the most consistent in giving high optical yields, they also consistently gave the lowest chemical yields, probably due to side reactions. It is likely that leaving groups could be designed to give substantially higher chiral reaction efficiencies than those reported here.

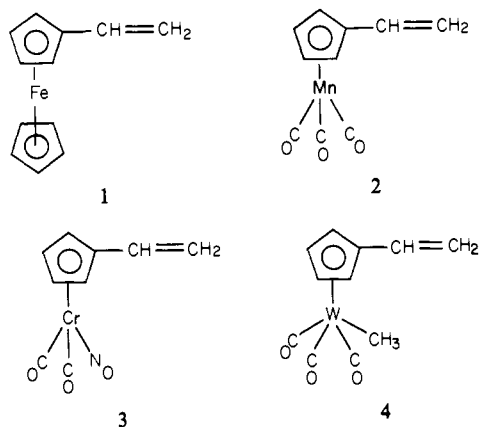## A New, General Route to η⁵-Vinylcyclopentadienyl Organometallic Monomers

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Organometallic polymers are useful in a variety of applications such as catalysts, UV absorbers, semiconductors, and antifouling agents.[1-3] In spite of these potential applications, very few η⁵-vinylcyclopentadienyl organometallic monomers are known. Indeed, only vinylferrocene (**1**),[4] vinylcymantrene (**2**),[5,6] vinylcynichrodene (**3**),[7,8] and (η⁵-vinylcyclopentadienyl)tricarbonylmethyltungsten (**4**)[9,10] have been studied in detail under homo- and copolymerization conditions. The paucity of η⁵-vinylcyclo-

1

2

3

4

pentadienyl monomers stems in part from a lack of suitable synthetic methods, which, in turn, is due to the failure of most

η⁵-cyclopentadienylmetal compounds to undergo aromatic-type ring substitution reactions. We have recently overcome part of this problem with the development of a new method for the formation of various functionally substituted η⁵-cyclopentadienylmetal compounds.[11]

We now report the development of a new and apparently general route for the synthesis of a wide variety of η⁵-vinylcyclopentadienyl organometallic monomers. This method provides a convenient means of introducing vinyl substituents directly onto η⁵-cyclopentadienyl rings in systems which are incapable of undergoing electrophilic aromatic substitution.

6,6-Dimethylfulvene and 6-methylfulvene react with lithium diisopropylamide in THF at 25 °C to produce isopropenylcyclopentadienyllithium (**5**) and vinylcyclopentadienyllithium (**6**), respectively, in yields of 80–90%. The solid products are air

5 (80–90%)

6 (80–90%)
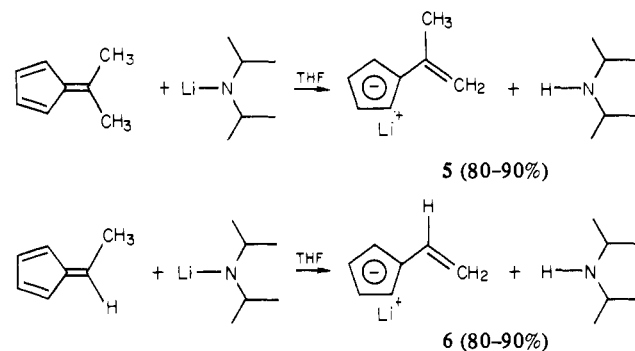
sensitive, as is cyclopentadienyllithium itself. The ¹H NMR spectrum of **5**[12] is in agreement with a recent report by Schore et al.[13] The ¹H NMR spectrum of the previously unknown compound **6** exhibits two apparent triplets due to the cyclopentadienyl protons as well as the typical ABX pattern for a terminal vinyl group (Figure 1).

The reaction between organolithium reagent **6** and η⁵-cyclopentadienyltrichlorotitanium in ethyl ether produces (η⁵-vinylcyclopentadienyl)η⁵-cyclopentadienyldichlorotitanium (**7**) (mp 154–157 °C, 16%).[14] Polymers of **7** after reduction could function

6   7 (16%)
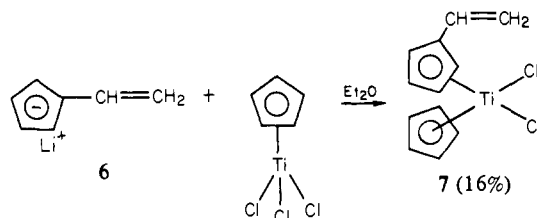
as hydrogenation catalysts similarly to polystyrene-bound titanocene dichloride.[15] Further investigations into the synthesis of other titanocene-type monomers are in progress.[16]

Organolithium reagents **5** and **6** react with molybdenum hexacarbonyl and with tris(dimethylformamide)tricarbonyltungsten in refluxing THF to give η⁵-vinylcyclopentadienyl monomers of these metals. Nitrosylation of the intermediate metal carbonyl anions with N-methyl-N-nitroso-p-toluenesulfonamide has afforded monomers **8** (liquid, 58%), **9** (mp 27–29 °C, 93%), **10** (mp 22–23 °C, 36%), and **11** (mp 38–40 °C, 24%). This completes the series

(1) Carraher, C. E., Jr.; Sheats, J. E.; Pittman, C. U., Jr., "Organometallic Polymers"; Academic Press: New York, 1978.
(2) Pittman, C. U., Jr. *Organomet. React. Synth.* **1977**, *6*, 1–62.
(3) Pittman, C. U., Jr. In "Polymer Supported Reactions in Organic Synthesis"; Hodge, P.; Sherrington, D. C., Eds.; Wiley: New York, 1980.
(4) Lai, J. C.; Rounsefell, T. D.; Pittman, C. U., Jr. *J. Polym. Sci., Part A-1* **1971**, *9*, 651–662.
(5) Pittman, C. U., Jr.; Grube, P. L. *J. Polym. Sci., Part A-1* **1971**, *9*, 3175–3186.
(6) Pittman, C. U., Jr.; Marlin, G. V.; Rousefell, T. D. *Macromolecules* **1973**, *6*, 1–8.
(7) Pittman, C. U., Jr.; Rounsefell, T. D.; Lewis, E. A.; Sheats, J. E.; Edwards, B. H.; Rausch, M. D.; Mintz, E. A. *Macromolecules* **1978**, *11*, 560–565.
(8) Mintz, E. A.; Rausch, M. D.; Edwards, B. H.; Sheats, J. E.; Rounsefell, T. D.; Pittman, C. U., Jr. *J. Organomet. Chem.* **1977**, *137*, 199–205.
(9) Pittman, C. U., Jr.; Jayaraman, T. V.; Priester, R. D., Jr.; Spencer, S.; Rausch, M. D.; Macomber, D. W. *Macromolecules* **1981**, *14*, 237–241.
(10) Macomber, D. W.; Rausch, M. D.; Jayaraman, T. V.; Priester, R. D.; Pittman, C. U., Jr. *J. Organomet. Chem.* **1981**, *205*, 353–364.

(11) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196–1198.
(12) ¹H NMR spectral data for **5** (THF-d₈): δ 2.08 (s, 3 H, CH₃), 4.34 (m, 1 H, vinyl), 4.90 (m, 1 H, vinyl), 5.64 (t, 2 H, H₃,₄), 5.92 (t, 2 H, H₂,₅).
(13) Schore, N. E.; La Belle, B. E. *J. Org. Chem.* **1981**, *46*, 2306–2310.
(14) ¹H NMR spectral data for **7** (CDCl₃): δ 5.32–5.82 (m, 2 H, C═CH₂), 6.38–6.66 (m, 10 H, CH═C and Cp H₂-₅ and C₅H₅). Elemental analyses and spectroscopic data (¹H NMR, IR, MS) were consistent with the proposed structures of all η⁵-cyclopentadienylmetal compounds.
(15) Bonds, D. W., Jr.; Brubaker, C. H., Jr.; Chandrasekaran, E. S.; Gibbons, C.; Grubbs, R. H.; Kroll, L. C. *J. Am. Chem. Soc.* **1975**, *97*, 2128–2132.
(16) For example, treatment of **7** with Al/HgCl₂ in the presence of carbon monoxide has afforded (η⁵-vinylcyclopentadienyl)η⁵-cyclopentadienyldicarbonyltitanium [(η⁵-CH₂═CHC₅H₄)η⁵-C₅H₅Ti(CO)₂]: ν_CO 1980, 1910 cm⁻¹ (recorded in benzene).

Communications to the Editor
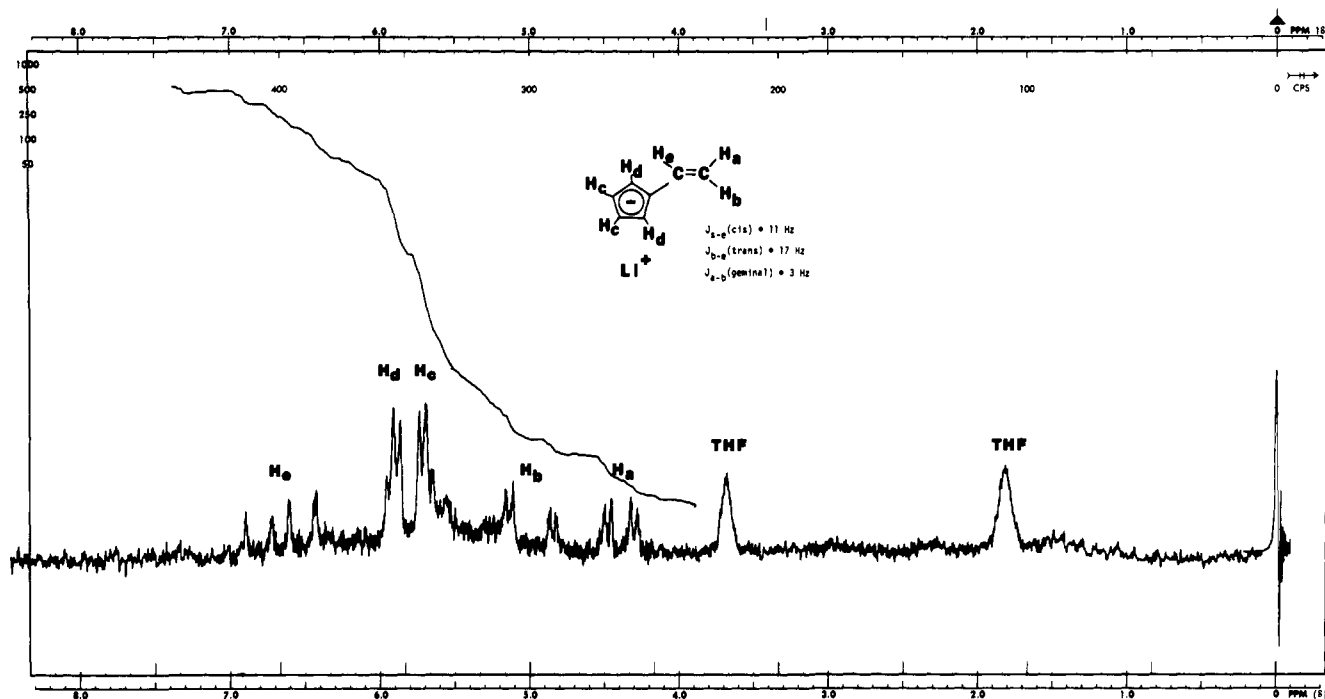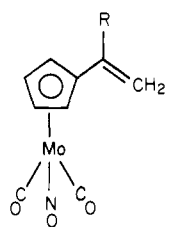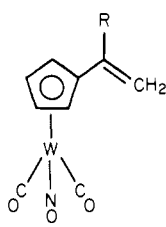
J. Am. Chem. Soc., Vol. 104, No. 3, 1982   885

Figure 1. ¹H NMR spectrum of vinylcyclopentadienyllithium (6) recorded in tetrahydrofuran-d_8 solution.

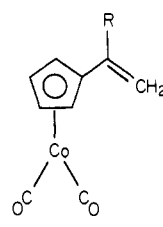of (η^5-vinylcyclopentadienyl)dicarbonylnitrosyl 6B metal monomers[17] and allows a comparison of the vinyl reactivity of monomers 3, 8, and 10 as a function of the metal.

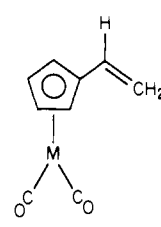8, R = H (58%)   10, R = H (36%)
9, R = CH₃ (93%)   11, R = CH₃ (24%)

Monomer 8 homopolymerizes and readily copolymerizes with styrene when initiated with AIBN in benzene (50–75 °C).[18] The reactivity ratios (m_1 = 8) for this copolymerization were r_1 = 0.31 and r_2 = 0.83, which are remarkably similar to those obtained for the copolymerization of the chromium analogue 3 with styrene (r_1 = 0.30, r_2 = 0.82).[7] Thus, the metal has little effect on the reactivity of the monomer.

8
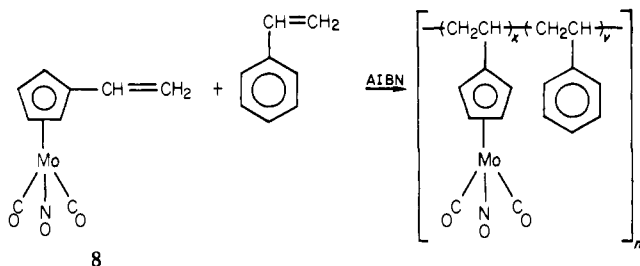
The use of polystyrene-bound η^5-cyclopentadienyldicarbonyl-cobalt as a catalyst[19-21] has prompted us to synthesize monomers

containing this metal. Reactions of 5 or 6 with an equimolar mixture of Co₂(CO)₈ and I₂ in THF at 25 °C give the cobalt monomers 12 (liquid, 15%), and 13 (liquid, 17%), respectively.[22]

12, R = H (15%)   14, M = Rh (47%)
13, R = CH₃ (17%)   15, M = Ir (91%)

Organolithium reagent 6 is also a convenient precursor to the analogous rhodium and iridium monomers. For example, the reaction of 6 with [Rh(CO)₂Cl]₂ in THF at 25 °C, or with Ir-(CO)₃Cl in refluxing hexane, affords monomers 14 (liquid, 47%) and 15 (liquid, 91%), respectively. Homopolymerizations and copolymerizations of 15 (with styrene = m₂) have been carried out. The homopolymer contains over 50 wt % iridium, and serves as a catalyst for 1,5-cyclooctadiene hydrogenation at 100 °C when first reduced by NaHBEt₃. Preliminary experiments place the reactivity ratios in styrene copolymerizations of 15 at r_1 = 0.28 and r_2 = 0.76.

Using reagents 5 and 6, we have now been able to synthesize the first organometallic monomers of copper. Thus, reactions of 5 or 6 with [ClCuPEt₃]₄ in ethyl ether give monomers 16 [mp 45 °C dec, 66%] and 17 [mp 42 °C, 90%], respectively.

The above reaction sequences demonstrate that the vinyl-substituted cyclopentadienyllithium reagents 5 and 6 serve as valuable intermediates for a wide variety of new organometallic monomers

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(17) The chromium analogue 3 has been studied in detail under both homo- and copolymerization conditions; see ref 7 and 8.
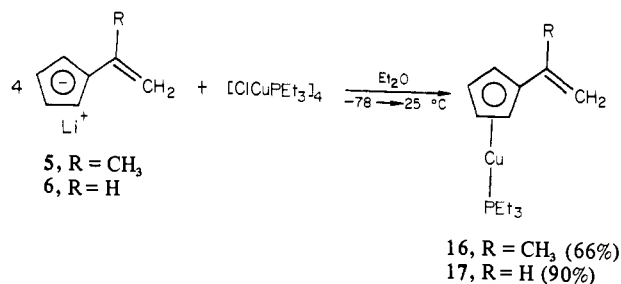
(18) Copolymers containing from 15–70 mol % of 8 have been isolated with molecular weights of ca. 3 × 10⁴. Bulk polymerizations lead to higher molecular weights. The Alfrey–Price value of e for 8 is –1.97, showing that this is an exceptionally electron-rich vinyl monomer like its chromium analogue 3 (e = –1.98⁷). The Q values for 8 and its chromium analogue are both 3.1, which is consistent with substantial delocalization in the α-cyclopentadienyl radicals.

(19) Bubitosa, G.; Boldt, M.; Brintzinger, H. H. J. Am. Chem. Soc. 1977, 99, 5174–5175.

(20) Chang, B.-H.; Grubbs, R. H.; Brubaker, C. H. J. Organomet. Chem. 1979, 172, 81–89.

(21) Perkins, P.; Vollhardt, K. P. C. J. Am. Chem. Soc. 1979, 101, 3985–3987.

(22) Compounds 12 and 13 have been previously described.[11] Compound 12 has also been prepared by a different method: Eilbracht, P.; Dahler, P.; Tiedtke, G. J. Organomet. Chem. 1980, 185, C25–C28. Monomer 13, like isopropenylferrocene, could not be polymerized by AIBN or benzoyl peroxide initiation.

16, R = CH₃ (66%)
17, R = H (90%)

Ion Pair Effects in an Intercalation Process. An Approach to the Bicyclo[5.3.1]undecyl System of Taxane

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Received September 8, 1981

Bifunctional reagents such as **1** containing electrophilic and nucleophilic reaction centers which do not self-annihilate offer a unique approach to ring formation.[1,2] The presence of an

(1)
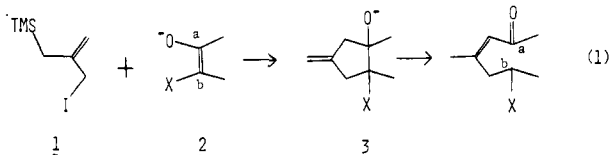
electron-withdrawing group in **2** (i.e., X = EWG) induces fragmentation of the initial adduct **3** and thus constitutes a three-carbon intercalation[3] between C(a) and C(b) (see eq 1).[2] In conjunction with a synthesis of the taxane system[4,5] (e.g., taxinine

(1) (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429. (b) Knapp, S.; O'Connor, U.; Mobilio, D. *Tetrahedron Lett.* **1980**, 4557. (c) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699.

(2) Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680.

(3) As suggested by a referee, in order to avoid confusion with the use of the term intercalation in nucleic acid chemistry, we are using intercalation to mean insertion of atoms *in a covalent manner* into an existing ring or chain.

(4) For a review, see: Miller, R. W. *J. Nat. Prod.* **1980**, *43*, 425.

(5) For formation of a bicyclo[5.3.1]undecanyl system, see: Prelog, V.; Barman, P.; Zimmermann, M. *Helv. Chim. Acta* **1949**, *32*, 1284. Roth, W. R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 503. Levine, S. G.; McDaniel, R. L., Jr. *J. Org. Chem.* **1981**, *46*, 2199. Kahn, M. *Tetrahedron Lett.* **1980**, 4547.

Scheme I. Synthesis of Fragmentation Substrates[a]
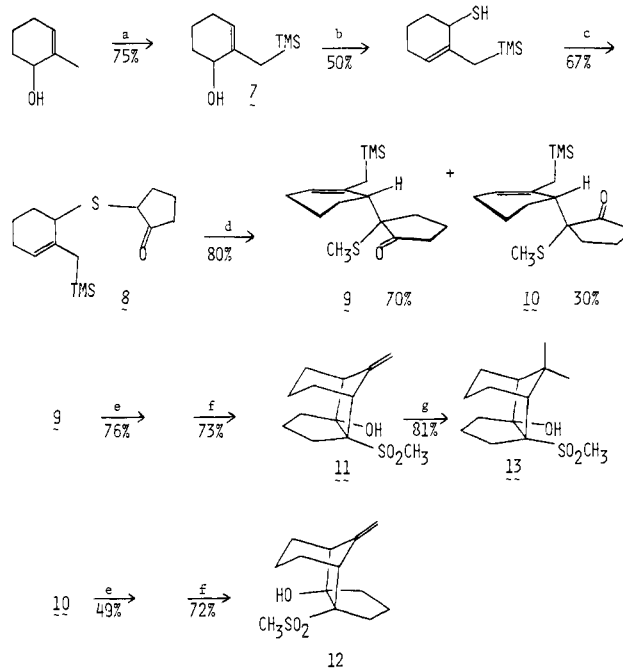
[a] (a) (i) n-C₄H₉Li, TMEDA, hexane, room temperature. (ii) Me₃SiCl, 0 °C. (iii) 1% H₂SO₄, H₂O, THF, room temperature. (b) (i) n-C₄H₉Li, ether, CS₂, CH₃I, room temperature, then warm to 60 °C neat. (ii) LAH, ether, reflux. (c) NaH, 2-chlorocyclopentanone, DMF, 0 °C, room temperature. (d) KH, DME, reflux, 1.5 min, then room temperature, CH₃I. (e) m-CPBA, CH₂Cl₂, NaHCO₃, H₂O, 0 °C. (f) C₂H₅AlCl₂, PhCH₃, room temperature. (g) (i) CH₂I₂, (C₂H₅)₂Zn, PhCH₃, dry air, 50–55 °C. (ii) H₂, PtO₂, HOAc.

4), we envisioned application of this strategy in which the critical step is the fragmentation of **6** to create the very sterically congested 11,11-dimethylbicyclo[5.3.1]undecyl system **5**. The factors that govern this type of fragmentation reaction remain to be established. We wish to report an unusual ion pair effect on this fragmentation, the utilization of the ability to invert thermodynamic acidities and thereby control the course of a reaction and the successful realization of the synthesis of the critical bridged bicyclic ring system of the taxane nucleus.
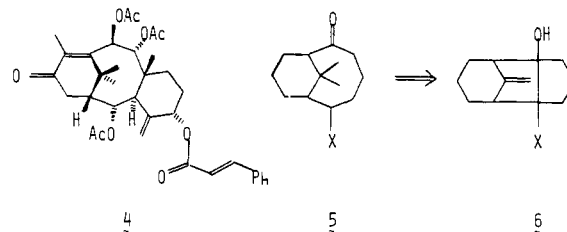
Scheme I outlines the synthesis of the fragmentation substrates **11–13**. The bifunctional conjunctive reagent **7**[6] smoothly formed by the direct metalation approach.[1a] Since attempts to effect direct displacement of leaving groups derived from alcohol **7** failed, the requisite C–C bond was formed via sigmatropic rearrangements—initially an O → S conversion via a [3.3] rearrangement of the xanthate[7] and then a S → C conversion via a [2.3] rearrangement of a sulfur stabilized carbanion derived from **8**.[6,8] The great facility of these rearrangements should be noted

(6) This compound has been fully characterized by spectral means and has a satisfactory elemental composition determined by either high-resolution mass spectroscopy or combustion analysis.

(7) Taguchi, T.; Kawazoe, Y.; Yoshihira, K.; Kanayama, H.; Mori, M.; Tabata, K.; Harano, K. *Tetrahedron Lett.* **1965**, 2717. Ferrier, R. J.; Vethaviyasar, N. *Chem. Commun.* **1970**, 1385. Also see: Hackler, R. E.; Balko, T. W. *J. Org. Chem.* **1973**, *38*, 2106. Nakai, T.; Mimura, T.; Kurokawa, T. *Tetrahedron Lett.* **1978**, 2895.