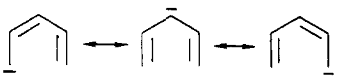
together with energy differences ΔE and MO coefficients c_z^2, c_{xz}, and c_{yz} from INDO calculations[17b] lead to the estimates $g_1 = 2.085$, $g_2 = 2.074$, and $g_3 = 2.0023$, if for the spin-orbit coupling constant somewhat intuitively the value of $\lambda[Fe(I)] = 356\ cm^{-1}$ is adopted.[19] While quantitative agreement is not to be expected for this crude treatment,[20] there is reasonable accord in that one g value is predicted to be close to the free spin value, while the other two are predicted to be substantially larger. In addition, this treatment illustrates the sources of the widely divergent ESR properties of closed and open ferrocenes. In particular, the totally different orbital compositions and energetic sequences for the open ferrocene MO's, a consequence of lower molecular symmetry, lead to orbitally nondegenerate ^2A ground states for the open cations $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$. Furthermore, the more extensive metal-ligand mixing in the open ferrocenes reduces the impact of spin-orbital coupling on $g_{1,2,3}$. Ironically, ESR spectra of the open ferricinium ions bear more resemblance to octahedral complexes of low-spin $Fe^{3+}(d^5)$[21] than to closed ferricinium species, thereby justifying a description of the open ferrocenes in terms of two eclipsed pentadienyl ligands which provide a distorted octahedral ligand field on iron(II) by means of the charged centers at $C_{1,3,5}$. Further experimental and theoretical studies on these and related molecules are in progress.



Acknowledgment. We are grateful to Professor Rolf Gleiter for providing results of INDO calculations on the open ferrocene cations. This work was supported by Deutsche Forschungsgemeinschaft (Grant El 62/4-2 to C.E.) and by grants from the National Science Foundation (CHE-8120683 and CHE-8419271 to R.D.E.) and from the donors of the Petroleum Research Fund, administered by the American Chemical Society (to R.D.E.).

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(19) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* 1970, *13*, 135.

(20) As calculations on open-shell complexes such as the "open ferrocene" radical cations are much more difficult than for similar diamagnetic species, the calculations were simplified by retaining for the cations the same orbital compositions as were found for the "open ferrocenes". While this treatment should lead to fairly reliable orbital energies and to a correct prediction regarding the localization of the radical character (in this case, metal rather than ligand), the actual values of the various coefficients (c_{xz}, c_{yz}, etc.) will change somewhat.[17b] Hence, a more involved theoretical calculation will need to be attempted if more quantitative agreement is to be achieved. We thank Professor Gleiter for providing the relevant information for the radical cations, and for permission to quote his results.

(21) Examples include: (a) $[Fe^{III}(S_2C_2(CN)_2)_3]^{3-}$ $g_1 = 2.225$, $g_2 = 2.114$, and $g_3 = 1.986$: Cotton, S. A.; Gibson, J. F. *J. Chem. Soc., Chem. Commun.* 1968, 883. (b) $[Fe^{III}(CH_3)_2C_3S_2)_3]$ $g_1 = 2.14$, $g_2 = 2.09$, and $g_3 = 2.01$; Knauer, K.; Hemmerich, P.; van Voorst, J. D. W. *Angew. Chem.* 1967, *79*, 273; *Angew. Chem., Int. Ed. Engl.* 1967, *6*, 262.

Reactions of Coordinated Molecules. 46. Formation of Pivaloin by the Reductive Coupling of Two Pivaloyl Ligands

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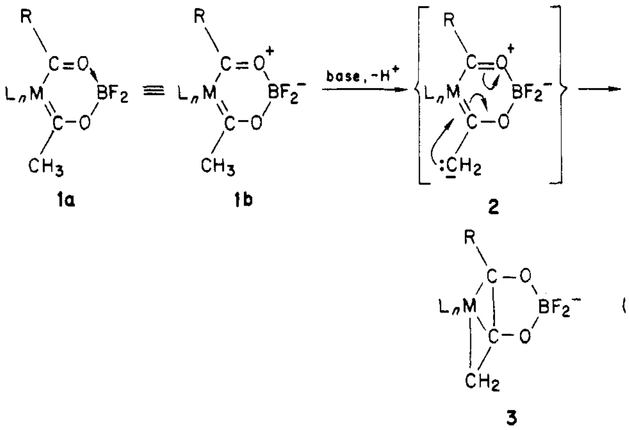
Summary: Chemical or electrochemical reduction of the complex $[(\eta\text{-}C_5H_5)(OC)Fe(Me_3C\overline{CO})_2]BF_2$ followed by removal of the Fe and BF_2 moieties gives pivaloin in yields ranging from 26 to 58%. A formal mechanism for this reductive coupling of two adjacent acyl carbon donor atoms is proposed.

We have reported previously that the α-enolate anions of (metalla-β-diketonato)BF_2 complexes,[1,2] metalla-β-diketonate anions,[3] and (triacylrhenato)BX complexes[4] undergo reductive coupling of two acyl carbon donor atoms to give η^3-allyl complexes. One representation of this C-C coupling reaction for a (metalla-β-diketonato)BF_2 complex is shown in eq 1. Deprotonation of the methyl substituent of **1b** generates the α-enolate anion **2** which apparently rearranges spontaneously to give the η^3-allyl complex **3**. An isolobal analysis of this type of rearrangement has been published earlier.[5]

Within the formal representation shown in eq 1, the crucial C-C bond coupling is initiated by formal reduction at M by the lone pair of electrons on the exo-methylene carbon atom. The metal undergoes a concomitant formal oxidation when the C-C bond is formed. The electron count of M in going from **1b** to **3**, therefore, remains the same.



(1)

We have examined the intriguing possibility that C-C coupling in these molecules might be initiated by *external* reduction of the metal atom rather than by an intramolecular electronic rearrangement as shown in eq 1. We now report that either chemical or electrochemical reduction of the complex $[(\eta\text{-}C_5H_5)(OC)Fe(Me_3C\overline{CO})_2]BF_2$,[6] **4**, occurs to give C-C coupling. This coupling is verified by the isolation of pivaloin (the organic coupling product).

When 0.8-4.1-g samples of **4** are treated with an excess of chemical reducing agent (Na/Hg in THF, or sodium naphthalenide, NaNp, in THF, or sodium benzophenone ketyl, NaBZK, in dioxane) for 2 h at 25 °C, the reaction solution changes color from red-orange to black. The reaction residue then is refluxed with 50 mL of 0.5 M NaOH for 2 h to remove the BF_2 and Fe moieties. Following neutralization with aqueous HCl, the neutral reaction products are extracted into methylene chloride. Pivaloin is isolated by sublimation from the extraction residue or

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(1) Lukehart, C. M.; Srinivasan, K. *J. Am. Chem. Soc.* 1981, *103*, 4166-4170.

(2) Lenhert, P. G.; Lukehart, C. M.; Srinivasan, K. *J. Am. Chem. Soc.* 1984, *106*, 124-130.

(3) Lukehart, C. M.; Srinivasan, K. *Organometallics* 1983, *2*, 1640-1642.

(4) Lukehart, C. M.; Magnuson, W. L. *J. Am. Chem. Soc.* 1984, *106*, 1333-1335.

(5) Lukehart, C. M.; Srinivasan, K. *Organometallics* 1982, *1*, 1247-1249.

(6) The preparation and X-ray structure of complex 4 is reported elsewhere; see: Afzal, D.; Lenhert, P. G.; Lukehart, C. M.; Srinivasan, R. *Inorg. Chem.*, submitted for publication.

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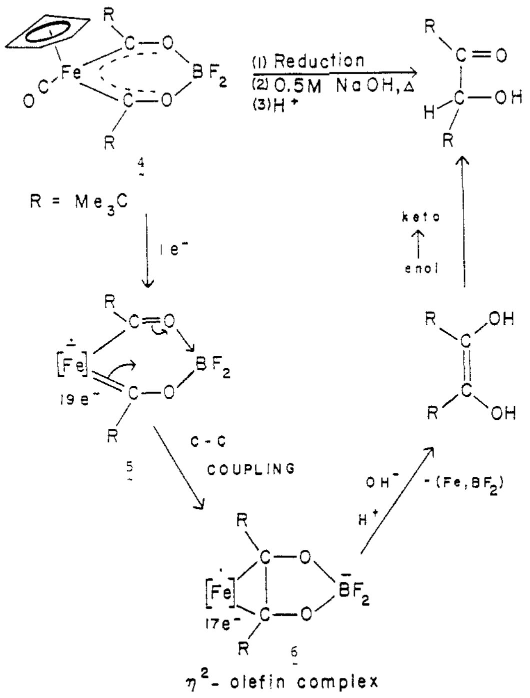
Scheme I. A Representation of Interligand C–C Coupling by External Reduction



[Fe] = (η-C_5H_5)(OC)Fe

is characterized as a component of the extraction residue.

In the Na/Hg reductions, *analytically pure* pivaloin is obtained by sublimation (under different conditions of temperature and pressure a small amount of pure ferrocene is obtained). With Na/Hg to 4 molar ratios of 3:1 and 5:1, the isolated yields of pivaloin are 28% and 44%, respectively. In the sodium naphthalenide reductions, the final sublimate contained pivaloin, naphthalene, and a trace amount of ferrocene. Yields of pivaloin (determined by ^{1}H NMR) for NaNp to 4 molar ratios of 3:1, 5:1, and 10:1 are 31%, 45%, and 58%, respectively. In a NaBZK reduction of 4 at a 5:1 molar ratio of reactants, respectively, the yield of pivaloin was 56% (determined by ^{1}H NMR of the extraction residue).

In a blank reaction, in which complex 4 was subjected to all of the reaction and workup procedures except for the chemical reduction step at room temperature, pivaloin was *not* formed and complex 4 was recovered as a crystalline solid in 93% yield. Therefore, the pivaloin is presumably formed from a reduction process and not via a reductive elimination or thermal degradation reaction.

When 0.8 g of 4 in THF is reduced electrochemically[7] for 4 h at 25 °C and the resulting black cathodic solution hydrolyzed as stated above, *analytically pure* pivaloin is isolated by sublimation. Pivaloin is obtained in 26% yield based on one C–C coupling per electron consumed.

No attempt was made to optimize the yield of pivaloin in either the chemical or electrochemical reductions.

Complex 4 was chosen to test the feasibility of effecting C–C coupling via external reduction because the lack of enolizable hydrogen atoms in 4 would preclude interligand C–C coupling by the mechanism shown in eq 1. On the basis of the formalism discussed above, we represent this reductive coupling of the two acyl carbon donor atoms of 4 as shown in Scheme I. One-electron reduction of 4 would give a formal 19-electron complex 5. As shown in eq 1, electronic rearrangement of this reduced species would give the C–C coupled product 6 (which is now a 17-electron η^2-alkene complex). Base hydrolysis at reflux would dissociate the alkene ligand from the Fe atom and remove the BF_2 moiety.[8] Enol–keto tautomerization of the alkene after neutralization would give free pivaloin. The 17-electron Fe moiety might be further reduced by one electron to return to its original electron count, thereby making the overall transformation a two-electron reduction. Other applications of this unusual coupling of "acyl" carbon donor atoms are being pursued to determine the generality of this reaction and to synthesize a variety of organic molecules from organometallic reagents.

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(7) The electrochemical reduction was conducted in an "H" cell with a glass frit separating the anodic and cathodic compartments. A pool of Hg (agitated by a gaseous N_2 flow) constituted the cathode while a Ag electrode in the presence of (n-butyl)$_4N^+Cl^-$ constituted the anode. The supporting electrolyte was (n-butyl)$_4N^+ClO_4^-$. A Heathkit Regulated Power Supply Model IP-32 was used as a potential source (400 V). Integration of a plot of current vs. time gave the number of coulombs of current passed through the electrolyte solution. No correction for solvent or electrolyte reduction was applied. A preliminary cyclic voltammogram revealed an irreversible reduction of 4 at −0.83 V (vs. the Ag/AgCl electrode) in CH_2Cl_2 solution.

(8) For other examples of base hydrolysis of a BF_2 moiety from oxygen donor groups see: Hanessian, S. "27th National Organic Chemistry Symposium", June 21–25, 1981 (abstracts of papers).