

REACTIONS OF COORDINATED MOLECULES

XLIX *. CARBON–CARBON BOND FORMATION BETWEEN THE DONOR ATOMS OF ADJACENT ACYL AND ALKENYL LIGANDS

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Summary

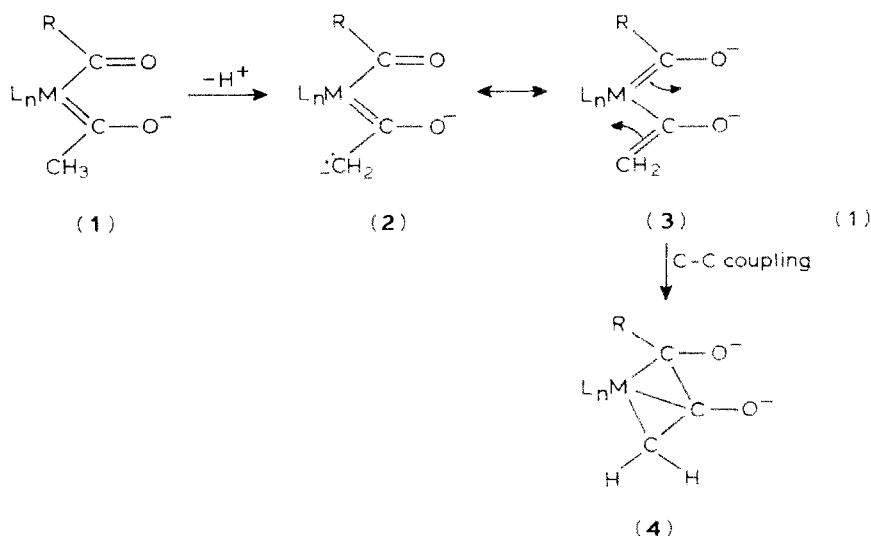
When the ferraenolate anion, $(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{FeC}(\text{O})\text{CH}_2^-$, is treated sequentially with methyllithium/TMEDA and benzoyl chloride, the known η^3 -allyl complex, $(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}\{\eta^3\text{-CH}_2\text{C}[\text{OC}(\text{O})\text{Ph}]\text{C}[\text{OC}(\text{O})\text{Ph}](\text{CH}_3)\}$, is isolated in 36% yield. When the neutral alkenyl complexes, $(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{Fe}[\text{C}(\text{Me})\text{CH}_2]$ and $(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{Fe}[\text{C}(\text{OMe})\text{CH}_2]$, were treated sequentially with methyllithium and benzoyl chloride, the η^3 -allyl complexes, $(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}\{\eta^3\text{-CH}_2\text{C}(\text{Me})\text{C}[\text{OC}(\text{O})\text{Ph}](\text{Me})\}$ and $(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}\{\eta^3\text{-CH}_2\text{C}(\text{OMe})\text{C}[\text{OC}(\text{O})\text{Ph}](\text{Me})\}$ are isolated in 8 and 11% yield, respectively. These η^3 -allyl ligands are presumably formed via C–C coupling of the donor atoms of the formal acyl and alkenyl ligands in the intermediate complexes.

Introduction

We have reported recently that the α -enolate anions of (metalla- β -diketonato)BF₂ complexes, metalla- β -diketonate anions, and (triacylrhenato)BX complexes undergo reductive coupling of two adjacent acyl carbon donor atoms to give η^3 -allyl complexes [1]. This type of acyl C–C coupling can be effected also by using external reducing agents [2].

A proposed mechanism for these interligand C–C coupling reactions is shown in eq. 1 for metalla- β -diketonate anions. Deprotonation of the metalla- β -diketonate anion (1) gives the α -enolate anion (2) (which can be represented also as the “acyl”/alkenyl dianion 3).

* For part XLVIII see Ref. 15.

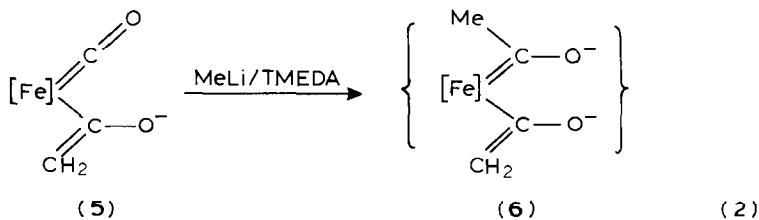


The conversion of **3** to **4** (where **4** depicts an η^3 -allyl complex in an “all- σ ” representation) occurs by interligand C–C coupling. An isolobal analysis of this type of rearrangement has been reported [3]. Diacylation of dianion **4** affords neutral η^3 -allyl complexes. This procedure has been used as a one-pot conversion of acyl/carbonyl complexes to η^3 -allyl complexes for manganese and iron compounds [1c].

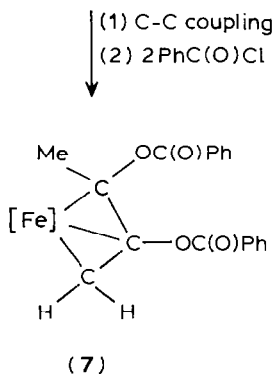
To probe the mechanism of this unusual C–C coupling reaction, we now report that anionic “acyl”/alkenyl intermediate species, such as **3**, can be prepared by an independent route and that neutral η^3 -allyl complexes can be isolated from these reactions after acylation. The conversion of **3** to **4** proceeds readily only for oxy dianions directly analogous to **3**, although related “acyl”/alkenyl intermediates give η^3 -allyl products in low yield. This report completes our study of this rearrangement via this synthetic route.

Results and discussion

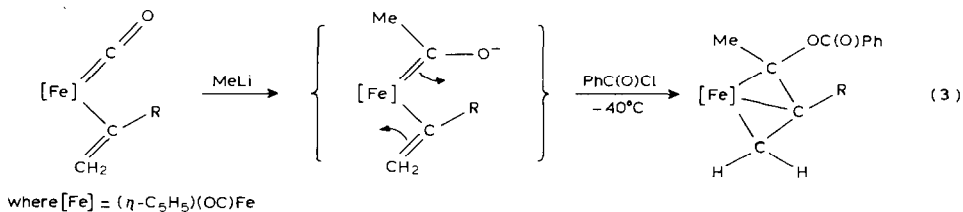
Recent reports indicate the nearly quantitative formation of the ferraenolate anion (**5**) upon treating $(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{FeC}(\text{O})\text{Me}$ with $\text{LiN}(\text{SiMe}_3)_2$ in THF solution at low temperatures [4,5]. When anion **5** is treated with MeLi/tetramethylethylenediamine (TMEDA) in THF solution at -63 to -50°C for 3.75 h followed by acylation with benzoyl chloride, the neutral η^3 -allyl complex **7** is isolated as a recrystallized solid in 38% yield (59% crude yield), as shown in eq. 2 [7]. We suggest that methyllithium adds to one of the carbonyl ligands of **5** to give the dianionic “acyl”/alkenyl intermediate **6**. Carbon–carbon coupling like that shown in the conversion of **3** to **4** followed by diacylation affords the known η^3 -allyl complex **7** [1c]. The formation of dianionic organometallic complexes by successive additions of alkyllithium or Grignard reagents to carbonyl ligands is well documented [1d,8]. By this procedure, intermediate **6** (which is of type **3**) is prepared directly by a route different from that utilized in previous studies (*vide supra*), and the interligand C–C coupling reaction occurs to give the η^3 -allyl product.



where $[\text{Fe}] = (\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}$



When the known iron alkenyl complexes, **8** [9,10] and **9** [11], are treated similarly with methyllithium followed by monoacylation, the neutral η^3 -allyl products **10** and **11** are formed also, see eq. 3. Unfortunately, complexes **10** and **11** are very unstable thermally. After purification by chromatography, **10** and **11** are obtained as oils in only 8 and 11% yield, respectively. Further attempts to purify **10** and **11** were



(R = Me (**8**) ;

R = MeO (**9**)

(R = Me (**10**) ;

R = MeO (**11**))

unsuccessful. However, the ^1H NMR spectra of both complexes are consistent with the structures shown, and the presence of the η^3 -allyl ligands is confirmed unambiguously by the observation of *anti* and *syn* allylic proton doublet resonances at, respectively, δ 0.62 and 2.66 for complex **10** and at δ 1.00 and 3.19 for complex **11** [1]. Both complexes exhibit a single carbonyl stretching band in the IR spectrum, as expected (at 1965 for **10** and at 1977 cm^{-1} for **11**) [1]. Furthermore, complex **10** has sufficient thermal stability that it could be characterized by exact mass spectroscopy.

We suggest that methyllithium adds to a carbonyl ligand of **8** and **9** to give "acyl"/alkenyl intermediates similar to **6** (where one of the oxy anion substituents

in **6** is replaced by the R groups). Subsequent C–C coupling and acylation affords **10** and **11**. The low yield of these reactions could be attributed to (i) the experimental difficulty in handling complexes **10** and **11**, (ii) the inability of these intermediates to coordinate to lithium ion as effectively as does **6** thereby inhibiting the interligand C–C coupling reaction [1,3], or (iii) the presence of competing reactions between **8** or **9** and methyllithium [12]. However, we believe that these results demonstrate an independent synthesis of anionic "acyl"/alkenyl complexes as intermediates which undergo interligand C–C coupling to give η^3 -allyl compounds. Due to the paucity of known alkenyl complexes having the desired reactivity with methyllithium and the apparent thermal instability of these highly substituted, neutral η^3 -allyl product compounds, a more general study of this synthetic method is not intended [13].

Experimental

Solvent purification methods and instrumental specifications have been provided previously [1c]. The reactant complexes were prepared according to the published methods referenced above. Exact mass spectra were obtained on a VG 70/250 GC/MS system with high-field magnet at 70 eV. Samples were introduced by using a direct introduction probe.

*Preparation of $(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}\{\eta^3\text{-CH}_2\text{C}[\text{OC}(\text{O})\text{Ph}]_2\text{C}[\text{OC}(\text{O})\text{Ph}](\text{CH}_3)\}$ (**7**)*

A solution of **5** in THF was prepared at -63°C according to literature procedures [4,5]. After a 20-min period, 2.1 equiv. of methyllithium solution (a molar excess to compensate for any possible in situ reaction with $\text{HN}(\text{SiMe}_3)_2$) followed by a similar amount of TMEDA were added successively to the solution of **5**. After stirring the reaction solution at -63 to -50°C for 3.75 h, 3.1 equiv. of benzoyl chloride were added, and then the solution was stirred for an additional 3 h. The solvent was removed at reduced pressure. The reaction residue was extracted with toluene and then was chromatographed on alumina. Complex **7** was eluted with toluene as a red band (59% crude yield). The yield of **7** after recrystallization from hexane solution was 38% (0.26 g). This product was identified spectroscopically to be identical to the known complex [1c].

*General preparation for $(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}\{\eta^3\text{-CH}_2\text{C}(\text{R})\text{C}[\text{OC}(\text{O})\text{Ph}](\text{CH}_3)\}$, where R = CH_3 (**10**) or CH_2O (**11**)*

To ca. 0.5 g solutions of **8** and **9** in THF or ether solutions at -78 or -20°C were added 1.2 equiv. of methyllithium solution. The reaction solutions were warmed to 10 or 0°C over a 1.75 or 0.75 h period affording dark red-brown solutions. The reaction solutions were cooled to -78°C and 1.4 equiv. of benzoyl chloride were added to these solutions. The solutions were warmed to room temperature, and then the solvent was removed at reduced pressure. The reaction residues were extracted with toluene, and these extracts were chromatographed on alumina. Complex **10** was isolated as a red oil from an ether/hexane (1/4) eluate in 8% yield, and complex **11** was isolated as a red oil from an ether/hexane (3/7) eluate in 11% yield. Detailed characterization data are provided below.

Complex 10. IR(pentane) $\nu(\text{CO})$ 1965, $\nu(\text{ester})$ 1723 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.62 (d, 1, CH_2 anti-H, J 2.4 Hz), 1.20 (s, 3, CH_3 allyl terminus), 2.17 (s, 3, CH_3), 2.66 (d, 1, CH_2 syn-H, J 2.4 Hz), 4.43 (s, 5, C_5H_5), 7.23–8.27 (m, 5, C_6H_5); exact mass 338.0616 $\text{C}_{18}\text{H}_{15}\text{O}_3\text{Fe}$ calcd.: 338.0605).

Complex II. IR(hexane) $\nu(\text{CO})$ 1977, $\nu(\text{ester})$ 1740 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.00 (d, 1, CH_2 *anti*-H, J 4.8 Hz), 1.28 (s, 3, CH_3 allyl terminus), 3.19 (d, 1, CH_2 *syn*-H, J 4.8 Hz), 3.66 (s, 3, CH_3O), 4.47 (s, 5, C_5H_5), 7.40, 7.82, 7.91 (m, 5, C_6H_5).

Acknowledgments

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References

- 1 (a) C.M. Lukehart and K. Srinivasan, *J. Am. Chem. Soc.*, 103 (1981) 4166; (b) P.G. Lenhart, C.M. Lukehart and K. Srinivasan, *J. Am. Chem. Soc.*, 106 (1984) 124; (c) C.M. Lukehart and K. Srinivasan, *Organometallics*, 2 (1983) 1640; (d) C.M. Lukehart and W.L. Magnuson, *J. Am. Chem. Soc.*, 106 (1984) 1333.
- 2 L.C. Hall, C.M. Lukehart and R. Srinivasan, *Organometallics*, 4 (1985) 2071.
- 3 C.M. Lukehart and K. Srinivasan, *Organometallics*, 1 (1982) 1247.
- 4 K. Brinkman and P. Helquist, *Tetrahedron Lett.*, (1985) 2845.
- 5 M. Akita and A. Kondoh, *J. Organomet. Chem.*, 299 (1986) 369. For related iron enolate preparations see ref. 6.
- 6 (a) N. Aktogu, H. Felkin and S.G. Davies, *J. Chem. Soc., Chem. Commun.*, (1982) 1303; (b) N. Aktogu, H. Felkin, G.J. Baird, S.G. Davies and O. Watts, *J. Organomet. Chem.*, 262 (1984) 49; (c) L.S. Liebeskind and M.E. Welker, *Organometallics*, 2 (1983) 194; (d) L.S. Liebeskind, M.E. Welker and V. Goedken, *J. Am. Chem. Soc.*, 106 (1984) 441.
- 7 In a control experiment, one-half of the solution containing anion **5** was quenched with MeI and the expected propionyl product was isolated in 75% yield after chromatography on alumina.
- 8 (a) F. L'Eplattenier, *Inorg. Chem.*, 8 (1969) 965; (b) D. Drew, M.Y. Darenbourg and D.J. Darenbourg, *J. Organomet. Chem.*, 85 (1975) 73; (c) D.T. Hobbs and C.M. Lukehart, *J. Am. Chem. Soc.*, 99 (1977) 8357; (d) D.T. Hobbs and C.M. Lukehart, *Inorg. Chem.*, 18 (1979) 1297; (e) D.T. Hobbs and C.M. Lukehart, *Inorg. Chem.*, 19 (1980) 1811.
- 9 K.A.M. Kremer, G.-H. Kuo, E.J. O'Conner, P. Helquist and R.C. Kerber, *J. Am. Chem. Soc.*, 104 (1982) 6119.
- 10 C.P. Casey, W.H. Miles, H. Tukada and J.M. O'Conner, *J. Am. Chem. Soc.*, 104 (1982) 3761.
- 11 C.P. Casey, H. Tukada and W.H. Miles, *Organometallics*, 1 (1982) 1083.
- 12 The reaction of **8** with MeLi afforded a small amount of ferrocene, a large amount of $[\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ which is a decomposition product of the ferrocenolate anion [5], and a trace amount of unreacted **8** in addition to **10** as products after acylation and chromatography on alumina. The reaction of **9** with MeLi gave a reaction solution containing more than one compound as evidenced by the number of carbonyl stretching bands in the IR spectrum of this solution.
- 13 For example, $(\eta\text{-C}_5\text{H}_5)(\text{Ph}_3\text{P})(\text{OC})\text{FeC}(\text{OEt})=\text{CH}_2$ [14] does not react similarly with MeLi as determined by monitoring the reaction solution by IR spectroscopy and by recovering this unreacted alkenyl complex in 74% yield.
- 14 (a) A. Davison and D.L. Reger, *J. Am. Chem. Soc.*, 94 (1972) 9237; (b) G. Grottsch and W. Malisch, *J. Organomet. Chem.*, 246 (1983) C42.
- 15 J.H. Davis, Jr., P.G. Lenhart, C.M. Lukehart and L.A. Sacksteder, *Acta Cryst.*, in press.