*Organometallics* **1985**, *4*, 1594–1601

M–H–M bonds in these compounds: ~1700 $cm^{-1}$ for the asymmetric stretch (IR active), ~850 $cm^{-1}$ for the out-of-plane deformation modes (Raman active), and <150 $cm^{-1}$ for the symmetric stretch (Raman active). The first and third assignments are basically in agreement with those of Harris and Gray.[13] The bent configuration provides a partial explanation for the puzzling phenomenon, first noticed by Kirtley,[28] that most $[HW_2(CO)_{10}]^-$ ions seem to exhibit more bands assignable to hydrogen motion than expected on the basis of a linear M–H–M model.

In solution it is generally agreed that all $[HM_2(CO)_{10}]^-$ ions adopt a common geometry of high symmetry: The simple three-band infrared pattern[7] in the carbonyl stretching region may be interpreted on the basis of a structure having a linear *non-hydrogen* skeleton, in which the two $M(CO)_5$ moieties are freely rotating about each other. Whether the M–H–M core itself remains bent in *solution* is not clear. It is our guess that it should be, but there are insufficient vibrational data to settle this point.

**Acknowledgment.** This research was supported by NSF grants CHE-81-01122 and CHE-83-20484 (R.B.). Work at Brookhaven National Laboratory was performed under Contract DE-AC02-76CH00016 with the U.S. Department of Energy, Office of Basic Energy Sciences. Special thanks go to Richard K. McMullan for assistance with the neutron data collection and to Joseph Henriques for technical help.

**Registry No.** $[Ph_4P]^+[HW_2(CO)_{10}]^-$, 97012-34-5.

**Supplementary Material Available:** Listings of the final atomic positions and thermal parameters from the X-ray analysis (Table A), the geometry of the $[Ph_4P]^+$ cation (Table B), final thermal parameters from the neutron analysis (Table C), and the observed and calculated squared structure factor amplitudes (Table D) from the neutron analysis (7 pages). Ordering information is given on any current masthead page.

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# Synthesis, Structure, and Redox Properties of $[(\eta\text{-}C_5H_5)Fe\{\mu\text{-}\sigma{:}\eta^4\text{-}NiC_4R_4(\eta\text{-}C_5H_5)\}]$. A Ferrocene Analogue with a Nickelapentadiene Ring

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*Received December 12, 1984*

The reaction of $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma{:}\eta^3\text{-}(CO)C_2RR'\}(\eta\text{-}C_5H_5)_2]$ (R = Ph or H; R′ = Ph) with nickelocene or $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with nickelocene and alkyne gave the brown heterodinuclear $[\eta\text{-}C_5H_5Fe\{\mu\text{-}\sigma{:}\eta^4\text{-}NiC_4R_2R_2'(\eta\text{-}C_5H_5)\}]$ (R = H, R′ = Ph (**1**); R = R′ = Ph (**2**)), the first examples of compounds with a nickelapentadiene ring. Compound **2**, as a benzene solvate, crystallizes in space group *C*2/*m* with *Z* = 4 and lattice constants of *a* = 22.153 (8) Å, *b* = 18.850 (7) Å, *c* = 9.816 (4) Å, and *β* = 116.06 (3)°. The structure consists of an iron atom sandwiched between approximately coplanar $\eta\text{-}C_5H_5$ and $\sigma{:}\eta^4\text{-}NiC_4Ph_4$ rings. The Fe atom is slightly displaced toward the nickel atom of the nickelapentadiene ring with Ni–Fe = 2.419 (2) Å. Compound **2** has a reversible one-electron oxidation at $E_{1/2}$ = 0.67 V vs. Ag/AgCl, and green salts of $\mathbf{2}^+$ have been prepared by chemical and electrochemical oxidation. An acid-mediated oxidation by $O_2$ is described. The $^1H$ NMR and electronic spectra of **1**, **2**, and $\mathbf{2}^+$ are analyzed, and options for assignments of the near-infrared band in $\mathbf{2}^+$ at 1110 nm are given. Photolysis of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $PhC_2H$ gives a differracyclopentadiene, $[Fe_2(CO)(\mu\text{-}C_4Ph_2H_2)(\eta\text{-}C_5H_5)_2]$, a possible intermediate in the above synthesis.

*Homonuclear* low-valent metal clusters can function as oxidizable or reducible centers depending on the type of peripheral group bound to the metal atoms.[1] In general the redox properties of reducible heteronuclear clusters (where the peripheral group is CO) are less attractive and electron transfer usually results in fragmentation of the cluster;[2] an exception is $(\eta\text{-}C_5H_{5-n}Me_n)CONi_2(\mu_3\text{-}CO)_2(\eta\text{-}C_5H_5)_2$ (*n* = 1–5).[3] Whether this is true for oxidizable heteronuclear clusters (where the peripheral group is probably cyclopentadienyl) is not known. This paper describes the products obtained in an attempt to prepare heteronuclear analogues of the bis(carbyne) cluster[4] $Co_3(\mu\text{-}CR)_2(\eta\text{-}C_5H_5)_3$ which can be[1] reversibly oxidized to $[Co_3(\mu\text{-}CR)_2(\eta\text{-}C_5H_5)_3]^+$. Key components in the syntheses of heteronuclear bis(carbyne) clusters would be heterometallic $\mu$-alkyne complexes which have labile CO groups—complexes similar to the intermediate $Co_2(\mu\text{-}C_2R_2)(CO)(\eta\text{-}C_5H_5)_2$ in the synthesis of $Co_3(\mu\text{-}CR)_2(\eta\text{-}C_5H_5)_3$[5]—where scission of the $\mu$-alkyne bond in the presence of another $M(CO)_x(\eta\text{-}C_5H_5)_y$ species would give the desired cluster.[6] These heterometallic $\mu$-alkyne complexes could be prepared via a dimetallacyclopentadiene or dimetallacyclopentadienone complex as these complexes

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[2] Bond, A. M.; Honrath, U.; Lindsay, P. N. T.; Robinson, B. H.; Simpson, J.; Vahrenkamp, H. *Organometallics* **1984**, *3*, 413.

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0276-7333/85/2304-1594$01.50/0

have been shown[7] to have labile metal centers. However, in the reaction described herein, between a ferracycle and nickelocene, the major product is a nickelapentadiene analogue of ferrocene.

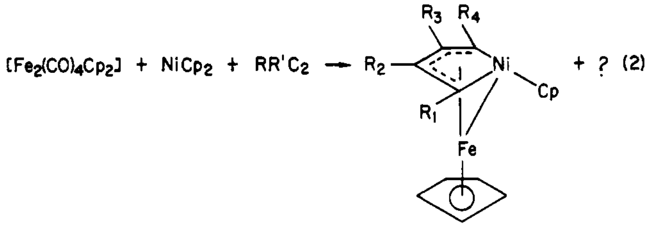
## Results and Discussion

The reaction of the dimetallacyclopentadienone[8] $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma{:}\eta^3\text{-}(CO)C_2Ph(H)\}(\eta\text{-}C_5H_5)_2]$ with nickelocene in refluxing undecane gave a brown compound which from the elemental and mass spectral analysis could be formulated as a new heterometallic dimetallacycle, $[Fe(\eta\text{-}C_5H_5)\{\mu\text{-}\sigma{:}\eta^4\text{-}NiC_4Ph_2H_2(\eta\text{-}C_5H_5)\}]$ (**1**). An analogous

$$2[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma{:}\eta^3\text{-}(CO)C_2Ph(H)\}(\eta\text{-}C_5H_5)_2] + Ni(\eta\text{-}C_5H_5)_2 \rightarrow \underset{\mathbf{1}}{Fe(\eta\text{-}C_5H_5)\{\mu\text{-}\sigma{:}\eta^4\text{-}NiC_4Ph_2H_2(\eta\text{-}C_5H_5)\}]} + (CO)_5Fe + 2Cp_2Fe \quad (1)$$

dimetallacycle $[Fe(\eta\text{-}C_5H_5)\{\mu\text{-}\sigma{:}\eta^4\text{-}NiC_4Ph_4(\eta\text{-}C_5H_5)\}]$ (**2**) was produced in low yield in a reaction designed to give a heteronuclear bis(carbyne) complex directly. Formulation **1** or **2** suggested that complexes of this type might be synthesized directly from $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, nickelocene, and alkyne, as indeed was the case; yields of 60% were achieved (Cp = $\eta\text{-}C_5H_5$).

$$CpCo(CO)_2 + Cp_2Fe_2(CO)_4 + Cp_2Ni + Ph_2C_2 \rightarrow \mathbf{2} + FeCp_2 + Co_3(CPh)_2Cp_3 + ?$$

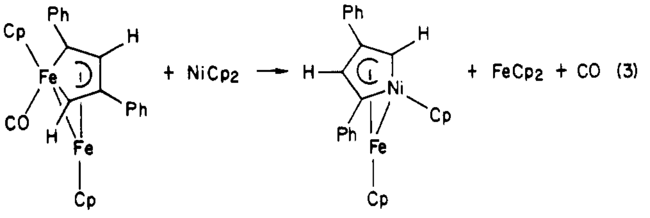


**1a**, $R_1 = R_3 = H$; $R_2 = R_4 = Ph$
**b**, $R_1 = R_4 = Ph$; $R_2 = R_3 = H$
**c**, $R_1 = R_4 = H$; $R_2 = R_3 = Ph$
**2**, $R_1 = R_2 = R_3 = R_4 = Ph$

Complexes **1** and **2** are air-stable in both solid and solution. The 18-electron structure as indicated above where a nickelacyclopentadiene ring is symmetrically bound to a $Fe(\eta\text{-}C_5H_5)$ moiety is consistent with the $^1H$ NMR and IR spectra. No $\nu(CO)$ bands were observed in the IR spectra. In the $^1H$ NMR spectrum of **2** the resonances at $\delta$ 4.82 and 4.93 and the grouping at $\delta$ 6.80, 7.07, and 7.37 can be assigned to the $Fe\text{–}C_5H_5$, $Ni\text{–}C_5H_5$, and Ph groups, respectively. The distinction between the $C_5H_5$ resonances is made on two criteria: (a) because of its association with a metallocycle the $C_5H_5(Ni)$ resonance should be shifted to lower field then $C_5H_5(Fe)$, (b) $C_5H_5(Ni)$ resonances generally tend to be to lower fields, especially when the Ni is attached to electron-withdrawing groups.[9] Juxtaposition of the Ph and H substituents on the nickelacyclopentadiene ring of **1** leads to three isomers **1a–c**, and the fact that six cyclopentadienyl resonances were observed in the $^1H$ NMR spectra from different preparations and after chromatographic separation shows that all three isomers are present in solution. Interconversion between isomers to give a thermodynamically dictated isomer ratio is not surprising in view of the known stereochemical nonrigidity of metallocyclopentadiene complexes.[7,8] Isomer **1c**, with two protons adjacent to the nickel atom can be assigned to the typical[8] low-field resonance at $\delta$ 9.30; the other low-field resonance at $\delta$ 8.93 is assigned to **1a**. Working from the relative intensities of these low-field resonances and the assumption that $\delta\ [C_5H_5(Ni)] > \delta\ [C_5H_5(Fe)]$, one arrives at an assignment for the cyclopentadienyl resonances (see Experimental Section) and the isomer ratio **1a**:**1b**:**1c** of 0.9:0.5:1.0. The ratio presumably reflects a preference for the least sterically demanding isomer.

Other minor products were identified but reaction 2 is unusually specific. Many years ago Tilney-Bassett[10] carried out similar reactions using $Fe(CO)_5$ but noted that the products—for example, $[(\eta\text{-}C_5H_5)Ni]_2(\mu\text{-}Ph_2C_2)Fe(CO)_3$ and $[(\eta\text{-}C_5H_5)NiC_2R_2]_2Fe(CO)_3$—readily disproportionated to $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[(\eta\text{-}C_5H_5)Ni]_2C_2R_2$. By ensuring that the nickelocene concentration remained high throughout the reaction, we were able to obviate this problem.

In an endeavor to prepare a heteronuclear bis(carbyne) cluster by scission of the nickelacyclopentadiene ring, **2** was heated in decalin with $[Co(CO)_2(\eta\text{-}C_5H_5)]$. A slow decomposition reaction took place to give small yields of $Co_3(\mu_3\text{-}CPh)_2(\eta\text{-}C_5H_5)_3$ and $[Co(\eta\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)]$, which accounts for most of the reacted $Co(CO)_2(\eta\text{-}C_5H_5)$ and ferrocene. This underlines the remarkable thermal stability of **1** and **2** under conditions where thermal scission of $\mu$-alkyne complexes normally occurs.[6] Consequently, it is unlikely that $\mu$-alkyne complexes are intermediates, and it is probable that **1** and **2** arise from insertion of a $Ni\text{–}C_5H_5$ group into a labile ferracyclopentadiene ring (eq 3). Indeed, in the preparation[8] of the diferracyclopentadienone precursor for reaction 1 via the photolysis of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, we noted that short irradiation times gave reasonable yields of a green complex identified as **3**, which gives **1** on reaction with $NiCp_2$. The structure of **3** was deduced by a spectral comparison with the data for the analogous $[Fe_2(CO)(\mu\text{-}C_4H_4)(\eta\text{-}C_5H_5)_2]$ characterized by Knox et al.[8] As expected, the $^1H$ NMR indicated that **3** exists as an isomeric mixture, but chromatographic separation was not possible.



**3**

Complexes **1** and **2** are members of the metallametallocene subset[11] of a rare class[12] of heterometallacyclopentadiene compounds which are thought to be involved in many reactions (often catalytic) of alkynes with organometallic substrates. Known representatives of this class are $CpM[C_4H_4Fe(CO)_3]$ (M = Co, Rh),[11] $CpCoFeC_4H_4$,[13] $[Me_4C_4Fe(CO)_3]Ni[C_4Me_4]$,[14] and $[CpMC_4R_4(CO)_2]Co(CO)_2$ (M = Mo, W).[15]

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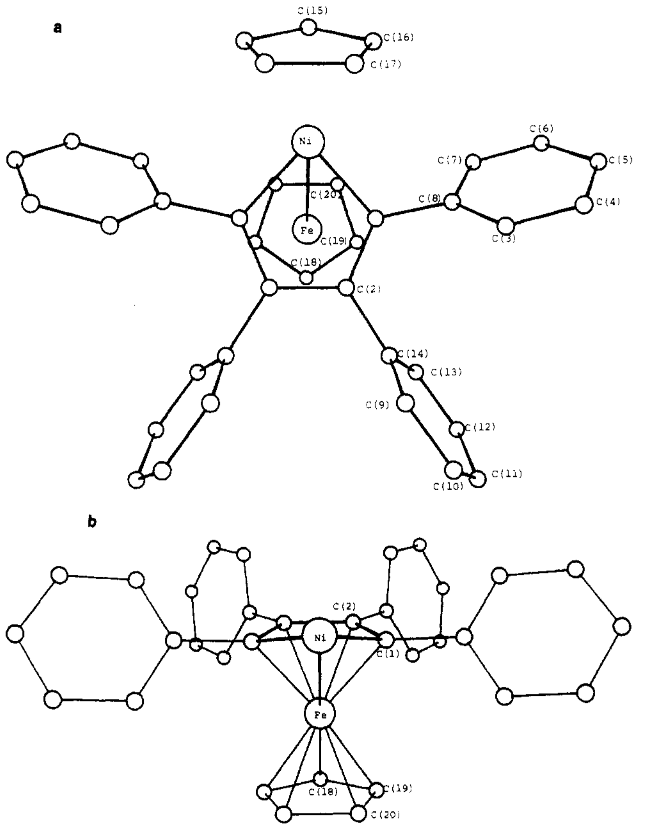

**Figure 1.** (a) Perspective drawing of 2 showing the atom numbering scheme. (The atoms defining the alternative corientation of the disordered cyclopentadienyl ring [C(151)–C(171)] are omitted.) (b) Perspective drawing of 2 showing the "sandwich" structure. (Atoms of the nickel-bound cyclopentadienyl ring are omitted for clarity.)

**Table I. Selected Bond Lengths and Angles and Mean Plane Data for 2**

Bond Lengths (Å)

| | | | |
|---|---|---|---|
| Ni–Fe | 2.419 (2) | C(1)–C(2) | 1.43 (1) |
| Ni–C(1) | 1.932 (8) | C(1)–C(8) | 1.48 (1) |
| Ni–C(15) | 2.19 (2) | C(2)–C(2) | 1.45 (2) |
| Ni–C(16) | 2.14 (1) | C(2)–C(14) | 1.503 (9) |
| Ni–C(17) | 2.10 (2) | C(15)–C(16) | 1.420 (9) |
| Ni–C(151) | 2.14 (2) | C(16)–C(17) | 1.419 (9) |
| Ni–C(161) | 2.18 (2) | C(17)–C(17) | 1.48 (3) |
| Ni–C(171) | 2.18 (2) | C(151)–C(161) | 1.411 (9) |
| Fe–C(1) | 1.979 (8) | C(161)–C(171) | 1.412 (9) |
| Fe–C(2) | 2.106 (7) | C(171)–C(171) | 1.48 (5) |
| Fe–C(18) | 2.08 (1) | C(18)–C(19) | 1.43 (1) |
| Fe–C(19) | 2.101 (9) | C(19)–C(20) | 1.39 (1) |
| Fe–C(20) | 2.089 (9) | C(20)–C(20) | 1.42 (1) |

Bond Angles (deg)

| | | | |
|---|---|---|---|
| C(15)–Ni(1)–C(16) | 38.3 (3) | C(19)–Fe(1)–C(20) | 38.7 (2) |
| C(15)–Ni(1)–C(17) | 65.0 (4) | C(20)–Fe(1)–C(20) | 39.8 (2) |
| C(16)–Ni(1)–C(17) | 39.1 (3) | Ni(1)–C(1)–C(2) | 111.9 (6) |
| C(17)–Ni(1)–C(17) | 41.2 (9) | Ni(1)–C(1)–C(8) | 119.3 (5) |
| C(151)–Ni(1)–C(161) | 38.2 (4) | C(2)–C(1)–C(8) | 125.0 (6) |
| C(151)–Ni(1)–C(171) | 64.5 (5) | C(1)–C(2)–C(14) | 123.5 (7) |
| C(161)–Ni(1)–C(171) | 37.8 (4) | C(1)–C(8)–C(3) | 119.9 (3) |
| C(171)–Ni(1)–C(171) | 39 (1) | C(1)–C(8)–C(7) | 120.0 (3) |
| Ni(1)–Fe(1)–C(1) | 50.9 (2) | C(2)–C(14)–C(9) | 117.9 (3) |
| Ni(1)–Fe(1)–C(2) | 76.0 (2) | C(2)–C(14)–C(13) | 122.0 (3) |
| Ni(1)–Fe(1)–C(18) | 170.7 (3) | Ni(1)–C(15)–C(16) | 69.0 (8) |
| Ni(1)–Fe(1)–C(19) | 134.8 (2) | Ni(1)–C(16)–C(15) | 72.7 (8) |
| Ni(1)–Fe(1)–C(20) | 106.1 (2) | Ni(1)–C(16)–C(17) | 69.0 (8) |
| C(1)–Fe(1)–C(18) | 133.6 (3) | C(15)–C(16)–C(17) | 108.5 (8) |
| C(1)–Fe(1)–C(19) | 105.4 (3) | Ni(1)–C(17)–C(16) | 71.9 (8) |
| C(1)–Fe(1)–C(20) | 109.2 (3) | Ni(1)–C(151)–C(161) | 72 (1) |
| C(1)–Fe(1)–C(2) | 40.7 (3) | Ni(1)–C(161)–C(151) | 69 (1) |
| C(2)–Fe(1)–C(18) | 112.7 (3) | Ni(1)–C(161)–C(171) | 71 (1) |
| C(2)–Fe(1)–C(19) | 112.3 (3) | C(151)–C(161)–C(171) | 109.4 (9) |
| C(2)–Fe(1)–C(20) | 139.9 (2) | Ni(1)–C(171)–C(161) | 71 (1) |
| C(2)–Fe(1)–C(2) | 40.3 (4) | Fe(1)–C(18)–C(19) | 70.9 (1) |
| C(18)–Fe(1)–C(19) | 39.9 (2) | Fe(1)–C(19)–C(18) | 69.2 (2) |
| C(18)–Fe(1)–C(20) | 65.3 (3) | Fe(1)–C(19)–C(20) | 70.2 (2) |
| | | Fe(1)–C(20)–C(19) | 71.1 (2) |

Least-Squares Planes and Distances of Atoms (Å) from the Planes[a]

1. Plane through C(1)C(2)C(1)′C(2)′

$$(-0.6985)X + (0.0000)Y + (-0.7156)Z - (-3.0654) = 0$$

| | |
|---|---|
| Ni | 0.500 (2) |
| Fe | −1.498 (2) |
| C8 | 0.130 (6) |
| C14 | −0.098 (6) |

2. Plane through C(15)C(16)C(17)C(16)′C(17)′

$$(0.9901)X + (-0.0004)Y + (-0.1401)Z - (-0.8927) = 0$$

| | |
|---|---|
| Ni | 1.751 (2) |

3. Plane through C(18)C(19)C(20)C(19)′C(20)′

$$(-0.5729)Z + (-0.0001)Y + (-0.8197)Z - (-6.1277) = 0$$

| | |
|---|---|
| Fe | 1.714 (2) |

[a] The equation of each plane is defined as $AX + BY + CY + D = 0$.

The molecular structure of the benzene solvate of $[(\eta^5\text{-}C_5H_5)Fe\{\mu\text{-}\sigma{:}\eta^4\text{-}NiC_4Ph_4(\eta^5\text{-}C_5H_5)\}]$ can be described as that of an iron atom sandwiched between approximately parallel $\eta^5$-cyclopentadienyl and nickelacyclopentadiene rings (Figure 1). The dihedral angle between the Cp(Fe) ring plane and that of the butadiene fragment of the $NiC_4$ ring is 9°. The formal relationship of this molecule to the metallocenes is obvious, and its discovery extends the limited range of heteronuclear metallametallocenes previously reported.[11] As far as we are aware, this is the first example of a compound containing a nickelacyclopentadiene ring.

The molecule has a crystallographically imposed mirror plane of symmetry passing through the Ni and Fe atoms and bisecting the Cp(Fe), Cp(Ni), and nickelacyclopentadiene rings; the phenyl substituents on the butadiene portion of the nickelacyclic ring are also related by this plane. The CpNi and CpFe units are linked by a Ni–Fe bond of length 2.419 (2) Å. An $\eta^4$-interaction of the Fe atom with the $NiC_4$ ring completes the structural picture such that each metal atom attains an 18-electron configuration. Selected intramolecular bond distances and angles and mean plane data are given in Table I, the numbering scheme is that of Figure 1. The shortest intermolecular contact not involving hydrogen atoms is 3.46 Å so the influence of packing forces on the overall molecular structure may be discounted.

Dimensions within the CpNi and CpFe moieties are unexceptional with mean values of Ni–C(Cp) = 2.15 Å and Fe–C(Cp) = 2.09 Å. The plane of the nickel-bound cyclopentadiene ring is inclined at 124° to the plane of the butadiene portion of the $NiC_4$ ring. It is interesting to note that the calculated, minimum energy configuration for the equivalent rings in the $CpCoC_6H_4$ system was found to be 126°.[16] It would appear therefore that metallocene formation does not impose additional steric demand on the CpNi fragment of the metallocycle.

Interest in the structure of 2 centers on the nickelacyclic ring, its coordination to the FeCp moiety, and the possible aromaticity of the resulting metallametallocene. The bu-

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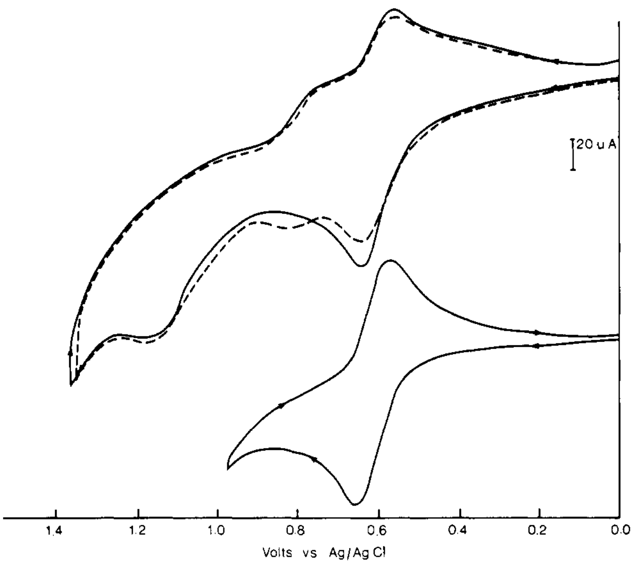


**Figure 2.** Cyclic voltammograms of 2 in acetone at 293 K on Pt (scan rate, 200 mV $s^{-1}$; potentials vs. Ag/AgCl. Scan range: 0–1.4 V, initial scan (—), subsequent scans (- - -); 0–1.0 V, initial scan showing chemical reversibility.

tadiene fragment of the $NiC_4$ ring, comprising C(1), C(2), and the mirror-plane related atoms C(1)′ and C(2)′, is strictly coplanar with the pivot atoms of the phenyl substituents displaced from this plane by +0.13 (1), C(8), and −0.10 (1) Å, C(14), respectively. (A positive displacement is in the direction away from the Fe atom.) The perpendicular displacement of the Ni atom, 0.500 (2) Å, represents a much greater departure from the butadiene plane than is observed in a number of similar dinuclear metallacyclopentadiene complexes.[13-15,17] On the other hand, the displacement of the Fe atom from the butadiene plane is only −1.498 (2) Å compared to values of 1.6–1.7 Å reported for a number of related complexes.[13,14,17] Even allowing for the smaller covalent radius of nickel (1.149 Å for Ni vs. 1.165 Å for Fe),[14] this reduction is significant and may be indicative of substantial Fe–butadiene back-donation in the molecule.[18] The displacements of the Ni and Fe atoms from the butadiene plane are complementary in the sense that the relatively close approach of the Fe atom to the $NiC_4$ ring requires a contrary displacement of the Ni atom to maintain a reasonable bonding separation between the two metal atoms. The observed Ni–Fe bond distance, 2.419 (2) Å, is somewhat shorter than the 2.45 Å observed in the ferrole complex $[Me_4C_4Fe(CO)_3]$-$Ni[C_4Me_4]$[14] but falls within the range of values observed more recently in a number of heterometallic Ni–Fe cluster compounds.[19]

The diene carbon fragment of the nickelapentadiene ring is not symmetrically disposed with respect to the Fe atom in contrast to many analogous ferra- and cobaltapentadiene ring interactions. Thus the two independent Fe-C(diene)

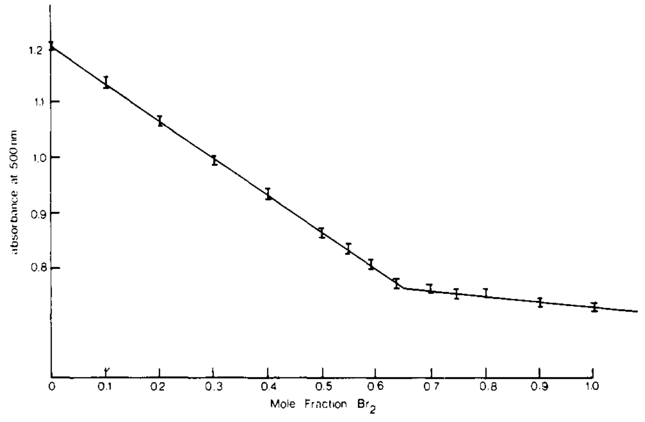
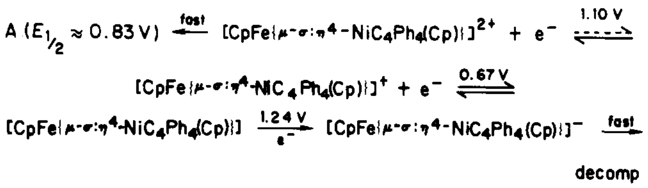


**Figure 3.** Job plot of absorbance vs. mole fraction of $Br_2$ in $CHCl_3$ at 293 K.

### Scheme I



distances, Fe–C(1) = 1.979 (8) Å and Fe–C(2) = 2.106 (7) Å, indicate that the Fe atom is displaced from the centroid of the $C_4Ph_4$ fragment toward the Ni atom. This displacement is 0.64 Å from the perpendicular Fe–ring axis. Since the Fe–C(2) distance is similar to those found in related molecules,[14,17,20] this displacement presumably arises from a need to satisfy the overlap requirements of the Ni–Fe bond rather than from an asymmetry inherent in the Fe–butadiene interaction.

Two features of the nickelacyclopentadiene ring deserve further comment. The two independent C–C bond distances, C(1)–C(2) = 1.43 (1) Å and C(2)–C(2)′ = 1.45 (2) Å, are the same within experimental error. Furthermore the Ni–C σ bond is relatively short, Ni–C(1) = 1.932 (8) Å, compared to values in the range 1.94–2.00 Å usually found for Ni–C σ bonds.[21] These observations point to a significant delocalization in the nickelapentadiene ring[18] and strengthen the analogy between compound 2 and ferrocene compounds. To test this analogy further, we investigated the redox chemistry of compound 2.

**Redox Chemistry of 2.** In acetone 2 undergoes an electrochemically reversible one-electron oxidation on Hg at $E_{1/2}^{ox}$ = 0.67 V (slope $(i_d - i)/i$ = 60 mV). Chemical reversibility of this diffusion-controlled oxidation process is achieved on Pt ($E_p^{ox}$ = 0.70 V; $E_p^{red}$ = 0.62 V; $i_p^{red}/i_p^{ox}$ = 1.0) (Figure 2). A second one-electron oxidation step occurs at more positive potentials ($E_p^{ox}$ = 1.10 V), but it is chemically irreversible. Current–voltage curves from repeat scans on Pt between 0 → 1.3 V show the growth of additional waves at $E_p^{ox}$ = 0.88 V and $E_p^{red}$ = 0.79 V which can be ascribed to a quasi-reversible couple of $E_{1/2}^{ox}$ ~ 0.83 V. The peak current for this feature a does not reach more than 20% of the peak current at 200 mV $s^{-1}$ for the first reversible couple and the new couple is not seen if the

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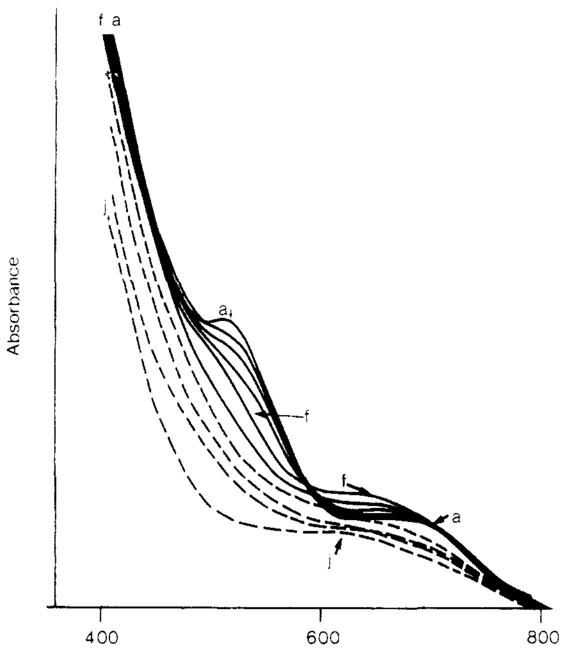

**Figure 4.** Electronic spectra (400–800 nm) of 2 in $CF_3CO_2H$ at 293 K: (a) under argon, brown solution, no reaction; (b–e) in air, green solution, arrows; (f) correspond to $2^+$; (g–j) in air, solution becomes yellow, species unknown.

repeat scan range is 0 → 1.0 V. Clearly a rapid chemical reaction follows the second oxidation step. An irreversible reduction process is observed at −1.24 V. Interestly, the analogous metallametallocenes $CpM[C_4H_4Fe(CO)_3]$ (M = Co, Rh) undergo reversible one-electron reductions at more negative potentials,[11] but their oxidative electrochemistry was not reported. In summary, the electron transfer steps for 2 are shown in Scheme I.

Green solutions of the cation $2^+$ were obtained by the controlled potential electrolysis of 2 (0.65 V vs. Ag/AgCl in $CH_2Cl_2$, 1 F $mol^{-1}$ passed) or by chemical oxidation with Ag[I] in $CH_2Cl_2$ or $CH_3CN$, or $Br_2$ in $CHCl_3$. A Job plot[12] of the reaction of 2 with $Br_2$ gave a stoichiometry of $2:Br_2$ at 1:0.55 (Figure 3), and the associated spectra showed a well-defined isosbestic point at 585 nm (eq 4). The cation

$$2[CpFe\{NiC_4Ph_4(Cp)\}] + Br_2 \rightarrow 2[CpFe\{NiC_4Ph_4(Cp)\}]^+Br^- \quad (4)$$

was isolated as its green-brown $PF_6^-$ salt, and its molar conductivity in $CH_3CN$ is consistent with a 1:1 electrolyte. A further reaction occurs with excess $Br_2$ leading to decomposition; the major product, a brown solid, is currently under investigation, but most likely results from the irreversible two-electron oxidation of 2. An interesting observation was made with $CF_3COOH$ solutions of 2. In the absence of molecular oxygen there is no reaction but in air the solution turns green after a few minutes, and, after 15–20 min, there is a further color change to yellow. These color changes correlate with the initial appearance of bands in the visible spectrum characteristic of the green cation $2^+$ (vide infra) and isosbestic points at 480 and 585 nm (Figure 4) followed by the disappearance of these bands at the onset of the yellow color. This suggests that there is an acid-mediated oxidation of 2, possibly with the prior coordination of molecular oxygen and/or a proton. Kinetic studies currently underway should provide further mechanistic details (eq 5).

$$4[CpFe\{NiC_4Ph_4(Cp)\}] + 4H^+ + O_2 \rightleftharpoons 4[CpFe\{NiC_4Ph_4(Cp)\}]^+ + 2H_2O \quad (5)$$

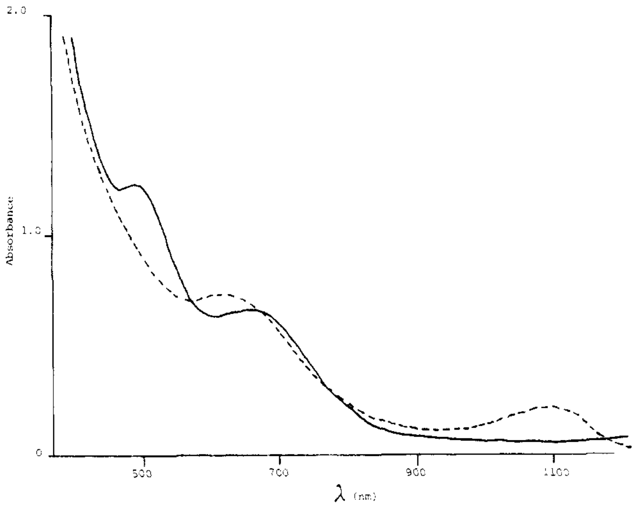

**Figure 5.** Electronic spectra of 2 (—) and $2^+$ $PF_6^-$ (---) in $CH_2Cl_2$ at 293 K.

In view of the relationship of 2 to ferrocene a characterization of the oxidation site in $2^+$ is important. $E_{1/2}{}^{ox}$ is remarkably close to that of ferrocene in the same solvent ($E_{1/2}[Fc]^{1,0}$ = 0.63 V),[5] and this fact, given that the first redox couple is reversible, favors an Fe-based redox site. The two uppermost bonding levels in ferrocene are primarily d in character,[23,24] and the ferricenium ion has the orbitally degenerate $(e_{2g})^3(a_{1g})^2$ configuration.[24] The electrochemical data for 2 are therefore indicating a similar energy gap between the upper bonding 3d levels, relative to the hypothetical electrode energy level,[2] in both FcH and 2.

Electronic spectra substantiate these conclusions. Two bands at 500 ($\epsilon$ 1837) and 665 nm ($\epsilon$ 636) are observed in the spectra of 2 in $CH_2Cl_2$ (Figure 5), together with an intense band at 325 nm in the ultraviolet envelope. The extinction coefficients of the visible bands indicate that the electronic levels responsible for the transition have considerable metal character although they are more intense than those found in ferrocene. In ferrocene weak bands at 440 ($\epsilon$ 91) and 325 nm ($\epsilon$ 52) are assigned to the transitions ${}'A_{1g} \rightarrow a'E_{1g}('E_{2g})$ and $A_{1g} \rightarrow b'E_{1g}$.[25] Obviously the change from a $\eta^5$-$C_5H_5$ ring to a $\mu$-$\sigma$:$\eta^4$-$NiC_4Ph_4$ ring does perturb the d levels on the iron, but there is sufficient correlation between the bands of 2 and FcH to assign those at 500 and 325 nm in 2 to the iron center transitions between Fe-dominated energy levels. Support for this assignment comes from their shift in energy on oxidation to $2^+$ (vide infra). Presumably the weaker band at 665 nm is associated with d transitions on the nickelapentadiene ring. On oxidation to $2^+$ the 500 and 325 nm bands disappear, the band at 665 nm shifts to 636 nm, and, surprisingly, a new band appears in the near-infrared at 1110 nm (Figure 5). Ferricenium compounds characteristically have a band at 620 nm ($\epsilon$ ~340), and the weaker higher energy bands of FcH are lost. Consequently, the three interpretations for the band at 636 nm in $2^+$ are as follows: (a) it is due to a shift of the nickelacycle absorption from 665 nm; (b) it is a ferricenium-type transition; (c) it is a combination of a and b. Since the extinction coefficient

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does not change on oxidation, we favor a, but the band is very broad and asymmetric ($\nu_{1/2} \approx 4000$ cm$^{-1}$) so the ferricenium transition could be hidden. Nonetheless, whatever the interpretation, the data place the iron atom as the major metal component of the orbitals involved in the oxidation process.

Charge transfer of the type shown in eq 6 could be assigned to the band in the near-infrared at 1110 cm$^{-1}$, and

$$[\mathrm{CpFe^{+}\{\mu\text{-}\sigma{:}\eta^{4}\text{-}NiC_4Ph_4(Cp)\}}] \xrightarrow{h\nu} [\mathrm{CpFe\{\mu\text{-}\sigma{:}\eta^{4}\text{-}Ni^{+}C_4Ph_4(Cp)\}}]^{*} \quad (6)$$

this would be consistent with the electrochemistry and the absence of a near-infrared absorption in **2**. This implies that the mixed-valence ion **2**$^+$ has more than one center of similar valence chemistry;[26] that is, the positive charge is partially localized on one metal ion (say Fe). Despite the analogy drawn between FcH$^+$ and **2**$^+$ in the discussion of the spectra and electrochemistry one *could not* conclude that the $\eta$-$C_5H_5$Fe and Ni$C_4Ph_4$($\eta$-$C_5H_5$) moieties acted as independent valence sites. There is a direct Fe–Ni bond! Support for orbital transmission comes from the observation that the phenyl resonances, although broadened, are still seen in the $^1$H NMR of **2**$^+$ whereas both M–($\eta$-$C_5H_5$) resonances collapse.

Two possibilities for the near-IR band are as follows: (i) a ligand–metal charge transfer from the phenyl groups via the $\pi$-system to the electron-deficient metal centers—this is the same type of transition observed[1] in the near-infrared spectra of [$Co_3$($\mu_3$-CPh)$_2$($\eta$-$C_5H_5$)$_3$]$^+$ (is it a general feature where phenyl groups are bonded by a $\pi$-system to electron-deficient metal centers?), (ii) a transition from a filled energy level to the singly occupied HOMO in **2**$^+$ (perhaps a low-energy metal–metal transition becomes allowed with the lower symmetry in **2**$^+$; it would then be comparable to the $^2E_{1u} \leftarrow {}^2E_{2g}$ transition in FcH$^+$).

## Conclusion

The compounds **1** and **2** reported herein represent a new type of heterometallic dimetallacyclopentadiene but more significantly, metallacycle analogues of ferrocene. Mercuration of an $\eta$-$C_5H_5$ ring in **2**, which is possible in poor yield,[27] serves to reinforce this analogy and suggests that the wealth of known ferrocene reaction chemistry may be accessible to the heterometallic complexes.

## Experimental Section

All preparations and manipulations were carried out under an atmosphere or argon. $^1$H NMR, infrared, and electronic spectra were recorded on Perkin-Elmer EM-390, Nicolet MX-9 or PE225, and Schimadzu 290 spectrometers, respectively. Electrochemical measurements were carried out as outlined previously;[1] potentials are vs. Ag/AgCl with ferrocene as reference.

Nickelocene, Co($\eta$-$C_5H_5$)(CO)$_2$,[28] and [$Fe_2$(CO)($\mu$-CO){$\mu$-$\sigma$:$\eta^3$-(CO)$C_2$Ph(H)} ($\eta$-$C_5H_5$)$_2$][8] were prepared by literature methods [Fe($\eta$-$C_5H_5$)(CO)$_2$][2] and alkynes were commercial materials. Solvents were dried by established procedures.

**Table II. Crystal Data, Data Collection, and Refinement of 2**

Crystal Data for **2**
cryst system: monoclinic
space group: *C*2/*m*
$a = 22.153\ (8)$ Å
$b = 18.850\ (7)$ Å
$c = 9.816\ (4)$ Å
$\beta = 116.06\ (3)°$
$V = 3682.3$ Å$^3$
formula: $C_{44}H_{36}$FeNi
fw: 655.31 g mol$^{-1}$
$D$(measd) = 1.21 (1) g cm$^{-1}$ (flotation)
$D$(calcd) = 1.18 g cm$^{-1}$
$Z = 4$
$F(000) = 1415.92$
cryst size: 1.2 × 0.7 × 0.4 mm
$\mu$(Mo K$\alpha$) = 8.79 cm$^{-1}$

Data Collection and Refinement for **2**
diffractometer: Nicolet P3
radiation: Mo K$\alpha$ ($\lambda$ = 0.710 69 Å)
scan type: $\theta$–$2\theta$
data limits $3 < 2\theta < 43°$
reflctns measd: $\pm h,k,l$
cryst decay: <2%[a]
total obsd data: 2196
unique data: 1492 [$I > 3\sigma(I)$]
max transmission = 1.000[b]
min transmission = 0.408
no. of variables: 188
$R(\sum||F_o| - |F_c||/|F_o|) = 0.0665$
$R_w[\sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|] = 0.0733$
$w = [1.287/(\sigma^2(F) + 0.004\,387F^2)]$

[a] Standard reflections (8, 0, 0), (0, 8, 0), and (0, 0, 5) measured after every 100 reflections. [b] See ref 30.

**Preparation of 1 and 2.** (a) Nickelocene (0.60 g, 3.2 mmol), [Fe($\eta$-$C_5H_5$)(CO)$_2$]$_2$ (1.10 g, 3.25 mmol), and PhC≡CPh (1.40 g, 7.9 mmol) dissolved in decalin (50 cm$^3$) were heated at reflux under a slow argon flush for 1 h at which stage TLC analysis (5:1 hexane/$CH_2Cl_2$) showed complete consumption of [Fe($\eta$-$C_5H_5$)(CO)$_2$]$_2$. The solution was cooled and crudely separated by column chromatography on silica. Hexane eluted a mixture of the high boiling solvent (decalin) and ferrocene (identified by mp and $^1$H NMR). The column was then stripped successively with $CH_2Cl_2$ and then acetone.

The solvent was removed in vacuo from these combined extracts and the residue plated on silica chromatography plates. Elution with 5:1 hexane/$CH_2Cl_2$ gave ten distinct bands, the majority of which were in small quantity. The most intense of the bands (brown band, $R_f$ 0.5) yielded crude **2**. Recrystallization from hexane gave **2** as brown chunky crystals: mass spectrum M$^+$ = 601 (M$^+$, $^{59}$Ni calcd = 601); $^1$H NMR (CDCl$_3$) $\delta$ 7.37 (m, 4 H), 7.07 (m, 6 H), 6.80 (s, 10 H), 4.93 (s, 5 H), 4.62 (s, 5 H); IR no $\nu$(CO) bands; $\lambda_{max}$ 665, 500, 325 nm. Anal. Calcd for $C_{38}H_{30}$FeNi: C, 75.94; H, 5.00. Found: C, 75.66; H, 5.21.

A yellow band ($R_f$ 0.65) gave the only other compound isolated in appreciable quantity. This was recrystallized from ether/hexane as orange crystals. The data are consistent with the compound tetraphenylcyclobutene; mass spectrum, M$^+$ = 358; $^1$H NMR $\delta$ 7.23 (multiplet); mp 185–188 °C; IR, no $\nu$(CO). Several other products were detected by t.l.c. but all were of insufficient quantity to characterise. Anal. Calcd: C, 93.85; H, 6.15. Found: C, 93.87; H, 5.49.

(b) To a refluxing solution of $Fe_2$($\mu$-CO)(CO){$\mu$-$\sigma$:$\eta^3$-C(O)$C_2$(H)Ph}($\eta$-$C_5H_5$)$_2$ (200 mg, 0.47 mmol)[8] in undecane (25 cm$^3$) was added nickelocene (200 mg, 1.1 mmol) in (25 cm$^3$) undecane. After 2 h the solution was filtered and chromatographed on silica gel (4:1 hexane/$CH_2Cl_2$). Separation of the major band gave brown **1** (50 mg, 0.11 mmol): mass spectrum, M$^+$ = 499 (M$^+$, $^{59}$Ni, calcd = 499); IR, no $\nu$(CO) bands; $^1$H NMR (CDCl$_3$) (isomers in square brackets, relative amount of each isomer is italics after bracket): [$\delta$ 4.13 (s, 5 H), 4.74 (s, 5 H), 7.00, 7.40 (m, 10 H), 8.93 (s, 1 H)], *0.9*, [$\delta$ 4.23 (s, 5 H), 4.41 (s, 5 H), 7.40 (m, 10 H), 9.30 (s, 2 H)], *1.0* [$\delta$ 4.64 (s, 5 H), 5.00 (s, 5 H), 7.00, 7.40 (m, 10 H)], 0.5. The same procedure could be used with **3** as the reactant and **1** is produced in much the same yield.

(c) A solution decalin (50 cm$^3$) containing nickelocene (200 mg, 1.1 mmol), [Fe($\eta$-$C_5H_5$)(CO)$_2$]$_2$ (200 mg, 0.6 mmol), Co($\eta$-$C_5H_5$-(CO)$_2$ (180 mg), and diphenylacetylene (220 mg, 1.24 mmol) was

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**Table III. Final Positional Parameters for 2**

| atom | *x*/*a* | *y*/*b* | *z*/*c* | atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|---|---|---|---|
| Ni | 0.1076 (1) | 0.0000 | 0.2729 (1) | C(13) | 0.2634 (3) | 0.1172 (4) | 0.0782 (6) |
| Fe | 0.2252 (1) | 0.0000 | 0.3270 (2) | C(14) | 0.2020 (3) | 0.0817 (4) | 0.0114 (6) |
| C(1) | 0.1540 (4) | 0.0686 (4) | 0.2069 (8) | C(15) | 0.0707 (9) | 0.0000 | 0.446 (1) |
| C(2) | 0.1761 (4) | 0.0385 (4) | 0.1032 (8) | C(16) | 0.0485 (7) | 0.0612 (5) | 0.353 (2) |
| C(3) | 0.1044 (3) | 0.1846 (3) | 0.0902 (5) | C(17) | 0.0097 (8) | 0.0391 (9) | 0.201 (1) |
| C(4) | 0.0898 (3) | 0.2555 (3) | 0.1031 (5) | C(151) | 0.000 (1) | 0.0000 | 0.177 (2) |
| C(5) | 0.1137 (3) | 0.2871 (3) | 0.2458 (5) | C(161) | 0.023 (1) | 0.0605 (7) | 0.270 (2) |
| C(6) | 0.1521 (3) | 0.2478 (3) | 0.3756 (5) | C(171) | 0.065 (1) | 0.039 (1) | 0.421 (2) |
| C(7) | 0.1667 (3) | 0.1768 (3) | 0.3627 (5) | C(18) | 0.3292 (5) | 0.0000 | 0.410 (1) |
| C(8) | 0.1428 (3) | 0.1452 (3) | 0.2200 (5) | C(19) | 0.3090 (5) | 0.0619 | 0.463 (1) |
| C(9) | 0.1605 (3) | 0.0896 (4) | −0.1432 (6) | C(20) | 0.2772 (5) | 0.0377 | 0.549 (1) |
| C(10) | 0.1805 (3) | 0.1331 (4) | −0.2312 (6) | C(30) | 0.000 | 0.235 (1) | 0.500 |
| C(11) | 0.2419 (3) | 0.1687 (4) | −0.1644 (6) | C(31) | 0.038 (1) | 0.273 (1) | 0.633 (1) |
| C(12) | 0.2834 (3) | 0.1607 (4) | −0.0097 (6) | C(32) | 0.041 (1) | 0.346 (1) | 0.630 (2) |
|  |  |  |  | C(33) | 0.000 | 0.384 (1) | 0.500 |

heated to reflux for 4 h. The solution was filtered and then chromatographed on silica gel plates (5:1 hexane/$CH_2Cl_2$). A large number of products separated which necessitated further chromatographic separation of each fraction on silica gel plates. The major products identified were ferrocene (mp 186 °C; $^1H$ NMR), ($\mu$-PhC)$_2$Co$_3$($\eta$-C$_5$H$_5$)$_3$ (mp; $^1H$ NMR),[1] hexaphenylbenzene, and 2 (10 mg) (identified by mass spectrum).

**Reaction of 2 with Co($\eta$-C$_5$H$_5$)(CO)$_2$.** 2 (200 mg) and an excess of Co($\eta$-C$_5$H$_5$)(CO$_2$) (600 mg) in undecane (30 cm$^3$) were heated under reflux for 72 h. Chromatographic separation (silica plates 5:1 hexane/$CH_2Cl_2$) revealed that only a small amount of reaction had taken place. A 180-mg sample of 2 was recovered, the other products being derived from Co($\eta$-C$_5$H$_5$)(CO)$_2$—in very small yield ($\eta$-Ph$_4$C$_4$)CoCp, Co$_3$($\mu$-CPh)$_2$($\eta$-C$_5$H$_5$)$_3$, and large amounts of green (CpCo)$_x$(CO)$_n$ [$n < x$] compounds (identified by mass spectrum).

**Photolysis of [Fe($\eta$-C$_5$H$_5$)(CO)$_2$]$_2$ and PhC$_2$H.** A solution (200 cm$^3$) of phenylacetylene (4 g) and [Fe($\eta$-C$_5$H$_5$)(CO)$_2$]$_2$ (2 g) was photolyzed with a 450-W water-cooled UV lamp for 1 h. The solvent was stripped and the residue separated on preparative silica gel plates with $CH_2Cl_2$/hexane giving a green band, a small band due to unreacted compound followed by a brown band. The green band was replated by using 4:1 hexane/$CH_2Cl_2$ to remove a small amount of ferrocene. Unstable green crystals of [Fe$_2$(CO)($\mu$-C$_4$H$_2$Ph$_2$)($\eta$-C$_5$H$_5$)$_2$] were obtained from hexane at 0 °C: mass spectrum, M$^+$ = 474 (M$^+$ calcd = 474); $\nu$(CO) 1956 cm$^{-1}$; $^1H$ NMR $\delta$ 4.15 (s), 433 (s), 4.52 (s), 5.10 (s), 5.44 (s), 7.12 (m), 7.5 (m), 9.42 (s) (the relative ratio of the cyclopentadienyl resonances is 1.0:0.8:1.0; the relative ratio of the resonances $\delta$ 5.10, 5.44, and 8.42 is respectively 1:0.9:0.8).

Brown crystals of [Fe$_2$(CO)($\mu$-CO){$\mu$-$\sigma$:$\eta^3$-C(O)C$_2$Ph(H)}($\eta$-C$_5$H$_5$)$_2$] were obtained from the brown band, which had IR and $^1H$ NMR spectra identical with those reported by Knox et al.[8]

**Preparation of 2$^+$.** AgPF$_6$ (37.2 mg, 0.06 mmol) dissolved in $CH_2Cl_2$ (10 cm$^3$) was added, with stirring, to a $CH_2Cl_2$ solution (10 cm$^3$) of 2 (16 mg, 0.06 mmol). An immediate color change to green occurred, and metallic Ag precipitated. The Ag was removed by filtration and the solution reduced to a small volume (~2 cm$^3$). The solution was layered with hexane and left at 0 °C overnight. Green-Brown crystals of 2$^+$PF$_6^-$ were obtained in 90% yield: $^1H$ NMR, broad resonance centered at $\delta$ 7.1; $\Lambda_M$ ($CH_3CN$, $10^{-3}$ M) 69 $\Omega^{-1}$ mol$^{-1}$ cm$^2$; $\lambda_{max}$ 636, 1110 nm ($CH_2Cl_2$). Anal. Calcd: C, 61.13; H, 4.02. Found: C, 61.32; H, 4.19. The cation is stable in air as a solid but slowly decomposes in solution.

**Oxidation with Br$_2$.** This was carried out quantitatively as described in the text. Data points for the Job plot were obtained at 500 nm from spectra, obtained by titrating a $2.8 \times 10^{-4}$ mol dm$^{-3}$ solution of 2 in $CH_2Cl_2$ with Br$_2$ ($6.0 \times 10^{-4}$ mol dm$^{-3}$ in $CH_2Cl_2$).

**X-ray Analysis of 2.** A sample of 2, prepared as detailed above, was recrystallised from hexane/benzene yielding purple/black plates. Precession photography (Cu K$\alpha$ radiation) indicated a C-centered, monoclinic unit cell, and the space group was confirmed as *C*2/*m* (no. 12[29]) by the success of the structure refinement. Details of the crystals, data collection, and structure refinement are summarized in Table II.

The structure was solved by Patterson methods using the interpretation facilities in the SHELXTL[31] package. This revealed the coordinates of the nickel and iron atoms on the special positions *x*,*o*,*z* (*i* for *C*2/*m* in Wyckoff notation[29]) as required for *Z* = 4. The remaining non-hydrogen atoms in the ($\eta^5$-C$_5$H$_5$)Fe{$\mu$-$\sigma$:$\eta^4$-NiC$_4$Ph$_4$($\eta^5$-C$_5$H$_5$)} molecule were found in subsequent difference Fourier, least-squares refinement cycles using the program SHELX.[32] In addition to the metal atoms, the carbon atoms C(15) (C(151) vide infra) and C(18) of the metal-bound cyclopentadiene rings lie on the mirror plane and their coordinates were constrained appropriately. A difference electron density synthesis at this stage showed four high peaks, ~3.5 e Å$^{-3}$, which defined a second molecular unit. Examination of the bond distances and angles within this unit determined that they correspond to a molecule of benzene, with the first and fourth C atoms of the ring lying on the twofold axis. Hence the four observed peaks completely define the solvate molecule. Inclusion of this benzene of solvation significantly reduced the discrepancy between the observed and calculated crystal densities.

Further inspection of the difference Fourier map revealed additional high peaks, located approximately midway between the carbon atoms of the nickel-bound cyclopentadiene ring, indicating positional disorder in the CpNi unit. These peaks were included as carbon atoms with partial occupancy, with one of the carbon atoms, C(151), constrained to lie on the mirror plane. Refinement of the occupancy factors of the atoms in the complimentary rings converged with a 60:40 distribution between the two rings [C(15),C(16),C(17)]:[C(151),C(161),C(171)], and their site occupancy factors were fixed appropriately.

Refinement continued with the phenyl substituents on the nickelacyclopentadiene ring treated as planar, rigid groups (C–C = 1.40 Å), and the C–C distances in the cyclopentadiene rings constrained to 1.42 Å. The hydrogen atoms on the phenyl rings and the iron-bound cyclopentadiene ring were included in calculated positions (C–H = 1.08 Å), with common, isotropic temperature factors. No attempt was made to locate the hydrogen atoms on thee disordered cyclopentadiene ring or on the solvate molecule.

The metal atoms, the carbon atoms of the nickelapentadiene ring, its phenyl substituents, the iron-bound cyclopentadiene ring, and the benzene solvate were assigned anisotropic temperature factors, and a weighting scheme based on counting statistics was

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(29) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. 1.

(30) Data were collected in two blocks using the same crystal in different orientations. Block 1 (1345 reflections) was corrected for absorbtion empirically by using the XEMP program from SHELXTL, giving maximum and minimum transmission 1.00 and 0.408. Block 2 (1025 reflections) was subject to analytical correction by using SHELX, giving maximum and minimum transmission 0.823 and 0.685, respectively. The data were merged, equivalent reflections averaged, and batch scale factors applied (0.8617, block 1; 1.1606 block 2). The internal consistency *R* index was *R* = 0.0446.

(31) Sheldrick, G. M. "SHELXTL", An integrated system for solving, refining, and displaying crystal structures from diffraction data; University of Gottingen, 1979.

(32) Sheldrick, G. M. "SHELX Program for Crystal Structure Determination"; University of Cambridge, 1976.

introduced. This model of the structure converged with $R = 0.0665$ and $R_w = 0.0733$ with a data to parameter ratio of 7.9. The high-temperature factors of the benzene carbon atoms suggest either some positional disorder or partial occupancy or both, but this was not investigated further. A final difference Fourier synthesis revealed no peaks higher than those previously assigned to hydrogen atoms, and the weighting scheme appeared reasonable.

In these refinements anomalous disperson effects for Ni and Fe were included in the calculation of $F_c$ using the values of Cromer and Liberman.[33] The atomic scattering factors were those of Cromer and Mann.[34] Final positional parameters for 2 are given in Table III. Tables of anisotropic temperature factors and positional parameters of calculated hydrogen atoms and a list of observed and calculated structure factor amplitudes are also available.[35]

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**Registry No.** **1a**, 96897-79-9; **1b**, 96897-80-2; **1c**, 96897-81-3; **2**, 96913-28-9; $\mathbf{2}^+PF_6^-$, 96913-31-4; $\mathbf{2}^+Br^-$, 96913-32-5; **3**, 96913-29-0; $Ni(\eta\text{-}C_5H_5)_2$, 1271-28-9; $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$, 12154-95-9; $Co(\eta\text{-}C_5H_5)(CO)_2$, 12078-25-0; $(\eta\text{-}Ph_4C_4)CoCp$, 1278-02-0; $Co_3(\mu\text{-}CPh)_2(\eta\text{-}C_5H_5)_3$, 72271-50-2; $[Fe_2(CO)(\mu\text{-}C_4H_2Ph_2)(\eta\text{-}C_5H_5)_2]$, 96928-54-0; $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma{:}\eta^3\text{-}ClO)C_2Ph(H)\}(\eta\text{-}C_5H_5)_2]$, 83691-33-2; $PhC{\equiv}CPh$, 501-65-5; Fe, 7439-89-6; Ni, 7440-02-0.

**Supplementary Material Available:** Listings of anisostropic temperature factors (Table S1), positional and thermal parameters for calculated hydrogen atoms (Table S2), and observed and calculated structure factors (Table S3) (10 pages). Ordering information is given on any current masthead page.

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(33) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(34) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(35) See paragraph at end of paper regarding supplementary material.

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# Early/Late Metal Binuclear Complexes Bridged by $\mu$-$OCH_2Ph_2P$: Structure of $(\eta^5\text{-}C_5Me_5)Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO{\cdot}C_7H_8$

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Methodology enabling the linkage of Ni and Zr via $\mu$-$OCH_2Ph_2P$ bridges has been explored. Treatment of $(COD)_2Ni$ with 4 equiv of $HOCH_2Ph_2P$ provided $(HOCH_2Ph_2P)_4Ni$ (**1**), which, upon stoichiometric addition of $Cp^*ZrMe_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$), was converted to $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPPh_2CH_2OH$ (**2**) with the concomitant formation of $CH_4$. Heterobimetallic **2** was derivatized with $PMe_3$, $P(OMe)_3$, and CO to obtain $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiPMe_3$ (**3**), $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiP(OMe)_3$ (**4**), and $Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_3NiCO$ (**5**), respectively, in good yield. An X-ray structure determination of $\mathbf{5}{\cdot}C_7H_8$ exhibited the expected pseudo-Td coordination about Zr and Ni. Crystal data: monoclinic, $P2_1/n$, $a = 14.189$ (3) Å, $b = 27.603$ (4) Å, $c = 13.448$ (3) Å, $\beta = 97.240$ (10)°, $Z = 4$, and $T = 25$ °C. Standard refinement procedures yielded an $R$ of 0.061 from 5866 data where $|F_o| \geq 3\sigma(F_o)$. Examination of the bridging unit suggests that the $\mu$-$OCH_2Ph_2P$ ligand should serve to bring two disparate metal centers together for the activation of small molecules.

## Introduction

In examining the composition of heterogeneous catalysts which make[1] or break[2] carbon–carbon bonds, it becomes evident that the combination of electron rich and electron poor metals is quite common. Typical Fischer–Tropsch (e.g., Co, Fe, Ru/$TiO_2$, $Al_2O_3$, $SiO_2$)[1,3] and reforming (e.g., Pt/Re/$Al_2O_3$)[2,4] catalysts exemplify such heterogeneous materials. Although it is clear that an important role of the support is to keep the electron-rich metal dispersed, these cocatalysts may play a more direct role[5] in the forming or breaking of C–C bonds, given the fact that certain zeolites (e.g., ZSM-5) possess the ability to catalyze the formation of hydrocarbons from methanol.[6]

In order to more fully understand the relationship between disparate metal centers, homogeneous analogues[7] to these heterogeneous species need to be constructed. In this manner, the potential cooperative reactivity of two widely different (early–late) metals[8–16] may be more clearly

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