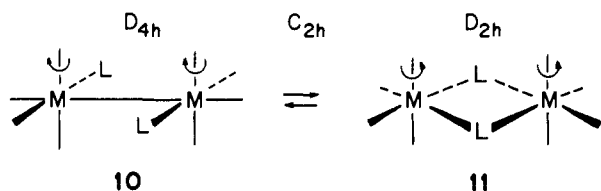


already in the literature for $\text{Mn}_2(\text{CO})_{10}$ ^{6a} and $\text{Re}_2(\text{CO})_{10}$ ^{6b} and is supported by spectroscopic evidence.^{6,7} Behind the high energy of the σ level are two factors: (a) the greater σ , π , and δ splitting in the acceptor-substituted monomer fragment and (b) the greater localization of the orbitals on the metal when the substituents are donors. If the level ordering of $\text{Re}_2(\text{CO})_{10}$ can be extrapolated back to a similarly substituted d^4 - d^4 dimer, as we think it can, then we believe there is no chance of a quadruple bond in a d^4 - d^4 $L_5\text{MML}_5$ dimer with acceptor substituents.

Thus the Vahrenkamp compounds do not open up because there is nothing especially good waiting for them in the unbridged alternative. The Cotton complexes do not go into the bridged double-bonded structure because core steric effects make inaccessible the region where a double bond could exist. Interestingly the concerted conversion of a Cotton complex into a Vahrenkamp type structure, $10 \rightleftharpoons 11$, is a forbidden reaction.



If the steric troubles of the bridged alternative could be relieved, perhaps by bidentate bonding across axial sites, it is conceivable that bridged, double-bonded and unbridged, quadruple-bonded d^4 - d^4 isomers might coexist.⁸

The forbiddenness of the interconversion is specific to a d^4 - d^4 electron count and donor substituents. It is allowed for d^7 - d^7 , an important class of molecules including the well-studied $[\text{CpFe}(\text{CO})_2]_2$.

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Sason Shaik, Roald Hoffmann*⁹

Department of Chemistry, Cornell University
Ithaca, New York 14853

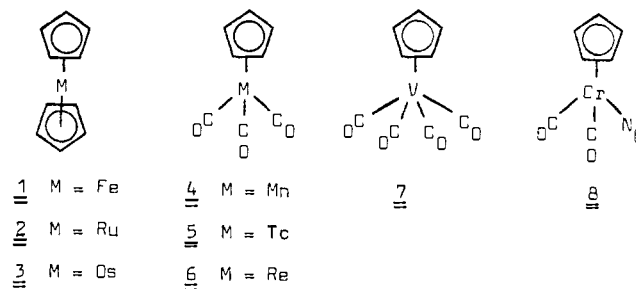
Received September 19, 1979

A New, General Route to Functionally Substituted η^5 -Cyclopentadienyl Metal Compounds

Sir:

The very extensive chemistry associated with bis(η^5 -cyclopentadienyl)iron (ferrocene) (**1**) has been due in large measure to the fact that this remarkable organometallic compound undergoes certain aromatic-type electrophilic substitution reactions,¹ resulting in products which often possess unique chemical and physical properties.² In spite of considerable additional research efforts along these lines, however, only a

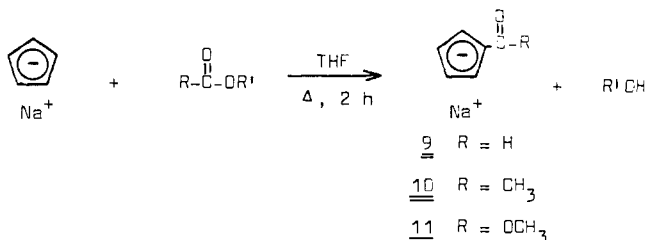
very few other η^5 -cyclopentadienyl metal compounds have ever been found to undergo analogous aromatic-type substitutions. These include the related sandwich compounds bis(η^5 -cyclopentadienyl)ruthenium (ruthenocene, **2**),³ bis(η^5 -cyclopentadienyl)osmium (osmocene, **3**),³ (η^5 -cyclopentadienyl)tricarboxylmanganese (cymantrene, **4**)⁴ and its technetium (**5**)⁵ and rhenium (**6**)^{5,6} analogues, (η^5 -cyclopentadienyl)tetracarboxylvanadium (**7**),⁷ and (η^5 -cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene, **8**).^{8,9} The failure of most η^5 -cyclopentadienyl metal compounds to undergo ring substitution may be ascribed either to their inherent lack of aromatic character or to more facile reaction pathways under the reaction conditions involved. In any event, the inability of most η^5 -cyclopentadienyl metal compounds to form functionally substituted derivatives by ring-substitution routes has severely impeded the development of η^5 -cyclopentadienyl metal chemistry of the type shown by compounds **1**-**8**.



tadienyl)osmium (osmocene, **3**),³ (η^5 -cyclopentadienyl)tricarboxylmanganese (cymantrene, **4**)⁴ and its technetium (**5**)⁵ and rhenium (**6**)^{5,6} analogues, (η^5 -cyclopentadienyl)tetracarboxylvanadium (**7**),⁷ and (η^5 -cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene, **8**).^{8,9} The failure of most η^5 -cyclopentadienyl metal compounds to undergo ring substitution may be ascribed either to their inherent lack of aromatic character or to more facile reaction pathways under the reaction conditions involved. In any event, the inability of most η^5 -cyclopentadienyl metal compounds to form functionally substituted derivatives by ring-substitution routes has severely impeded the development of η^5 -cyclopentadienyl metal chemistry of the type shown by compounds **1**-**8**.

We now report the development of a new and apparently general route for the formation of a wide variety of functionally substituted η^5 -cyclopentadienyl metal compounds. The method provides a convenient means of introducing functional substituents on η^5 -cyclopentadienyl rings in systems which are incapable of undergoing electrophilic aromatic substitution, and as such should greatly stimulate research in this branch of chemistry.

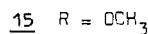
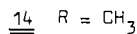
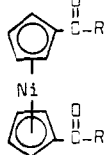
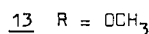
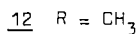
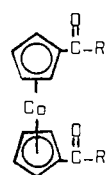
We find that the reactions of cyclopentadienylsodium with either ethyl formate, methyl acetate, or dimethyl carbonate in refluxing tetrahydrofuran solution for 2 h produces 60-90% yields of the respective compounds formyl- (**9**), acetyl- (**10**), or methoxycarbonylcyclopentadienylsodium (**11**).¹⁰ The solid



products **9**-**11** are moisture sensitive but are generally stable in air for short periods of time, in contrast to cyclopentadienylsodium itself. The generation of **9**-**11** likely proceeds via intermediate formation of the corresponding 1-substituted cyclopentadienes, the latter being rapidly metalated by the sodium alkoxide produced concurrently in the reaction. The ¹H NMR spectra of **9**-**11**¹¹ are of interest in that resonances for the substituted cyclopentadienyl hydrogens occur as unresolved multiplets rather than as apparent triplets as in the case of most η^5 -cyclopentadienyl transition metal compounds substituted with analogous electron-withdrawing substituents.¹² Additional NMR investigations as well as X-ray diffraction studies on **9**-**11** are underway in order to elucidate the nature of the ring-metal bonding in solution and in the crystal state, respectively.¹³

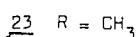
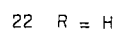
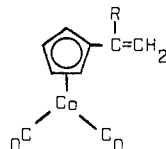
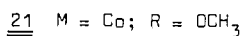
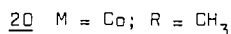
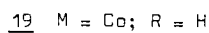
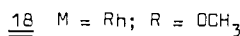
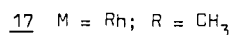
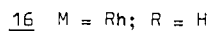
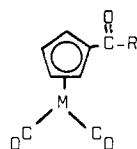
The utility of these organosodium reagents in organometallic chemistry is aptly demonstrated by their reactions with cobalt or nickel salts to form functionally substituted sandwich

compounds of these metals. Thus, reactions between either **10** or **11** with CoCl_2 in THF solution (25 °C) produce 1,1'-bis(η^5 -acetylcyclopentadienyl)cobalt (1,1'-diacetylcobaltocene, **12**) (ν_{CO} 1650 cm^{-1} , $M^+ = m/e$ 273, mp 139–141 °C)

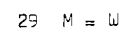
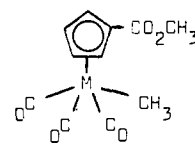
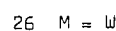
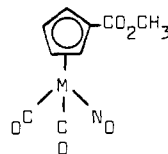


and 1,1'-bis(η^5 -methoxycarbonylcyclopentadienyl)cobalt (1,1'-dicarbomethoxycobaltocene, **13**) (ν_{CO} 1710 cm^{-1} , $M^+ = m/e$ 305, mp 134–136 °C) in yields of 30–40%, respectively, whereas analogous reactions of **10** or **11** with $\text{NiBr}_2 \cdot 2\text{DME}$ in DME solution under similar conditions afford 1,1'-bis(η^5 -acetylcyclopentadienyl)nickel (1,1'-diacetylnickelocene, **14**) (ν_{CO} 1640 cm^{-1} , $M^+ = m/e$ 272, mp 114–115 °C) and 1,1'-bis(η^5 -methoxycarbonylcyclopentadienyl)nickel (1,1'-dicarbomethoxynickelocene, **15**) (ν_{CO} 1710 cm^{-1} , $M^+ = m/e$ 304, mp 115–117 °C), respectively, in yields of 40–45%.^{14,15} In contrast, all attempts to prepare functionally substituted cobaltocenes and nickelocenes by electrophilic substitution techniques have proved to be unsuccessful.^{2a,b,16}

Organosodium reagents **9–11** are also convenient precursors to functionally substituted η^5 -cyclopentadienyldicarbonyl metal derivatives, products which likewise are unavailable through electrophilic substitution reactions of the parent compounds. For example, reactions of **9**, **10**, or **11** with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in THF at 25 °C readily produce the corresponding formyl (**16**), acetyl (**17**), and methoxycarbonyl (**18**) analogues, whereas the respective cobalt counterparts (**19–21**) are available via reactions of **9–11**, with an equimolar mixture of $\text{Co}_2(\text{CO})_8$ and I_2 in THF at 25 °C. These products are ob-

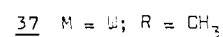
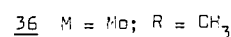
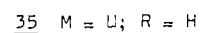
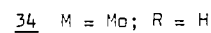
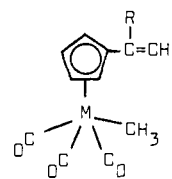
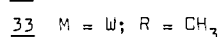
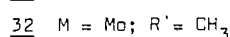
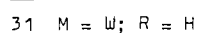
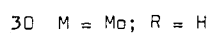
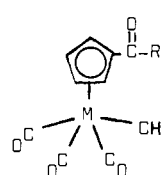


Reactions of **9–11** with group 6b metal hexacarbonyls have led to a wide variety of functionally substituted η^5 -cyclopentadienyl derivatives of these metals. For example, reactions of **11** with $\text{Cr}(\text{CO})_6$ (DMF, reflux), $\text{Mo}(\text{CO})_6$ (THF, reflux), or $\text{W}(\text{CO})_6$ (DME, reflux), followed by acidification with acetic acid and subsequent nitrosylation with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, have afforded the respective methoxycarbonyl derivatives **24** (liquid, 79%), **25** (mp 67–69 °C, 12%), and **26** (mp 89–91 °C, 41%).²¹ The chromium an-



alogue **24** is available less directly via electrophilic substitution of the parent compound ($\eta^5\text{-C}_5\text{H}_5$) $\text{Cr}(\text{CO})_2\text{NO}$;^{9c} however, the present route is far preferable in terms of overall yield and facility. In contrast, all attempts to carry out analogous ring-substitution reactions of ($\eta^5\text{-C}_5\text{H}_5$) $\text{Mo}(\text{CO})_2\text{NO}$ and ($\eta^5\text{-C}_5\text{H}_5$) $\text{W}(\text{CO})_2\text{NO}$ have proven unsuccessful.¹⁶

In a similar manner, treatment of the metal carbonyl anions generated as above with methyl iodide (THF, 25 °C) leads to a new family of functionally substituted η^5 -cyclopentadienyl derivatives of chromium, molybdenum, and tungsten, in which the products also contain a metal-methyl σ bond.²¹ In the methoxycarbonyl series, for example, the relative thermal stabilities of the chromium (**27**) (dec pt >40 °C), molybdenum (**28**) (mp 61–62 °C), and tungsten (**29**) (mp 76–78 °C) derivatives parallel the stabilities found earlier for the parent members ($\eta^5\text{-C}_5\text{H}_5$) $\text{M}(\text{CO})_3\text{CH}_3$ (M = Cr, Mo, W).²² Starting from the metal carbonyl anions derived from **9** or **11** and either $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$, the respective formyl (**30**, **31**) and acetyl (**32**, **33**) analogues are also readily accessible via methylation with methyl iodide.²³ Furthermore, conversions of **30–33** under Wittig conditions as described previously



tained in yields up to 50% as dark red liquids that are distillable under reduced pressure.^{17,18}

The availability of the functionally substituted organorhodium and -cobalt derivatives **16–21** provides valuable new routes to organometallic monomers and polymers of these metals. For example, **19** and **20** are readily converted by means of methylenetriphenylphosphorane (ethyl ether, 25 °C) to the corresponding vinyl (**22**) and isopropenyl (**23**) analogues, respectively.¹⁹ The latter product can also be obtained by reaction of **20** with methylmagnesium iodide followed by dehydration (benzene, *p*-toluenesulfonic acid). Polymerization reactions of these new monomers under free-radical and cationic conditions are in progress and should lead to new types of organometallic polymers with potential catalytic properties.²⁰

lead to an additional series of new vinyl monomers (**34–37**) which appear capable of undergoing cationic and free-radical polymerizations.^{23,24}

The above reaction sequences demonstrate that functionally substituted cyclopentadienylsodium reagents such as **9–11** and related compounds can lead to a wide variety of new products of potential importance to organic, inorganic and polymer chemistry. Functionally substituted analogues of other transition and main group metals also appear feasible.²⁵ Reactions of intermediates such as **24–26** with phosphines, followed by hydrolysis and standard resolution techniques, offer promising routes to new classes of chiral organometallic compounds.²⁴ The availability of new functionally substituted η^5 -cyclopent-

tadienyl derivatives of the transition metals also opens for study many new systems in terms of metal-stabilized carbocations and related species.²⁶ Further investigations along these lines are in progress in our laboratory.

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- (15) Spectral evidence indicates that 1,1'-diformylcobaltocene can likewise be produced in low yields from an analogous reaction between **9** and CoCl₂ in THF solution, although the product has not yet been isolated in pure form.
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- (17) Compounds **13** and **21** have been previously prepared by alternative, although less convenient procedure: Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 1239–1246. ¹H NMR data have also been reported for compounds **16** and **18**: Arthur, M.; Nelson, S. M.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 779.
- (18) Spectral data for **16–23** (¹H NMR, CDCl₃, and IR, CDCl₃, unless otherwise indicated): **16**, δ 5.84 (m, 4 H, C₅H₄), 8.90 ppm (s, 1 H, CHO), and ν_{CO} 2030, 1995, 1675 cm⁻¹; **17**, δ 2.34 (s, 3 H, CH₃), 5.69 (t, 2 H, H_{3,4}), 5.90 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2050, 1990, 1660 cm⁻¹; **18**, δ 3.78 (s, 3 H, CH₃), 5.63 (t, 2 H, H_{3,4}), 5.95 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2035, 1985, 1715 cm⁻¹; **19**, δ 5.40 (s, 4 H, C₅H₄), 9.40 ppm (s, 1 H, CHO), and ν_{CO} 2015, 1980, 1675 cm⁻¹; **20**, δ 2.38 (s, 3 H, CH₃), 5.39 ppm (m, 4 H, C₅H₄), and ν_{CO} 2020, 1960, 1660 cm⁻¹; **21**, δ 3.80 (s, 3 H, CH₃), 5.24 (t, 2 H, H_{3,4}), 5.45 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2020, 1990, 1715 cm⁻¹; **22**, δ 5.10 (t, 2 H, H_{3,4}), 5.25 (t, 2 H, H_{2,5}), 5.2–6.6 ppm (m, 2 H, vinyl), and ν_{CO} 2020, 1960 cm⁻¹; **23** (¹H NMR recorded in C₆D₆), δ 1.74 (s, 3 H, CH₃), 4.55 (t, 2 H, H_{3,4}), 4.84 (t, 2 H, H_{2,5}), 4.8–5.2 ppm (m, 2 H, CH₂), and ν_{CO} 2020, 1960 cm⁻¹.
- (19) Formation of a mixture containing **23** has been reported earlier: Altman, J.; Wilkinson, G. J. *Chem. Soc.* **1964**, 5654.
- (20) (a) Pittman, C. U., Jr. *Organomet. React.* **1977**, *6*, 1–62. (b) Carraher, C. E., Jr.; Sheats, J. E.; Pittman, C. U., Jr. "Organometallic Polymers"; Academic Press: New York, 1978.
- (21) Spectral data for **24–29** (¹H NMR, CDCl₃, and IR, KBr, unless otherwise noted): **24**, δ 3.81 (s, 3 H, CH₃), 5.14 (t, 2 H, H_{3,4}), 5.78 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2030, 1955 cm⁻¹; ν_{CO}, ν_{NO} 1710 cm⁻¹ (IR recorded neat); **25**, δ 3.80 (s, 3 H, CH₃), 5.62 (t, 2 H, H_{3,4}), 6.23 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2025, 1945, 1720 cm⁻¹; ν_{NO} 1665 cm⁻¹; **26**, δ 3.82 (s, 3 H, CH₃), 5.70 (t, 2 H, H_{3,4}), 6.26 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2005, 1930, 1715 cm⁻¹; ν_{NO} 1655 cm⁻¹; **27**, δ 0.82 ppm (s, 3 H, M-CH₃), and ν_{CO} 2030, 1950, 1735 cm⁻¹ (IR recorded in pentane); **28**, δ 0.45 (s, 3 H, M-CH₃), 3.83 (s, 3 H, OCH₃), 5.39 (t, 2 H, H_{3,4}), 5.78 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2010, 1915, 1710 cm⁻¹; **29**, δ 0.47 (s, 3 H, M-CH₃), 3.85 (s, 3 H, OCH₃), 5.49 (t, 2 H, H_{3,4}), 5.83 (t, 2 H, H_{2,5}), and ν_{CO} 2005, 1910, 1710 cm⁻¹.

- (22) (a) Piper, T. S.; Wilkinson, G. J. *Inorg. Nucl. Chem.* **1956**, *3*, 104–124. (b) Alt, H. G. *J. Organomet. Chem.* **1977**, *124*, 167–171.
- (23) Spectral data for **30–37** (¹H NMR, CDCl₃, and IR, KBr, unless otherwise noted): **30**, δ 0.45 (s, 3 H, M-CH₃), 5.52 (t, 2 H, H_{3,4}), 5.72 (t, 2 H, H_{2,5}), 9.58 ppm (s, 1 H, CHO), and ν_{CO} 2020, 1920, 1680 cm⁻¹; **31**, δ 0.47 (s, 3 H, M-CH₃), 5.62 (t, 2 H, H_{3,4}), 5.74 (t, 2 H, H_{2,5}), 9.57 ppm (s, 1 H, CHO), and ν_{CO} 2000, 1915, 1675 cm⁻¹; **32**, δ 0.44 (s, 3 H, M-CH₃), 2.35 (s, 3 H, COCH₃), 5.47 (t, 2 H, H_{3,4}), 5.73 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2020, 1920, 1665 cm⁻¹; **33**, δ 0.45 (s, 3 H, M-CH₃), 2.34 (s, 3 H, COCH₃), 5.52 (t, 2 H, H_{3,4}), 5.72 ppm (t, 2 H, H_{2,5}), and ν_{CO} 2010, 1920, 1670 cm⁻¹; **34**, δ 0.32 (s, 3 H, M-CH₃), 5.1–5.5 (m, 6 H, C₅H₄ + =CH₂), 5.9–6.5 ppm (m, 1 H, =CH), and ν_{CO} 2005, 1920 cm⁻¹; **35**, δ 0.40 (s, 3 H, M-CH₃), 5.1–5.5 (m, 6 H, C₅H₄ + =CH₂), 6.0–6.5 ppm (m, 1 H, =CH), and ν_{CO} 2000, 1915 cm⁻¹; **36**, δ 0.33 (s, 3 H, M-CH₃), 1.91 (d, 3 H, C(CH₃)), 5.0–5.2 (m, 2 H, =CH₂), 5.28 (m, 2 H, H_{3,4}), 5.38 ppm (m, 2 H, H_{2,5}), and ν_{CO} 2000, 1915 cm⁻¹; **37**, δ 0.39 (s, 3 H, M-CH₃), 1.92 (d, 3 H, C(CH₃)), 5.0–5.2 (m, 2 H, =CH₂), 5.34 (m, 2 H, H_{3,4}), 5.44 ppm (m, 2 H, H_{2,5}), and ν_{CO} 2005, 1910 cm⁻¹.
- (24) Macomber, D. W., unpublished studies.
- (25) For example, a reaction between **11** and (η⁵-C₅H₅)TiCl₃ (THF, 25 °C) has afforded (η⁵-methoxycarbonylcyclopentadienyl)(η⁵-cyclopentadienyl)dichlorotitanium [(η⁵-C₅H₄CO₂CH₃)(η⁵-C₅H₅)TiCl₂]: mp 188–190 °C, ν_{CO} 1725 cm⁻¹, M⁺ = m/e 308.¹⁹
- (26) Watts, W. E. *J. Organomet. Chem. Libr.* **1979**, *7*, 401–452.

William P. Hart, David W. Macomber, Marvin D. Rausch*

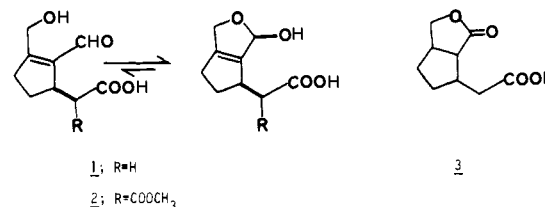
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01003

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Synthesis of the Alleged Genipic Acid by Photoannulation¹

Sir:

In 1964 Tallent proposed structures **1** and **2** for genipic acid and genepinic acid, respectively, two unstable antibiotics isolated from Puerto Rican jagua fruit.² We now present an unambiguous synthesis of structure **1** and its methyl ester which suggest beyond reasonable doubt that genipic acid cannot be as originally formulated.



Tallent's assignment of structure **1** to genipic acid rests primarily on three pieces of evidence. First, exposure of **1** to prereduced PtO₂ and H₂ afforded a 16% yield of lactone **3**, identical with an "authentic" sample,³ suggesting the indicated carbon substitution pattern on a cyclopentane ring. Secondly, genipic acid undergoes mutarotation in basic solution, consistent with a hemiacetal structure. Finally, the NMR spectrum of genipic acid confirms the presence of the hemiacetal with a signal at δ 5.8 (no CHO), while a two-proton signal at δ 4.30 with no absorptions for vinyl hydrogens located the tetrasubstituted double bond between C-1 and C-2 as indicated. It is somewhat curious that genipic acid should exist in the lactol form because of the anticipated strain, but it is possible that sufficient stabilization is gained by hydrogen bonding with the carboxylic acid group to make such a structure energetically plausible. Unfortunately, such an explanation is not possible for the methyl ester of genipic acid (CH₂N₂) which persists as a hemiacetal (δ 5.88 and 4.17, no CHO).

During the intervening years only a single publication dealing with synthetic efforts in the genipic acid area has appeared.⁴ In 1978 Whitesell and Matthews reported an eminently rational approach to genipic acid, which, although unsuccessful, raised significant questions about the validity of the published structure. Problems seemed to rest primarily with the remarkable reluctance of a hydroxymethyl cyclopentene-