples of metal-mediated reductive coupling of terminal isocyanide and carbonyl ligands[7-9] to include acyl ligands.

We now wish to report that this interligand C–C coupling reaction occurs *directly with metalla-β-diketonate anions*, thereby precluding the need to use (metalla-β-diketonato)BF_2 complexes. As a "one-pot" synthesis, metal carbonyl acetyl complexes can be converted into neutral η^3-allyl complexes. This discovery represents a significant advance in the potential development of this reaction for designed organic syntheses.

Results and Discussion

The general synthetic results are summarized in eq 3. The neutral η^3-allyl complexes 8–12 are prepared in a

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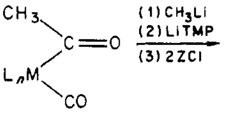
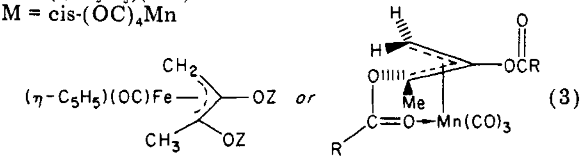


6, $L_nM = (\eta\text{-}C_5H_5)(OC)Fe$
7, $L_nM = cis\text{-}(OC)_4Mn$



8, Z = MeC(O)
9, Z = PhC(O)
10, Z = Me_3Si

11, R = Me
12, R = Ph

three-stage, "one-pot" synthesis. When the neutral metal carbonyl acetyl coomplexes **6** and **7** are treated with methyllithium, the corresponding metalla-β-diketonate anions are formed as intermediates.[10] Addition of 1 molar equiv of lithium tetramethylpiperidide (LiTMP) to these solutions effects deprotonation of one of the acetyl methyl groups with concomitant interligand C–C bond coupling of the two acyl carbon donor atoms, as shown in eq 2. The η^3-allyl complexes formed are dianionic because two of the allylic carbon atoms bear O^- substituents. Diacylation or disilylation affords the neutral η^3-allyl complexes **8–12** which are then isolated and characterized.

Complexes **8–12** are isolated in good yield after column chromatography as yellow solids, except that complex **10** is isolated as an unstable yellow liquid which darkens to a red liquid upon standing. The thermal stability of the solid complexes is excellent in that all melting or decomposition points are greater than 115 °C.

Infrared Spectra. The iron complexes **8** and **9** show a carbonyl stretching vibration at 1965 cm^{-1}. Complex **10** has a corresponding band at 1930 cm^{-1}. This lower energy band for **10** relative to **8** and **9** probably indicates that the acyl substituents withdraw more electron density from the allyl ligand than do the Me_3Si substituents. The carbonyl band of $(\eta\text{-}C_5H_5)(OC)Fe(\eta^3\text{-}C_3H_5)$ appears at 1950 cm^{-1} which indicates that **8–10** are also neutral η^3-allyl complexes of the same type.[11] In **8** and **9**, the ester carbonyl stretching vibrations appear as two bands in the normal range of 1725–1770 cm^{-1}.

For the manganese complexes **11** and **12**, an $Mn(CO)_3$ pattern is indicated by the three carbonyl stretching bands at 2030, 1952, 1930 cm^{-1}. Microanalytical data are also consistent with only three carbonyl ligands. An 18-electron complex is obtained in each case by the coordination of one of the ester carbonyl oxygen atoms to the manganese atom. This ester coordination is evident in the IR spectrum. In both **11** and **12**, the uncomplexed ester carbonyl stretching band occurs at ca. 1760 cm^{-1}, while the complexed ester carbonyl band at 1640 cm^{-1} appears at much lower energy, as expected. The structure assigned to **11** and **12** is presumed to be similar to that of the known, isoelectronic complex $\{(OC)_3Fe[\eta^3\text{-}CH_2C(H)C(H)(CH_2C{=}OMe)]\}PF_6$.[12] This complex, like several others,[13] has a ketonic or sulfoxide group attached β to an allylic terminal carbon atom, and this ketonic or sulfoxide oxygen atom coordinates to the metal atom to give an 18-electron, chelated allyl complex. The carbonyl stretching band for the coordinated acetyl group in the above-mentioned cationic iron complex appears at a low frequency of 1637 cm^{-1}, also.[14]

^1H and ^{13}C NMR Spectra. The diagnostic indication of the formation of η^3-allyl ligands in these complexes is the observation of the syn- and anti-proton doublets of the allyl CH_2 terminus in the ^1H NMR spectra. In the iron complexes **8–10** the anti-proton doublet occurs in the range of δ 0.52–1.21 and the syn-proton doublet occurs in the range of δ 2.85–3.20. The corresponding resonances in $(\eta\text{-}C_5H_5)(OC)Fe(\eta^3\text{-}C_3H_5)$ are observed similarly at δ 0.68 and 2.67, respectively.[11] The allyl methyl singlets of **8–10** appear in the range of δ 1.05–1.38. This methyl group is assigned to an anti site because the corresponding allyl methyl resonance of $Me_4N\{(\eta\text{-}C_5H_5)(OC)Fe[\eta^3\text{-}CH_2COCO(Me)BF_2]\}$, **13**, which is required to be located in an anti site, is observed at δ 1.27. Other ^1H NMR resonances of **8–10** appear at the expected chemical shifts. However, as expected from the low symmetry of these complexes, the methyl ester and silyl methyl resonances are anisochronous (by 0.07 and 0.09 ppm, respectively).

The ^{13}C NMR spectra of **8** and **9** reveal a CH_2 allyl terminus resonance at δ ca. 25.9 and the other two allyl carbon resonances at δ ca. 116.4 and 91.6. The corresponding allyl carbon resonances for complex **13** are observed at δ 15.6, 123.1, and 103.2. The *anti*-methyl resonances of **8** and **9** appear at an average value of δ ca. 25. The corresponding resonance of **13** is observed at δ ca. 30. The observed anisochronism for the two acyl carbon resonances of **8** and **9** are 2.3 and 2.7 ppm, respectively. The anisochronism for the two methyl ester carbons of **8** is 0.7 ppm.

In the ^1H NMR spectra of the manganese complexes **11** and **12**, the *anti*- and *syn*-allyl proton doublets occur at average values of δ ca. 1.34 and 3.84, respectively. The corresponding allyl proton resonances of $(\eta^3\text{-}C_3H_5)Mn(CO)_4$,[15] **14**, and $Me_4N\{cis\text{-}(OC)_4Mn[\eta^3\text{-}CH_2COCO(Me)BF_2]\}$,[2] **15**, apppear at δ 1.72, 2.69 and δ 1.53, 2.88, respectively. The allyl methyl group singlets of **11** and **12** appear at δ ca. 3.85. However, the allyl *anti*-methyl group resonance of **15** is observed at δ 1.88. Therefore, because the allyl methyl resonances of **11** and **12** appear at such low field, they are assigned to allyl methyl groups which occupy *syn*-allyl sites.[15] The observed anisochronism of the methyl ester methyl groups in **11** is 0.23 ppm. This anisochronism is over three times larger than the observed anisochronism for the same groups of complex **8**. This result might be expected because one of these ester groups is now coordinated to the manganese atom.

In the ^{13}C NMR spectra of **11** and **12**, the CH_2 allyl terminus and other allyl carbon appear at δ, ca. 57.9, 125.3, and 116.8, respectively. The corresponding allyl carbon resonances of **14** and its 1-ethyl and 1-isopropyl derivatives are observed at δ ca. 37.0, 91.9, and 75.6.[16] In complex **15**, these allyl carbon resonances appear similarly at δ 23.2, 127.2, and 124.8. The allyl methyl carbon resonances of **11** and **12** appear at δ ca. 20.5. The nonequivalent ester groups of **11** and **12** show separate carbon resonances in the normal chemical shift regions. The anisochronism

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observed for the acyl carbons of **11** and **12** are 10.3 and 9.4 ppm, respectively, while the methyl ester carbon resonances of **11** are separated by 1.4 ppm. As observed in the ^{1}H NMR spectra, the anisochronism of the ester carbon resonances of **11** are much larger than those of **8** where both ester groups are uncomplexed. The carbonyl ligand carbon resonances of **11** appear as one broad band; however, the CO resonances of **12** appear as two peaks of ca. 2:1 relative intensity which is consistent with a pseudosymmetrical $Mn(CO)_3$ structure.

A minor isomer is observed in the ^{1}H NMR spectra of **8** and **9**. These isomers are η^3-allyl complexes where the anti- and syn-allyl proton doublets centered at δ ca. 1.73 and 3.42, respectively, are shifted significantly to lower field relative to the corresponding resonances of the major isomer. For complex **8**, the minor isomer abundance does not exceed ca. 10%, while for **9**, the minor isomer abundance increases to ca. 40% after warming the complex in solution at ca. 40 °C for 1 day. The minor isomer of **9** shows an allyl methyl singlet resonance at δ 2.35. This resonance appears 0.97 ppm to lower field than the allyl methyl resonance of the major isomer. We assign both minor isomers to a structure where the allyl methyl group now occupies a syn-allyl site. These isomers are related by a simple syn–anti interconversion. This type of isomerization is known to be slow for $(\eta\text{-}C_5H_5)(OC)Fe(\eta^3\text{-allyl})$ complexes.[13]

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen. Glass apparatus were flame dried before use. Tetrahydrofuran (THF), pentane, and toluene were dried over Na/K alloy with added benzophenone. Methylene chloride was dried over P_2O_5.

Infrared (IR) spectra were recorded on a Perkin-Elmer 727 spectrometer as solutions in 0.10-mm sodium chloride cavity cells with the solvent as a reference and a polystyrene film as a calibration standard. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX90 Q F-T NMR spectrometer operating at a frequency of 90 MHz for ^{1}H NMR and 22.5 MHz for ^{13}C NMR at 36 °C. The ^{2}H signal of the solvent ($CDCl_3$) was used as a locking frequency. The pulse width repetition rate, and number of accumulations for ^{1}H NMR and ^{13}C NMR were 15 μs, 1.8 s, and 48 and 3 μs, 1.7 s, and ca. 9000, respectively. Preliminary ^{13}C NMR spectra were proton decoupled by using a 1000-Hz bandwidth decoupling frequency. Peak assignments and exact C–H coupling constants were obtained by gated decoupling. Samples consisted of ca. 50 mg of complex dissolved in 0.5 mL of solvent with Me_4Si as an internal standard. Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, TN, and by MicAnal Microanalysis, Tuscon, AR.

The complexes **6** and **7** were prepared by literature methods.[17,18]

General Preparation of the η^3-Allyl Complexes 8–12. To a stirred solution of 0.8–1.0 g of **6** or **7** in 40 mL of THF was added 1 molar equiv of methyllithium in ether solution (1.4 M) at −50 (for **6**) or at 0 °C (for **7**). For **6**, the reaction solution was warmed slowly to −30 °C and was stirred for 1 h. For **7**, the reaction solution was stirred at 0 °C for 1 h. At this point, 1 molar equivalent of lithium tetramethylpiperidide[19] in 20 mL of THF was added to the reaction solution at −78 °C over a 5-min period through a cannula needle. The solution was warmed to −20 °C over a period of 90 min. After the solution was cooled to −78 °C, 3 equiv of Me_3SiCl, acetyl chloride, or benzoyl chloride were added. The solution was warmed to 25 °C over 2 h, and then the solvent was removed at reduced pressure. The product was extracted into 40 mL of toluene (50 mL of pentane for **10**) and was chromatographed on a florisil column (100–200 mesh, 12 mm × 75 mm column). A yellow band was eluted in all cases. Removal of the solvent at reduced pressure gave the crude product. Complexes **8**, **9**, and **11** were crystallized from hexane, while complex **5** was crystallized from a mixture of hexane and methylene chloride. Complex **3** was isolated as an impure red liquid upon removing the pentane solvent. The detailed characterization data for each complex are provided below.

$(\eta\text{-}C_5H_5)(OC)Fe\{\eta^3\text{-}CH_2C[OC(O)Me]C[OC(O)Me](CH_3)\}$, 8: yield 36%; mp 115–120 °C; IR (ether) ν(CO) 1965 (s), ν(ester) 1770 (w), 1755 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (d, 1, CH_2 anti-H, J = 4.9 Hz), 1.16 (s, 3, CH_3 allyl), 2.11 (s, 3 , CH_3 acetyl), 2. 18 (s, 3, CH_3 acetyl), 2.97 (d, 1, CH_2 syn-H), 4.51 (s, 5, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 20.9 (q, CH_3 acetyl, J = 129 Hz), 21.6 (q, CH_3 acetyl, J = 129 Hz), 24.9 (q, CH_3 allyl, J = 129 Hz), 25.8 (d of d, CH_2, J = 159, 166 Hz), 82.3 (d of t, C_5H_5, J_α = 175 Hz, J_β = 6 Hz), 91.4 (s, C allyl), 115.9 (s, C allyl), 168.3 (s, C acyl), 170.6 (s, C acyl), 219.3 (s, CO). Anal. Calcd for $C_{14}H_{16}O_5Fe$: C, 52.55; H, 5.00. Found: C, 52.69; H, 5.05.

$(\eta\text{-}C_5H_5)(OC)Fe\{\eta^3\text{-}CH_2C[OC(O)Ph]C[OC(O)Ph](CH_3)\}$, 9: yield 45%; mp 127–132 °C; IR(hexane) ν(CO) 1965 (s), ν(ester) 1740 (w), 1725 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 1, CH_2 anti-H, J = 4.9 Hz), 1.38 (s, 3, CH_3 allyl), 3.20 (d, 1, CH_2 syn-H, J = 4.9 Hz), 4.64 (s, 5, C_5H_5), 7.26–8.10 (m, 10, 2 Ph); ^{13}C NMR ($CDCl_3$) δ 25.0 (q, CH_3 allyl, J = 129 Hz), 26.1 (d of d, CH_2, J = 159, 164 Hz), 82.2 (d of t, C_5H_5, J_α = 178 Hz, J_β = 7 Hz), 91.9 (s, C allyl), 116.9 (s, C allyl), 128.2–133.4 (2 Ph), 164.2 (s, C acyl), 166.9 (s, C acyl) 219.3 (s, CO). Anal. Calcd for $C_{24}H_{20}O_5Fe$: C, 64.86; H, 4.54. Found: C, 64.64; H, 4.55.

$(\eta\text{-}C_5H_5)(OC)Fe[\eta^3\text{-}CH_2C(OSiMe_3)C(OSiMe_3)(CH_3)]$, 10: yield 35%; IR (hexane) ν(CO) 1930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9, $SiMe_3$), 0.33 (s, 9, $SiMe_3$), 0.52 (d, 1, CH_2 anti-H, J = 4.4 Hz), 1.05 (s, 3, CH_3 allyl), 2.85 (d, 1, CH_2 syn-H, J = 4.4 Hz), 4.36 (s, 5, C_5H_5). Sample decomposition precluded further characterization.

$(OC)_3Mn\{\eta^3\text{-}CH_2C[OC(O)Me]C[OC(O)Me](CH_3)\}$, 11: yield 31%; mp 121–123 °C; IR(pentane) ν(CO) 2030 (m), 1955 (s), 1930 (s), ν(ester) 1770 (w), 1650 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 1, CH_2 anti-H, J = 4.9 Hz), 1.92 (s, 3, CH_3 acetyl), 2.15 (s, 3, CH_3 acetyl), 2.41 (s, 3, CH_3 allyl), 3.75 (d, 1, CH_2 syn-H, J = 4.9 Hz); ^{13}C NMR ($CDCl_3$) δ 18.7 (q, CH_3 acetyl, J = 130 Hz), 20.1 (q, CH_3 acetyl, J = 129 Hz), 20.3 (q, CH_3 allyl, J = 129 Hz), 57.4 (t, CH_2, J = 162 Hz), 116.6 (s, C allyl), 125.5 (s, C allyl), 169.8 (s, C acyl), 180.1 (C acyl), 221.2 (bs, CO ligands). Anal. Calcd for $C_{11}H_{11}O_7Mn$: C, 42.59; H, 3.54. Found: C, 42.30; H, 3.65.

$(OC)_3Mn\{\eta^3\text{-}CH_2C[OC(O)Ph]C[OC(O)Ph](CH_3)\}$, 12: yield 46%; mp 154–159 °C dec; IR (pentane) ν(CO) 2030 (m), 1950 (s), 1930 (s), ν(ester) 1750 (w), 1630 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46 (d, 1, CH_2 anti-H, J = 4.9 Hz), 2.59 (s, 3, CH_3 allyl), 3.94 (d, 1, CH_2 syn-H, J = 4.9 Hz), 7.39–8.12 (m, 10, 2 Ph); ^{13}C NMR ($CDCl_3$) δ 20.7 (s, CH_3 allyl), 58.3 (t, CH_2, J = 162 Hz), 116.9 (s, C allyl), 125.2 (s, C allyl), 126.3–134.7 (2 Ph), 165.7 (s, C allyl), 175.1 (s, C acyl), 221.3 (s, 1 CO), 222.1 (s, 2 CO). Anal. Calcd for $C_{21}H_{15}O_7Mn$: C, 58.07; H, 3.46. Found: C, 58.41; H, 3.56.

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Registry No. **6**, 12108-22-4; **7**, 13963-91-2; **8** (anti isomer), 87333-64-0; **8** (syn isomer), 87261-42-5; **9** (anti isomer), 87261-38-9; **9** (syn isomer), 87333-65-1; **10**, 87261-39-0; **11**, 87261-40-3; **12**, 87261-41-4.

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