case, the cationic character of C_α in (*E*)-3 certainly ameliorates this rearrangement; however, with the (trimethylsilyl)tropylium cation, the only previous example where a partial formal cationic change is present on C_α in a stable compound, introduction of fluoride is reported to give desilation.[10]

The synthetic utility of chiral vinyl trimethylsilanes[4] and chiral allyldimethylfluorosilanes[11] has recently been of interest. Work on the preparation and synthetic applications of chiral transition-metal [(trimethylsilyl)vinyl]carbene complexes as well as achiral and chiral (methoxyallyl)silane complexes[12] is currently being pursued.

Acknowledgment. We wish to thank the National Science Foundation (CHE-8313644) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. (*E*)-1, 112655-64-8; (*E*)-2, 112655-65-9; (*E*)-3, 112655-67-1; (*E*)-4 (isomer 1), 112655-68-2; (*E*)-4 (isomer 2), 112710-88-0; TAS-F, 59218-87-0; $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, 12078-28-3; (*E*)-1-(tri-*n*-butylstannyl)-2-(trimethylsilyl)ethene, 58207-97-9.

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Synthesis of Bis(3,4-dimethylcyclopentadienyl)acetylene and Bridged Metallocenes $(\eta^5\text{-}C_5Me_5)M[(\eta^5\text{-}C_5H_2Me_2)C{\equiv}C(\eta^5\text{-}C_5H_2Me_2)]M(\eta^5\text{-}C_5Me_5)$ (M = Fe, Ni) Derived Therefrom

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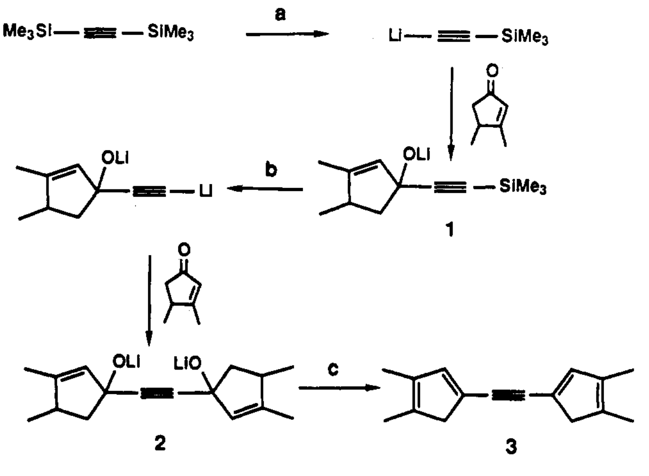
Summary: The synthesis of the binuclear cyclopentadienyl ligand $C_5H_3Me_2C{\equiv}CC_5H_3Me_2$ (**3**) is reported. Reaction of the dilithio salt of **3** with $(\eta^5\text{-}C_5Me_5)M(acac)$ (M = Fe, Ni; acac = acetylacetonate) gives $(\eta^5\text{-}C_5Me_5)M[(C_5H_2Me_2)C{\equiv}C(C_5H_2Me_2)]M(\eta^5\text{-}C_5Me_5)$ (**4a,b**). Cyclic voltammetry reveals two reversible waves with $\Delta E_{1/2}$ = 160 mV for M = Fe and 265 mV for M = Ni. Compound **4b** has been characterized by X-ray crystallography.

Bridged biferrocenes play a central role in the chemistry of mixed-valence compounds.[1] Since the metallocenes of the first-row transition elements exhibit high stabilities and interesting electronic structures, the bimetallocenes of these metals may be expected to provide additional insights into the nature of metal–metal interactions in coupled binuclear compounds. Owing to the special stability of ferrocene, a number of bridged ferrocenes have been prepared by direct functionalization of the cyclopentadienyl groups. Compounds such as biferrocene,[2] bis(fulvalene)diiron,[3] and bis(ferrocenyl)acetylene[4] were prepared and their properties have been extensively studied over the past years. Unfortunately, this same chemistry cannot be applied to the synthesis of the analogous bridged metallocenes of other metals. As a result, the series of such isostructural compounds is restricted to the bis(fulvalene)dimetal compounds of V,[5] Cr,[6] Fe,[7] Co,[8] Ni,[9] bis(pentalenyl)dinickel,[10] and bis(pentalenyl)dicobalt.[10]

Scheme I



a: MeLi, b: MeLi, c: 1. H_2O 2. p-TosOH

We wish to report a different synthetic strategy to binuclear systems, in which the bridging ligand is prepared by using standard organic procedures for the synthesis of methyl-substituted cyclopentadienes. Reaction of the dilithio salt of the ligand with 2 equiv of $(\eta^5\text{-}C_5Me_5)M(acac)$ (acac = acetylacetonate)[11] provides a clean entry into bridged bimetallocenes. The general utility of this synthetic strategy for preparing bridged derivatives depends upon the availability of the (cyclopentadienyl)–X–(cyclopentadienyl) linking group. Thus, we have undertaken the syntheses of a number of such linked cyclopentadienyl ligands in which the unsaturated organic group X is varied systematically. In the present communication we describe the synthesis of bis(3,4-dimethylcyclopentadienyl)acetylene

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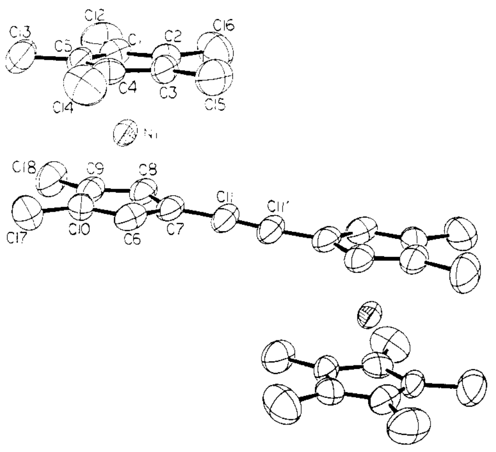
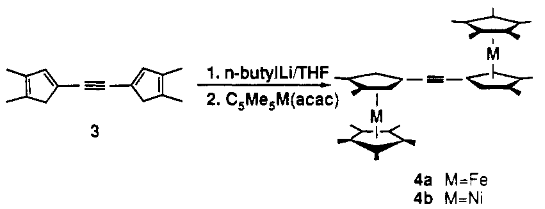


Figure 1. Molecular geometry and atom labeling scheme for **4b**. Selected bond distances (Å) include the following: Ni–C(6) = 2.183 (7), Ni–C(7) = 2.230 (7), Ni–C(8) = 2.187 (7), Ni–C(9) = 2.159 (8), Ni–C(10) = 2.139 (7), C(7)–C(11) = 1.425 (9), C(11)–C(11)′ = 1.184 (9), C(6)–C(7) = 1.422 (9), C(7)–C(8) = 1.422 (10), C(8)–C(9) = 1.395 (9), C(9)–C(10) = 1.438 (11), C(10)–C(6) = 1.397 (10).

and the bridged metallocenes of the formula (η^5-C_5Me_5)M[(η^5-$C_5H_2Me_2$)C≡C(η^5-$C_5H_2Me_2$)]M(η^5-C_5Me_5) (M = Fe, Ni).

The clean displacement of a trimethylsilyl group from bis(trimethylsilyl)acetylene by methyllithium reported by Holmes[12] provides a straightforward route to the lithium alkoxide **1** (Scheme I). Addition of a second equivalent of methyllithium in situ, followed by addition of another mole of 3,4-dimethylcyclopent-2-en-1-one,[13] affords the symmetric dilithium dialkoxide **2**. Hydrolysis of dialkoxide **2** to the corresponding diol, followed by dehydration and recrystallization from pentane, affords pale yellow crystals of bis(3,4-dimethylcyclopentadienyl)acetylene[14] (**3**) in 20% overall yield. Isomeric purity is confirmed by NMR spectroscopy.[14] Compound **3** appears to be moderately air sensitive and should be recrystallized under nitrogen and stored below 0 °C in the absence of air.

When doubly deprotonated **3** is added to a tetrahydrofuran solution of (η^5-C_5Me_5)M(acac) (M = Fe, Ni), highly colored (M = Fe, red; M = Ni, violet) bridged metallocene derivatives are formed. Crystalline **4a** (M = Fe) and **4b** (M = Ni) are obtained from methylcyclohexane in 40% yield (eq 1).[14] Red-orange **4a** is stable in air, whereas dark violet **4b** must be handled in an inert atmosphere.



(1)

The ^1H NMR spectrum of **4a** (C_6D_6, 25 °C) is consistent with the structure depicted above. The magnetic moment of **4b** as determined by the Evans method[15] suggests 3.8 unpaired electrons per dimer.

Single crystals of **4b** suitable for X-ray diffraction were grown by slowly cooling to room temperature a saturated solution of **4b** in methylcyclohexane, and the molecular structure was determined.[16] The molecule consists of two nickel atoms in a trans conformation, each sandwiched between an η^5-pentamethylcyclopentadienyl ligand and one dimethylcyclopentadienyl fragment of the disubstituted acetylene ligand (Figure 1). The dihedral angle between the two five-membered rings of the (η^5-C_5Me_5)Ni(η^5-$C_5H_2Me_2$) moiety is 3.2°. These two rings are staggered with respect to one another by 41.3°. A stereoview of the crystal packing is shown in Figure 2.

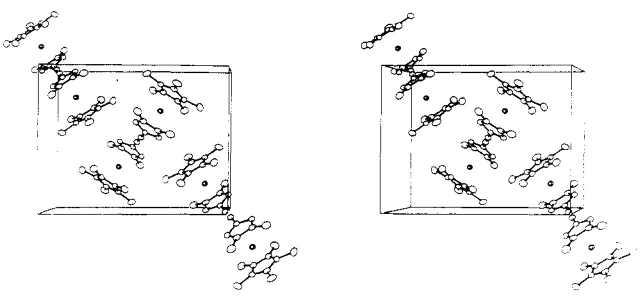


Figure 2. Stereoview of crystal packing of **4b**.

Table I. Cyclic Voltammetry Data[a]

compd	$E_{1/2}$[b]	$E_{1/2}$[c]	ΔE[d]
4a	0.165	0.330	0.160
4b	–0.480	–0.210	0.265

[a] Supporting electrolyte is 0.1 M NBu_4ClO_4. All potentials in V referenced to SCE. Temperature = 20 °C. Sweep rate = 20 mV/s. Solvent = CH_2Cl_2. [b] For the process M(II)/M(II) → M(II)/M(III) + e⁻. [c] For the process M(II)/M(III) → M(III)/M(III) + e⁻. [d] Obtained from differential-pulse voltammetry.

The nickel atom is bonded to the η^5-C_5Me_5 ligand (Cp*) in a symmetric fashion (average Ni–C = 2.156 (10) Å) similar to that displayed in $Cp^*_3Ni_3(\mu_3\text{-}CO)_2$[17] and in contrast to the coordination displayed in $(Cp^*Ni)_2C_{16}H_{24}$ (Ni–C = 2.089–2.176 Å).[18] The C–C bond lengths support the symmetrical η^5-type bonding as well (average C–C = 1.41 (1) Å).

Within the acetylene-bound cyclopentadienyl ring there are two short C–C bonds and three long C–C bonds. The Ni–C interactions vary from 2.230 (Ni–C(7)) to 2.139 Å. A bond arrangement such as that described suggests a resonance contribution from an η^4-cyclopentadienyl ligand.

Complexes **4a** and **4b** exhibit two reversible, one-electron oxidation waves in dichloromethane as shown in Table I. The first oxidation potential of **4a** is 0.5 V lower than that of the parent compound bis(ferrocenyl)acetylene.[4] This

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(14) **3**: ^1H NMR ($CDCl_3$, 25 °C) δ 1.83 (s, 3 H), 1.91 (s, 3 H), 3.04 (s, 2 H), 6.49 (s, 1 H); ^{13}C NMR ($CDCl_3$, 25 °C) δ 12.56 (q, J = 125 Hz), 13.61 (q, J = 125 Hz), 49.25 (t, J = 126 Hz), 89.52 (s), 123.19 (s), 134.98 (s), 136.89 (s), 141.10 (d, J = 164 Hz). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.25; H, 8.57. **4a**: ^1H NMR (C_6D_6, 25 °C) δ 1.64 (s, 6 H), 1.84 (s, 15 H), 3.77 (s, 2 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 10.73, 11.53, 66.60, 74.89, 80.48, 82.60, 85.25. Anal. Calcd for $C_{36}H_{46}Fe_2$ (**4a**): C, 73.23; H, 7.85. Found: C, 73.47; H, 7.62. Anal. Calcd for $C_{36}H_{46}Ni_2$ (**4b**): C, 72.53; H, 7.78. Found: C, 72.87; H, 7.68.

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(16) A crystal of **4b** of dimensions 0.20 × 0.25 × 0.40 mm was sealed in a glass capillary. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer. Crystallographic computations were carried out on a VAX 11/750 computer using the Enraf-Nonius structure determination package. The structure was solved by Patterson map and successive weighted Fourier syntheses. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized locations, assigned isotropic thermal parameters, and held fixed during refinement. Crystal data for $C_{36}H_{46}Ni_2$: space group C^5_{2h}—$P2_1/n$, a = 8.852 (3) Å, b = 11.884 (2) Å, c = 15.362 (2) Å, β = 99.05 (2)°, V = 1595.9 (6) Å^3, ρ (calcd) = 1.241 g cm^{-3}, Z = 2, T = 23 ± 1°, radiation Mo Kα. The structure was refined to R = 0.064 and R_w = 0.073 (172 variables) for 1815 independent reflections ($F_o^2 < 3\sigma(F_o^2)$) of 3657 unique reflections collected in the range $4.0 \le 2\theta \le 55.0°$.

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difference may be attributed to the increase in the charge density over the iron centers. This increase is brought about by the electron-donating effects induced by the methyl groups on the bridging and the C_5Me_5 ligands. The same behavior has been observed in the *p*-phenylene-bridged biferrocenes $(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}C_5Me_4\text{-}p\text{-}C_6H_4\text{-}\eta^5\text{-}C_5Me_4)Fe(\eta^5\text{-}C_5Me_5)$ and $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5Me_4\text{-}p\text{-}C_6H_4\text{-}\eta^5\text{-}C_5Me_4)Fe(\eta^5\text{-}C_5H_5)$ where the first oxidation occurs at 0.084 and 0.276 V, respectively.[19] Methyl substitution seems to affect noticeably the first oxidation potential; however, the second oxidation occurs at nearly identical potentials.

The synthesis of the mono- and dioxidized species, derived from **4a** and **4b**, and the study of their spectroscopic and magnetic properties are presently under way and will be reported in a future paper.

Acknowledgment. We are grateful to Professor John E. Bercaw for helpful discussion throughout the course of this work. We also wish to thank Pamela J. Shapiro for her help in the writing of this manuscript. We thank a reviewer for helpful comments.

Registry No. **2**, 112713-01-6; **3**, 112713-02-7; **4a**, 112713-03-8; **4b**, 112713-04-9; $(\eta^5\text{-}C_5Me_2)Fe(acac)$, 97210-26-9; $(\eta^5\text{-}C_5Me_5)Ni(acac)$, 97210-29-2; bis(trimethylsilyl)acetylene, 14630-40-1; 3,4-dimethylcyclopent-2-en-1-one, 30434-64-1.

Supplementary Material Available: Tables of data collection and structure solution details, atomic positional parameters, thermal parameters, root-mean-square amplitudes of vibration, and bond distances and angles for **4b** (7 pages); a listing of $10|F_o|$ vs. $10|F_c|$ for **4b** (6 pages). Ordering information is given on any current masthead page.

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Synthesis of $[Pd_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ and Its Reaction with Acids. Structure of $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^+[CF_3SO_3]^-$

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Summary: The complex $[Pd_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ (**1**) has been synthesized by the reaction of $[PdCl(CO)]_n$ with $C_5Me_5MgCl\cdot THF$. The dimer **1** reacts with HBF_4 or CF_3SO_3H to give $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^+$ whose structure as the $CF_3SO_3^-$ salt was solved by X-ray crystallography.

Nickel and platinum complexes of the type $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_2]$ have been observed when R is H or an alkyl group.[2,3] However, the corresponding palladium system has only been described when R = Ph.[4] Dimeric palladium complexes containing the stabilizing pentaphenylcyclopentadienyl group are not unusual, but they are primarily associated with alkyne oligomerization.[4] Similar palladium species containing $\eta^5\text{-}C_5R_5$ (R = H, Me) are far rarer. We have devised a synthesis of the pentamethylcyclopentadienyl dimer $[Pd_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]$ (**1**) and are investigating the chemistry associated with the metal–metal bond and the $Pd(\eta^5\text{-}C_5Me_5)(CO)$ molecular fragment. Herein, we describe the synthesis of **1** and its unusual reactivity with acids.

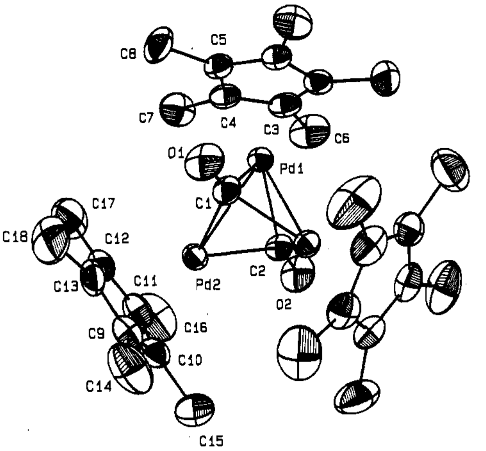

Figure 1. ORTEP drawing of $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^+$ (**2b**) with non-hydrogen atoms represented by thermal ellipsoids at the 50% probability level: Pd_1–Pd_2, 2.6254 (3) Å; Pd_2–$Pd_{2'}$, 2.6207 (4) Å; Pd_1–C_1, 2.171 (4) Å; Pd_1–C_2, 2.033 (4) Å; Pd_2–C_1, 2.061 (3) Å; Pd_2–C_2, 2.134 (3) Å; Pd_1–C_{g1} (center of gravity of Cp*), 1.926 Å; Pd_2–C_{g2} (center of gravity of Cp*), 1.939 Å; Pd_2–Pd_1–$Pd_{2'}$, 59.88 (1)°; Pd_1–Pd_2–$Pd_{2'}$, 60.059 (5)°.

Treatment at −30 °C of a THF slurry of the palladium(I) polymer $[PdCl(CO)]_n$ with $C_5Me_5MgCl\cdot THF$ affords purple, temperature-sensitive crystals of $[Pd_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ (**1**) in 44% yield.[5,6] This method contrasts with the synthesis of the pentaphenylcyclopentadienyl analogue which was prepared by reduction under CO of a Pd(II) precursor.[4]

The presence of a single band at 1839 cm^{-1} in the IR spectrum of hexane solutions of **1** indicates that the carbonyl groups bridge the two palladium atoms and that the carbon–oxygen vectors are coplanar. This contrasts with the related nickel complexes $[Ni_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_2]$ (R = H, Me), which, with one exception (C_5R_5 = C_5H_4Me), have a puckered central core and exhibit symmetric and asymmetric carbonyl absorption bands in their solution IR spectra,[7,8] and with the platinum complexes $[Pt_2(\eta^5\text{-}$

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(6) In a typical reaction, a suspension of $[PdCl(CO)]_n$ (1.0 g, 5.9 mmol) in THF (70 mL) at −25 °C was treated with a THF solution of $C_5Me_5MgCl\cdot THF$ (14.1 mL of a 0.418 M solution). The solution was stirred for 2 h at −25 °C and then stripped to dryness in vacuo at the same temperature. The residue was extracted with prechilled hexane (500 mL) at 0 °C and filtered rapidly through a Celite pad into a cooled vessel under dinitrogen. Cooling to −78 °C (2–3 days) afforded maroon crystals of $[Pd_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ (1) (0.696 g, 44%). Spectroscopic data for 1: IR (hexane) ν(CO) 1839 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) 1.87 ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz, −40 °C) 218.7 (CO), 106.7 *C*Me), 9.6 (Me) ppm. Anal. Calcd for $C_{22}H_{20}O_2Pd_2$: Pd, 39.5. Found: Pd, 39.4, 38.9.

0276-7333/88/2307-0791$01.50/0