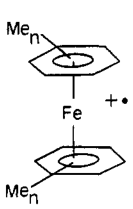
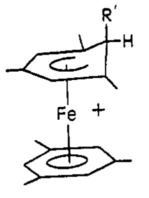


3a: $n = 0$
b: $n = 3$ (1,3,5)
c: $n = 5$
d: $n = 6$



2e: R′ = CH_2Cl
f: R′ = CH_2CH_2Cl

In summary, this paper details a one-step, high-yield method of carbon–carbon bond formation utilizing the readily accessible $[(arene)_2Fe]^{2+}$ series of dications and $AlEt_3$. $AlEt_3$ has therefore been shown to be an effective complement to more conventional carbanionic sources, presumably because of its tendency to engage in ET reactions with organotransition-metal substrates. We are extending this work in our laboratory by focusing upon other trialkylaluminum reagents and further functionalization of **2a–d**.[30]

Acknowledgment. We are indebted to NSERC (M. J.Z., T.S.C.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (M.J.Z.), for financial support and to Dr. Don Hooper of the Atlantic Regional Magnetic Resonance Centre (ARMRC) for recording ^{13}C NMR spectra.

Registry No. **1a**, 11108-19-3; **1b**, 31666-55-4; $\mathbf{1b}^+$ $(I^-)_2$, 12148-60-6; **1c**, 59688-09-4; **1d**, 53382-63-1; **2a** PF_6, 117340-92-8; **2b** PF_6, 117340-94-0; **2c** PF_6, 117340-96-2; **2d** PF_6, 117340-98-4; **2f** PF_6, 117341-00-1; **3d**, 53382-60-8; $AlEt_3$, 97-93-8; $AlMe_3$, 75-24-1; $[(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}exo\text{-}CH_2Cl_6Me_6)Fe]^+$, 117341-01-2.

Supplementary Material Available: Details of structure solution and refinement and tables of distances and angles and atomic coordinates and thermal parameters for **2b** and **2d** (17 pages); listings of observed and calculated structure factors for **2b** and **2d** (41 pages). Ordering information is given on any current masthead page.

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[30] Bis(cyclohexadienyl) complexes have been prepared from **2a**, **2b**, and **2c** and an η^4-triene containing a highly reactive exocyclic double bond has been synthesized from **2d**.

Synthesis and Structures of Dibenzometallacyclohexa-2,5-dienes

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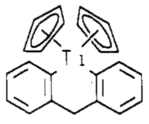
Received February 9, 1988

Summary: A study of the synthesis and structure of dibenzometallacyclohexa-2,5-dienes incorporating titanium, hafnium, and cobalt is reported. The crystal structures of the titanacycle and cobaltacycle exhibit boat conformations. Variable-temperature ^1H NMR data implicate fast-exchange spectra for boat–boat interconversion in the titanacycle and hafnacycle.

The importance of unsaturated transition metallacycles has been recently exemplified by their implication in stoichiometric and catalytic reactions.[1] Two stable metallacyclohexa-2,4-dienes have been reported. Hughes and co-workers recently reported the synthesis of a platinacyclohexadiene[2] and Bleeke and co-workers reported the isolation of an iridacyclohexadiene.[3] We here report a study of the preparation and characterization of the first metallacyclohexa-2,5-dienes—dibenzotitanacyclohexa-2,5-diene (**1**), dibenzohafnacyclohexa-2,5-diene (**2**), and dibenzocobaltacyclohexa-2,5-diene (**3**). The titana- and hafnacycles also constitute the first reported unsaturated six-membered metallacycles incorporating early transition metallacycles.[4]



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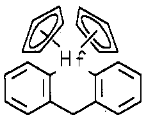

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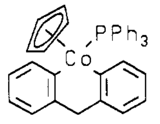
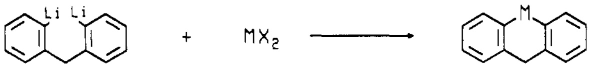


3

As a systematic approach toward the preparation of metallacyclohexadienes we sought a method which would favor forming both single bonds to the metal in one step. Much precedent is available in transition-metal chemistry in which dibenzometallacyclopenta-2,4-dienes may be prepared utilizing 2,2′-dilithiobiphenyl with transition-metal dihalides.[5] In that the kinetic stability of the diaryl transition-metal products is evident, we sought to react 2,2′-dilithiodiphenylmethane[6] with selected transition-metal dihalides to prepare the benzannulated six-membered metallacycles (eq 1). Initial attempts at this approach with titanocene dichloride gave mixtures of products with predominately unidentified yellow precipitates. However, slow addition of a solution (Et_2O) of the dilithium reagent to a cold (−78 °C) ether solution of titanocene dichloride, with *rigorous exclusion of light*, gave a red solution. After the solution was warmed to room temperature, washed with pentane and water, and dried with $MgSO_4$, removal of the solvent gave red needles



(1)

MX_2 = $(C_5H_5)_2TiCl_2$
$(C_5H_5)_2HfCl_2$
$(C_5H_5)(PPh_3)CoI_2$

1 M = $(C_5H_5)_2Ti$
2 M = $(C_5H_5)_2Hf$
3 M = $(C_5H_5)(PPh_3)Co$

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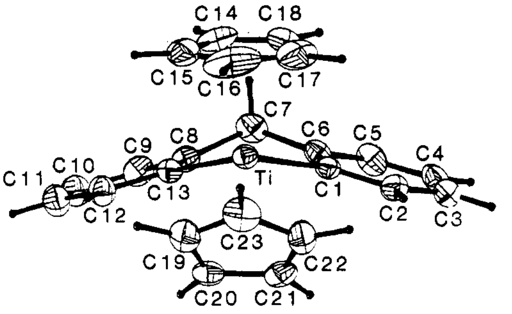

Figure 1. View of $(\eta^5\text{-}C_5H_5)_2Ti(C_{13}H_{10})$ (1). H atoms given arbitrary radii. C(1)–C(6), C(6)–C(7), C(7)–C(8), and C(8)–C(13) distances are 1.419 (7), 1.500 (8), 1.513 (7), and 1.408 (8) Å, respectively. Central ring angles at C(1), C(6), C(7), C(8), and C(13) are 121.9 (4), 122.7 (5), 121.0 (5), 122.4 (5), and 122.0 (4)°, respectively. The dihedral angle C(6)–C(7)–C(8)/C(1)–C(6)–C(8)–C(13) is 36.7°.

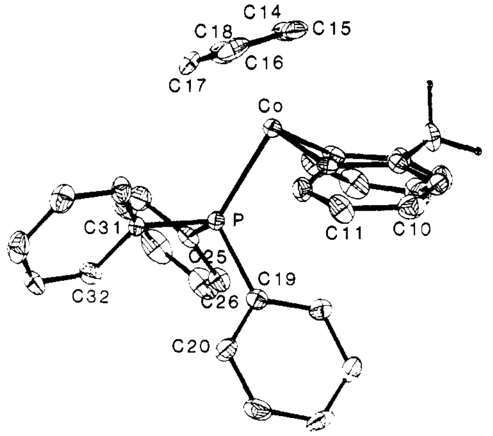

Figure 2. "Side" view of $(\eta^5\text{-}C_5H_5)(PPh_3)Co(C_{13}H_{10})$ (3). Same numbering scheme used in 1 is used for metallacycle moiety in 3. H atoms, except for those on C(7), which were refined, are omitted for clarity. C(1)–C(6), C(6)–(7), C(7)–C(8), C(8)–C(13) distances are 1.410 (9), 1.490 (10), 1.515 (10), and 1.416 (9) Å, respectively. Central ring angles at C(1), C(6), C(7), C(8), and C(13) are 120.6 (5), 121.9 (6), 115.2 (6), 121.0 (6), and 121.4 (5)°, respectively. The dihedral angle C(6)–C(7)–C(8)/C(1)–C(6)–C(8)–C(13) is 37.3°.

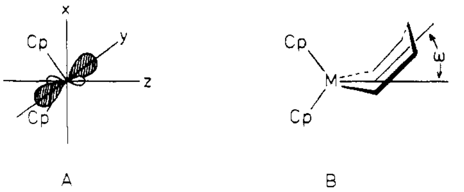

Figure 3. A: $1a_1$ frontier orbital (note Cp orbitals omitted.[12] B: angle ω in Cp_2M metallacyclic complexes.[12]

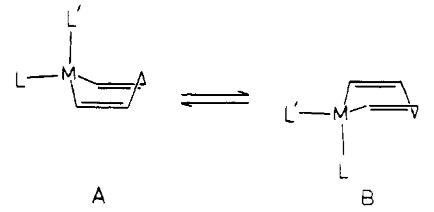

Figure 4. Boat–boat interconversion in 1 (L, L′ = $\eta^5\text{-}C_5H_5$), 2 (L, L′ = $\eta^5\text{-}C_5H_5$), and 3 (L = PPh_3, L′ = $\eta^5\text{-}C_5H_5$) (benzo substituents omitted for clarity).

identified as 1 (89%).[7]

As also shown in eq 1, introduction of 2,2′-dilithiodiphenylmethane to hafnocene dichloride and $(\eta^5\text{-}C_5H_5)(PPh_3)CoI_2$ gave **2** (white solid, 48%) and **3** (red needles, 32%), respectively.[8,9] Titanacycle 1 and hafnacycle **2** are air- and light-sensitive compounds. Hafnacycle **2** is thermally sensitive, decomposing at −10 °C, with a half life of ca. 1 week. As a solid, the cobaltacycle **3** exhibits high thermal and air stability but decomposes rapidly in halogenated solvents and benzene.

Crystals of 1 and **3** suitable for X-ray crystallographic analysis were obtained from solutions of pentane/ether and ether, respectively.[10] ORTEP views of both complexes are shown in Figures 1 and 2. In contrast to Bleek's iridacyclohexa-2,4-diene,[3] the central rings in 1 and **3** are not planar. The "phenylene butterfly" angle of 1 is 149.1°, the Cp-M-Cp bond angle is 133.9°, and the C-M-C bond angle is 90.5 (2)°. It is interesting to note the Ti-C(1) and Ti-C(13) bond distances of 2.185 (5) and 2.190 (5) Å, respectively, are significantly shorter than the $Ti\text{-}C_{ipso(phenyl)}$ bonds in $Cp_2Ti(phenyl)_2$ of 2.27 Å although they are similar to those found in five-membered titanacyclopentadienes.[11] Furthermore, in order to accommodate the metal in the six-membered ring, the methylene carbon has a large central ring angle of 121.0 (5)°. The cobaltacycle **3** exhibits similar structural characteristics. The nonplanar metal-

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(7) Preparation of 1. All manipulations were carried under a N_2 atmosphere with the exclusion of light. 2,2′-Dilithiodiphenylmethane (2.4 mmol) in 50 mL of diethyl ether was added dropwise to a cold (−78 °C) dark stirred slurry of titanocene dichloride (2.3 mmol) in 150 mL of diethyl ether. After the solution was stirred for 3 h and warmed to room temperature, the solvent was removed in vacuo. The resulting orange residue was washed thrice with pentane, extracted into diethyl ether, washed thrice with water, separated, and dried over $MgSO_4$. Removal of the solvent in vacuo gave 1 as red needles (89%): mp 145 °C dec; ^1H NMR ($CDCl_3$) δ 3.91 (s, CH_2, 2 H), 5.95 (dd, *J* = 9, 4 Hz, 2 H), 6.18 (s, Cp, 10 H), 6.23–7.30 (m, aromatic, 6 H). $^{13}C(\{^1H\}$ NMR ($CDCl_3$) δ 48.1 (CH_2), 114.7 (C_5H_5), 122.1, 122.7, 127.8, 132.2 (CH benzo), 142.4 (C quat benzo), 189.6 (C–Ti). Mass spectra: calcd, *m/z* 344.104; found, *m/z* 344.107. Anal. Calcd for $C_{23}H_{20}Ti$: C, 80.23; H, 5.85. Found C, 79.68; H, 5.85.

(8) Preparation of **2**. All manipulations were carried out under a N_2 atmosphere. 2,2′-Dilithiodiphenylmethane (1.2 mmol) in 25 mL of diethyl ether was added dropwise to a dark stirred cold (−78 °C) diethyl ether slurry (125 mL) of hafnocene dichloride (0.42 g, 1.2 mmol). The resulting mixture was stirred 2 h and warmed to 0 °C. After the solvent was removed in vacuo, the yellow residue was washed thrice with pentane. Extraction of the remaining solid with diethyl ether, filtration, and removal of the solvent in vacuo gave the white, air and thermally sensitive powder **2** (48%): ^1H NMR ($CDCl_3$) δ 3.88 (s, CH_2, 2 H), 6.13 (Cp, 10 H), 6.86 (m, aromatic, 8 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 48.7 (CH_2), 110.6 (C_5H_5), 122.5, 123.7, 127.8, 135.6 (CH benzo), 149.2 (C quat benzo), 190.0 (C–Hf).

(9) Preparation of **3**. All manipulations were carried out under a N_2 atmosphere. 2,2′-Dilithiodiphenylmethane (3.5 mmol) in diethyl ether (50 mL) was added dropwise to a stirred cool (0 °C) slurry of diiodo(triphenylphosphine)cyclopentadienylcobalt[14] (2.24 g, 3.5 mmol). The resulting mixture was warmed to room temperature and stirred 16 h. The red solution was then filtered and concentrated on neutral alumina. The coated alumina was then transferred to the top of the chromatography column. Chromatography (neutral alumina, diethyl ether/pentane, 1:3), collection of the red/orange band, and removal of the solvent, in vacuo, gave red needles identified as **3** (32%): mp 135–137 °C; X-ray quality crystals can be obtained from pentane/benzene; ^1H NMR (C_6D_6) δ 3.95 (d, 1 H, *J* = 15.8 Hz, CH_2), 4.22 (d, 1 H, *J* = 15.8 Hz, CH_2), 4.84 (s, 5 H, Cp), 6.62–7.45 (m, 24 H, Ar). Mass Spectra: calcd, *m/z* 552.142; found, *m/z* 552.142. This compound decomposes in solution ($CDCl_3$, C_6D_6), thus thwarting our efforts to obtain ^{13}C NMR data. Anal. Calcd for $C_{36}H_{30}CoP$: C, 78.26; H, 5.47. Found: C, 78.04; H, 5.42.

(10) X-ray structure determinations. 1: $TiC_{23}H_{20}$; $a = 8.041$ (2), $b = 11.787$ (2), $c = 18.170$ (2) Å; $V = 1722.1$ (9) Å^3, $R = 0.045$, for 1274 observed reflections. **3**: $CoPC_{36}H_{30}$, $a = 9.377$ (5), $b = 15.465$ (2), $c = 18.619$ (4) Å, $V = 2700$ (3) Å; $R = 0.039$, for 1778 observed reflections. For both crystals: orthorhombic; $P2_12_12_1$; $Z = 4$; intensities measured with an Enraf-Nonius CAD-4 diffractometer using ω–2θ scans of 4–16° min^{-1} in θ; λ(Mo Kα) = 0.71073 Å, $T = 293$ K; H atom positions idealized except for those on C(7) in **3** which were refined; and all non-H atoms refined anisotropically. Full-matrix least squares minimized $\sum(\Delta F)^2$. Tables of atomic coordinates, thermal factors, data collection and refinement details, bond distances and bond angles, and structure factors are available as supplementary material.

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lacycle has a butterfly angle of 144.7°, and the C–M–C bond angle is 93.4 (3)°. The Co–C(1) and Co–C(13) bond distances are 1.985 (6) and 1.959 (7) Å, respectively. Again, the methylene carbon has a large central ring bond angle of 115.2 (6)°. Selected bond angles and distances for 1 and 3 are provided in the captions of the figures.

The transition-metal molecular orbitals involved in bonding with Cp_2MR_2 complexes have been outlined by Hoffmann and co-workers.[12] Folding of the metallacycle (the angle ω in our metallacycle 1 is 19.9°, Figure 3) would be necessary for π overlap of the Cp_2M vacant Frontier $1a_1$ orbital (Figure 3) with the HOMO of the organic ligand. Such overlap could enhance the observed nonplanar conformation and shorten the Ti–C(1) and Ti–C(13) bond distances in 1. The crystal structures of 1 exhibits a boat conformation for the central ring where the methylene hydrogens are nonequivalent. In order to ascertain the relative boat vs planar conformational energies and hence the contribution of the $1a_1$–HOMO π overlap in 1 and 2, we turned to variable-temperature NMR studies. In the ^1H NMR spectrum (25 °C, THF-d_8, 90 MHz) of 1, the methylene hydrogens appear as a singlet at δ 3.91 ppm, indicative of a fast-exchange boat–boat interconversion process (Figure 4). At −50 °C, broadening was observed for the methylene hydrogen resonance; however, coalescence was not achieved with temperatures as low as −75 °C. Similar experiments were performed on our hafnacycle 2 (CD_2Cl_2/CF_2Br_2, 1:3, as solvent). Again, the methylene hydrogen resonance broadened, but coalescence was not obtained. These experiments suggest a low $\Delta G^{\ddagger}$ for boat–boat interconversion in 1 and 2. Furthermore, if π overlap plays a role in conformational stability (and concomitant shortening of the Ti–C bonds in 1), its contribution to the energy stabilization of the boat conformation is minimal.[13] Finally, in the case of cobaltacycle 3, its methylene protons give an AB spectrum at room temperature (H_A, δ 4.22 ppm, H_B, δ 3.95 ppm, J_{AB} = 15.8 Hz) consistent with a nonfluxional thermodynamically more stable boat structure (ω = 27.9° in the crystal structure) where the bulky triphenylphosphine ligand occupies an equatorial position (Figure 4A).[13]

Further work concerning the preparation, conformational analysis, and chemistry of metallacyclohexa-2,5-dienes is being pursued.

Acknowledgment. We thank Dr. J. Lay, Jr., at the National Center for Toxicological Research for the high-resolution mass spectral data. We would also like to thank the National Science Foundation (CHE-8312644) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial funding of this research.

Supplementary Material Available: Tables of crystallographic data collection and refinement details, atomic coordinates and equivalent isotropic thermal parameters, distances and angles in $C_{13}H_{10}Ti(cpd)_2$ and $C_{13}H_{10}Co(cpd)(PPh_3)$, and anisotropic thermal parameters (13 pages); listings of structure factor amplitudes for $C_{13}H_{10}Ti(cpd)_2$ and $C_{13}H_{10}Co(cpd)(PPh_3)$ (37 pages). Ordering information is given on any current masthead page.

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(13) MMX minimization of 1, 2, and 3 also gave boat conformations (ω = 25° and 17° for 1 and 2, respectively). Further calculations performed for simulation of the boat–boat interconversion of 1 and 2 gave barriers of 0.68 and 1.13 kcal/mol, respectively. Such calculations take into account steric and torsional contributions of the ligands with the metal torsional effects being negligible. The energy differences determined by MMX calculations between boat forms of 3 (parts A and B of Figure 4 with ω = 33°) was 21 kcal/mol in favor of the equatorial PPh_3 conformation. Cf. Bowen, J. P.; Pathiaseril, A.; Profeta, S., Jr.; Allinger, N. L. *J. Org. Chem.* **1987**, *52*, 5162 and references cited. PC Model/MMX molecular modeling program: Serena Software, Box 3076, Bloomington, IN 47402-3076.

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Redox-Induced Reversible Migration of Hydrogen from Metal to Alkene

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Summary: Reaction of the trihydride $(triphos)RhH_3$ (**1**) [triphos = $MeC(CH_2PPh_2)_3$] in benzene with dimethyl acetylenedicarboxylate (DMAD) (room temperature) or with excess dimethyl fumarate (DMFU) (reflux temperature) gives (triphos)RhH(π-DMFU) (**2**). Two-electron chemical or electrochemical oxidation of **2** in THF promotes hydride migration on the alkene. As a result, the succinyl complex $[(triphos)Rh\{CH(COOMe)CH_2(COOMe)\}]^{2+}$ forms, which can be isolated as an $SO_3CF_3^-$ (**3**) or ClO_4^- (**3a**) salt. One-electron reduction of **3** (or **3a**) in CH_2Cl_2 by macroelectrolysis at controlled potential permits one to obtain the square-pyramidal Rh(II) $[(triphos)Rh\{CH(COOMe)CH_2(COOMe)\}]^+$ (**4**), which has been characterized by ESR spectroscopy. Addition of one electron to **4** or two electrons to **3** (or **3a**) yields the starting hydride (fumarate) complex **2**.

The formal insertion of olefins into metal–hydrogen bonds and the microscopic reverse process, β-H elimination, are fundamental transformations in organometallic chemistry. Much is known about the kinetics and mechanism of these reactions; in particular, it is agreed that externally added ligands may promote the insertion and stabilize the alkyl complex with no variation of the formal oxidation state of the metal.[1] We now wish to report an example of hydride (alkene) → alkyl interconversion which is strictly controlled by the oxidation state of the metal.

The trihydride $[(triphos)RhH_3]^2$ (1) [triphos = $MeC(CH_2PPh_2)_3$] reacts in benzene with dimethyl acetylenedicarboxylate (DMAD) at room temperature or with excess dimethyl fumarate (DMFU) at reflux temperature yielding pale yellow crystals of $[(triphos)RhH(\pi\text{-DMFU})]^3$ (2) (yield 95%). The reaction with DMFU is accompanied by production of dimethyl succinate (DMSU) due to hydrogenation of excess olefin (Scheme I). Two-electron oxidation of the cis hydride (alkene) complex 2 in THF by chemical (2 equiv of $AgSO_3CF_3$) or electrochemical (ex-

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