Scheme I

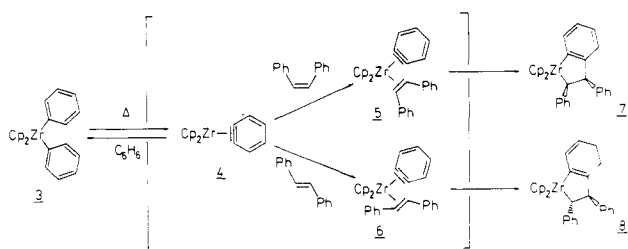**Scheme II**

Diphenylzirconocene (3) in benzene solution is a suitable starting material for the generation of the elusive (η^2-dehydrobenzene)dicyclopentadienylzirconium(II) (4) under sufficiently mild conditions.[4] We have recently been able to show that a variety of olefins can compete successfully with the aromatic solvent as scavengers and can trap intermediate 4 from this thermal equilibrium to form metallaindans.[5] Thermolysis of 1.8 g (4.8 mmol) of 3 in 20 mL of benzene for 18 h at 80 °C in the presence of a tenfold excess of *cis*-stilbene yielded a single organometallic product (7) which was isolated in 31% yield after recrystallization from *n*-hexane. In an argon atmosphere the orange-red crystalline material is stable to about 160 °C; above that temperature it rapidly decomposes before melting. The compound analyzes correctly for a 1:1 adduct of (η^2-dehydrobenzene)dicyclopentadienylzirconium(II) (4) with the added olefin [Calcd for $C_{30}H_{26}Zr$: C, 75.42; H, 5.49. Found: C, 75.33; H, 5.52. MS: *m/e* 476 $(M^+)^6$]. Treatment of a deep red benzene solution of 7 with HCl resulted in an almost quantitative yield of zirconocene dichloride and 1,1,2-triphenylethane.

The ^{13}C NMR spectrum (62.89 MHz, C_6D_6) of 7 shows carbon atoms of three chemically different aromatic frameworks[7] in addition to two nonidentical η^5-cyclopentadienylligands at δ_C 110.9 and 109.7. The presence of a metallacyclic σ structure becomes evident from resonances due to two benzylic carbons at δ_C 70.5 and 58.8 exhibiting coupling constants $^1J_{CH}$ = 126.9 and 122.3 Hz, respectively, characteristic for a saturated alkyl moiety in a five-membered metallacycle.[8] In the ^1H NMR spectrum (250 MHz, C_6D_6) 7 displays two Cp resonances at δ 5.63 and 5.00. Benzylic hydrogens appear as a well-separated AB system at δ 5.72 (ArCHPh) and 3.30 (ZrCHPh). An observed AB coupling constant $^3J_{HH}$ = 7.1 Hz does not by itself allow a clear distinction between a cis and trans arrangement of phenyl substituents at the five-membered ring system.[9] Tentatively, we assign a cis structure to this zirconocene complex 7 obtained from the reaction of in-

termediate 4 with added scavenger *cis*-stilbene.

We could not detect any trace of 7 upon thermolysis of 3 under similar conditions using a fivefold excess of *trans*-stilbene. A different organometallic compound 8 was formed instead which appears to be the configurational isomer of 7. This we deduce from the formation of the identical organic product, 1,1,2-triphenylethane, upon hydrolysis and a distinctly different although in general quite similar appearance of the ^1H NMR spectrum, exhibiting features at δ 8.20–6.80 (m, 14 H, aromatic), 5.83 and 5.10 (s, 5 H each, Cp), 5.00 and 3.95 (AB system, 2 H, CHPh, $^3J_{HH}$ = 10.5 Hz). Independent crossover experiments revealed that the formation of about 1% of the cis isomer accompanying *trans*-2,3-diphenyl-1-zirconaindan 8 would have been detected by the method of analysis applied (FT ^1H NMR, 250 MHz). However, in a direct comparison of crude reaction mixtures obtained from thermolyses of 3 and the respective stilbene isomers in C_6D_6 solvent in sealed NMR tubes, we have not been able to observe any formation of the "wrong" isomer of the particular metallacyclic reaction product.

Our observation of a >99% selective, stereospecific formation of phenyl-substituted five-membered metallacycles 7 and 8 provides a strong indication for a concerted course of the ring closure reaction of intermediate bis-(olefin)zirconocene complexes 5 and 6. This example, therefore, contrasts favorably with the reaction of (η^2-benzophenon)zirconocene with dimethyl fumarate and maleate, the latter forming a five-membered metallacycle with loss of stereochemistry as expected for a stepwise reaction mechanism.[3]

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(5) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659.

(6) A *m/e* value corresponding to naturally most abundant isotopes, i.e., ^{90}Zr (51.5%).

(7) NMR: δ 179.3 (s), 164.3 (s), 146.8 (s), 141.5 (s), 140.9 (d), 132.8 (d), 131.1 (d), 127.0 (d), 126.4 (d), 124.7 (d), 124.0 (d), 119.2 (d), two additional carbon resonances cannot be located accurately due to solvent signals.

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Reactions of Coordinated Molecules. 33. Conversion of a Metalla sp²-CH Analogue to a Metalla sp³-CH Analogue: A Comment about Structural and Electronic Formalism
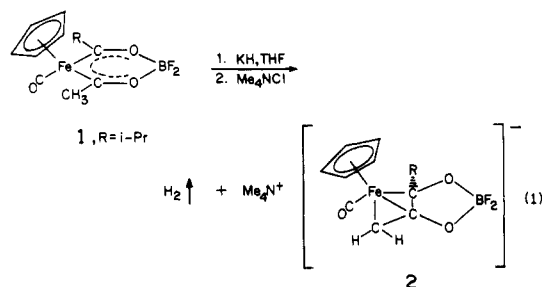
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Received May 18, 1982

Summary: The conversion of α-enolate anions of metalla-β-diketonate complexes to η^3-allylic complexes is analyzed by using an isolobal approach. These reactions are described as the conversion of a metalla sp²-CH moiety into a metalla sp³-CH moiety.

We reported recently an intramolecular, interligand C–C bond formation reaction which occurred between adjacent acylic ligands, as shown in eq 1.[1] When the (ferra-β-di-

ketonato)difluoroboron complex 1 is treated with KH, the methyl substituent of the ferra chelate ring is deprotonated, and complex 2 forms in essentially quantitative yield with concomitant elimination of hydrogen. Complex 2 is an η^3-allylic complex (written in an all-σ representation) as determined by X-ray crystallography.

We rationalized *how* the α-enolate anion of 1 rearranges to 2 by using a single set of Lewis structures, as shown in eq 2.[1] The initial enolate anion of 1 is represented as 3. Resonance 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 iron atom. Both of these ligand types are known to form stable complexes with cyclopentadienyliron carbonyl moieties. The conversion of 4 to the observed product 5 occurs as a metal-mediated,


3, M=(η^5-C$_5$H$_5$)(OC)Fe

R=i-Pr

(2)

5
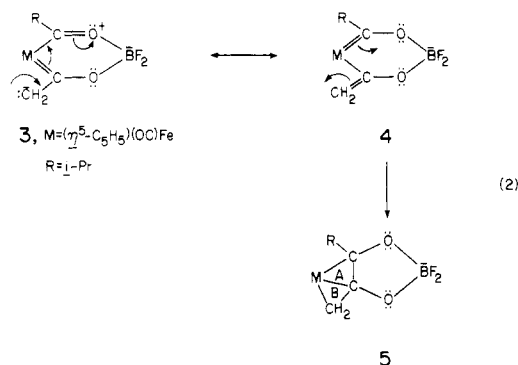
transannular C–C bond formation. The formal oxidation state of M does not change in going from 1 to 2 (or 5) nor has a reductive-elimination reaction occurred.

Two observations regarding reaction 1 are the following: (1) the reaction as shown, is a general one as demonstrated by effecting a clean 1 to 2 conversion when the *cis*-(OC)$_4$Mn and *cis*-(OC)$_4$Re analogues of 1 are used and (2) the deprotonation of the methyl substituent can be accomplished with such weak bases, as tetramethylpiperidine or even pyridine.[2] The first observation is expected since these metalla moieties are isovalent to the C$_5$H$_5$(OC)Fe moiety. However, the second observation is somewhat surprising, since the methyl substituent of 1 was not expected to be nearly as acidic as a methyl substituent on a Fischer-carbenoid ligand.[3] Since no intermediates are observed, the formation of anion 3 (or 4) appears to be direct and very facile, and the subsequent rearrangement to 5 is, apparently, very rapid. The question of *why* this final rearrangement is so facile is addressed in this communication.

A considerable amount of work has demonstrated that the metalla moieties, *cis*-(OC)$_4$Mn, *cis*-(OC)$_4$Re, and C$_5$-H$_5$(OC)Fe, in metalla-β-diketonate molecules can be considered as being isovalent to an sp^2-methine group.[4] Although theoretical calculations of metalla-β-diketonate complexes have not been performed, we propose that the metalla moieties *in these molecules* are isolobal[5] to an sp^2-CH group, as shown in 6 and 7 for the *cis*-(OC)$_4$Mn fragment.

A neutral sp^2-CH fragment, 6, is a 5-electron moiety

6   7
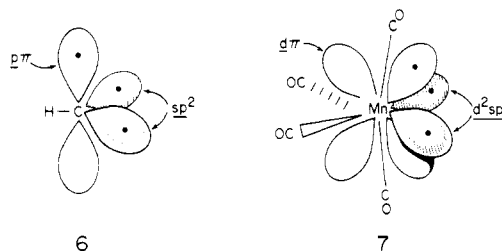
having two sp^2-σ orbitals and one pπ orbital each containing one unpaired electron formally. A neutral *cis*-(OC)$_4$Mn fragment is a d^7 M(CO)$_4$, 15-electron moiety which has two d^{2}sp^3-σ orbitals and one dπ orbital (d$_{yz}$) each containing one unpaired electron formally.[6] When the moieties 6 and 7 form a double bond to a two-electron substituent and a single bond to a one-electron substituent, the central C and Mn atoms became coordinately saturated.

Hoffmann's elegant work on the fragment orbitals of transition-metal carbonyl moieties[7] indicates that d^7 M-(CO)$_4$ moieties have an optimum C_{2v} geometry with a slight tetrahedral distortion. The X-ray structures of [*cis*-(OC)$_4$Mn(CH$_3$CO)$_2$]$_3$Al and [*cis*-(OC)$_4$Re(CH$_3$CO)$_2$]H reveal such a distortion of the axial CO ligands, as shown in 7.[8,9]

When this isolobal formalism is applied to the rearrangement of 4 to 5, an interesting analogy appears evident. *In structure 4, if the metalla moeity, M, is presumed to be isolobal to an sp^2-CH group, then in structure 5, it is now isolobal to an sp^3-CH group.* Structure 4 is a *trans*-2-metalla-1,3-butadiene, and 5 is *formally* a 1-metallabicyclo[1.1.0]butane.

This *formalism* implies an analogous relationship between the very facile conversion of 4 to 5, and the well-known, thermally allowed concerted [$_\sigma 2_a + {}_\sigma 2_s$] pericyclic ring opening of bicyclo[1.1.0]butanes to give *trans*-1,3-butadienes, as shown in eq 3 for a classic example.[10] The
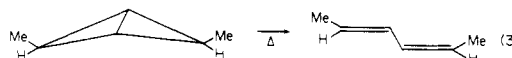
4 to 5 conversion is actually the *reverse* of this organic rearrangement, presumably because the η^3-allylic complex, 5, lacks ring strain and is more stable than 4. Notice, however, that the disrotatory closure of ring A and the conrotatory closure of ring B converts 4 to 5 by a thermally allowed mechanism.[11]

The analogy between the organometallic and organic conversions shown in eq 2 and 3, respectively, might help to explain *why* the α-enolate anions of (metalla-β-diketonato)difluoroboron complexes rearrange to η^3-allylic

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(11) Experimental verification of the thermally allowed [$_\sigma 2_a + {}_\sigma 2_s$] ring closure mechanism which converts 4 into 5 would be difficult. The BF$_2$ chelate ring ensures a disrotatory closure of ring A. The determinaion of conrotatory or disrotatory closure of ring B by introducing different substituents on the CH$_2$ group is thwarted by the transient stability of species like 4 and by the inability to selectively enolize the alkyl precursor to give an analogue to 4 as only one geometrical isomer. In the absence of a chelate ring formed by BF$_2$ or a coordinating metal ion, geometrical isomerization of the carbenoid acylmetalate ligand would preclude an unambiguous stereochemical interpretation of the closure of ring A. However, we intend to demonstrate that species like 4 can be prepared independently by treating (η^5-C$_5$H$_5$)Fe(CO)$_2$(η^1-vinyl) complexes with alkyllithium reagents. The resulting complexes should undergo interligand C–C bond formation to afford analogues to 5.

complexes so facilely. We would like to suggest that similar analogies might be useful in explaining otherwise unique or esoteric reactions of organometallic compounds. By using this formalism, one can predict several related reactions of various classes of metalla-β-diketonate complexes or other types of complexes which contain some degree of metal–carbon multiple bonding to adjacent ligands. A general *formal* representation of η^n ligands in an all-σ description rather than as a π-delocalized description may lead to a better understanding of how such ligands are formed, particularly when 18-electron metal moieties are involved.

Another interesting observation is evident from the molecular structure of anion **5**, where M is *cis*-(OC)$_4$Mn.[2] The Mn(CO)$_4$ moiety now has a slight square-pyramidal distortion where the axial OC–Mn–CO angle of 168° is now bent *away from* the η^3-allylic ligand. This gives a θ angle[7] and 96°, as shown in **8**. Although this angle does not have
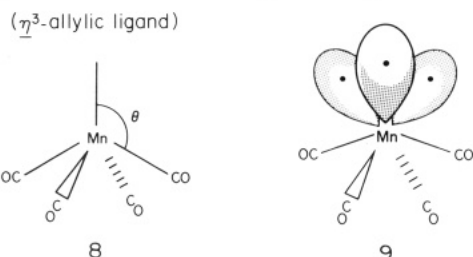
the preferred θ value of ca. 105°,[7] the distortion is in the correct direction for the Mn(CO)$_4$ moiety to attain a threefold set of three acceptor fragment orbitals.[7] As shown in **9**, this neutral, d^7 Mn(CO)$_4$ moiety is then quite analogous to a neutral sp^3-methine radical.

Registry No. 1, 73426-86-5; **2**, 82621-98-5.

Grignard-Type Carbonyl Addition of Allyl Unit with MnCl$_2$–LiAlH$_4$ Reagent

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Summary: The manganese reagent derived from equimolar amounts of MnCl$_2$ and LiAlH$_4$ is found to attain carbonyl addition of allylic bromides with characteristic stereoselectivities.

Manganese is one of most promising marine metallic resources for the future.[1] Because of the salient features of manganese species of high oxidation state,[2] the metal has been widely used for oxidation of organic compounds. The lower valent manganese species, on the other hand, remained unutilized possibly due to the instability of Mn(I)

species[3] and inactivity of metallic Mn.[4]   Herewith we report that manganese(II) chloride is readily reduced with lithium aluminum hydride and the resulting manganese reagent is capable of Grignard-type reaction (eq 1).

$$MnCl_2 + LiAlH_4 \xrightarrow[\text{THF}]{0\ °C} \text{“Mn(0)”} + H_2 \qquad (1)$$
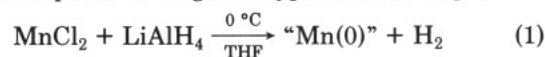
Anhydrous manganese(II) chloride[5] suspended in tetrahydrofuran (THF) was reduced with an equimolar amount of lithium aluminum hydride at 0 °C. The initial pink color of the reaction mixture turned black. Although details of the resulting species are not at hand, a brief note by Rice,[6] who records that the manganese(II) ion is reduced to Mn(0) by aluminum hydride or lithium aluminum hydride, is informative. Thus, we call it “Mn(0)” reagent.[7] When the reagent was treated with allyl bromide and then with aldehydes or ketones, the allyl unit was effectively added to the carbonyl groups of these compounds (eq 2). Our results are summarized in Table I.
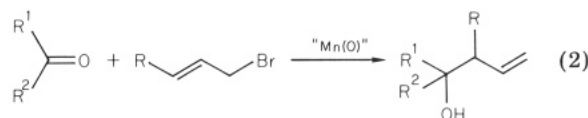
Characteristic features of the allyl addition by the “Mn(0)” reagent are as follows. (1) Both aldehydes and ketones give corresponding adducts in good yields. (2) α,β-Unsaturated aldehydes and ketones undergo 1,2 addition (runs 10, 11, 12, and 17). (3) With crotyl bromide carbonyl addition takes place at the γ-position exclusively, and the aldehyde adducts are in general erythro–threo mixture (runs 13, 14, 15, 16, and 17).[8] (4) α-Erythro induction[9,11] (run 7) was moderate. (5) Addition to 4-*tert*-butylcyclohexanone occurs predominantly from the equatorial direction. Particularly remarkably high selectivity is observed for crotyl addition, and hereby the axial alcohol[12] is produced almost exclusively in sharp contrast to the corresponding Grignard reagent.[12,13] (6) Reaction of prenyl bromide was less effective than allyl or crotyl

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(3) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189. Some Mn(–I) complexes stabilized by carbonyls have found synthetic applications recently. For example: Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417. See also: Marsi, M.; Gladysz, J. A. *Tetrahedron Lett.* **1982**, *23*, 631 and references cited therein.

(4) Reduction by means of manganese powder: Battaglia, L. P.; Nardelli, M.; Pelizzi, C.; Predieri, G. *J. Organomet. Chem.* **1981**, *209*, C7–C9. Synthetic application of reactive manganese metal: Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *Tetrahedron Lett.* **1981**, *21*, 3861–3865.

(5) Dehydration of commercially available manganese(II) chloride–water (1/4) was effected with thionyl chloride (cf. Pray, A. R. *Inorg. Synth.* **1954**, *5*, 153–156).

(6) Rice, M. J. *Nucl. Sci. Abstr.* **1956**, *10*, No. 1641. Gmelin, L. “Handbuch der anorganischen Chemie, Mn, Teil C5, Halogenverbindungen”; Verlag Chemie: Weinheim, 1978; p29.

(7) The reagent generated from 1:1 mixture of MnCl$_2$ and LiAlH$_4$ gave the best results in the reaction. When smaller or larger amounts of LiAlH$_4$ were used, the yields of the adducts were lower. For example, the reagent generated from MnCl$_2$–LiAlH$_4$ (2:1) gave the adduct of run 1 (Table I) in 75% yield. When the reagent from MnCl$_2$–LiAlH$_4$ (4:1) was used for the same reaciton, 1,2-diphenylethane-1,2-diol was produced in 35% yield. In the case of MnCl$_2$–LiAlH$_4$ (1:2), benzyl alcohol was the major product.

(8) The results surprisingly contrast with those of chromium (threo selective)[9] and tin (erythro selective).[10]

(9) Hiyama, T.; Kimura, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *21*, 1037–1040. Hiyama, T.; Okude, Y.; Kimura, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 561–568. See also: Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1981**, *22*, 2895–2899. Sato, F.; Iida, K.; Iijima, S.; Moriya, H.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1140–1141.

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(11) Buse, C. T.; Heathcock, C. H. *Tetrahedron Lett.* **1978**, 1685–1689.

(12) Cherest, M. *Tetrahedron* **1980**, *36*, 1593–1598. Selective equatorial attack is realized by alternative methods. See: ref 9 and Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919–923.

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(2) House, H. O. “Modern Synthetic Reactions”; Benjamin, W. A.: Menlo Park, CA, 1972; pp 257–291.