Synthesis, Characterization, and Theoretical Studies of New Alkynylferrocene and -biferrocene Ligands and Their Platinum-Containing Dimers and Oligomers

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A series of disubstituted alkynylferrocenyl and -biferrocenyl ligands (**1**−**4**) have been synthesized and these then utilized to form a number of di-, tri-, and oligomeric platinum-containing alkynyl species (**5**−**10**). Characterization by spectroscopy and X-ray crystal structure determinations of [{$C_5H_4FeC_5H_4C\equiv CH$}$_2$] (**3**), [C_6H_5{(C_2H_5)$_3$P}$_2$PtC$\equiv$CC$_5$H$_4$-FeC$_5$H$_4$C$\equiv$CPt{P(C_2H_5)$_3$}$_2$C$_6$H$_5$] (**5**), and [(C_6H_5Pt{P(C_2H_5)$_3$}$_2$C$\equiv$C{C_5H$_4$Fe(C_5H$_4$)$_2$FeC$_5$H$_4$}C$\equiv$CPt{P(C_2H_5)$_3$}$_2$C$_6$H$_5$)] (**8**) illustrates their "rigid-rod" symmetrical geometries, featuring staggered cyclopentadienyl rings and almost perfect *anti* geometry of the ethynyl linkages in each case. Electrochemical and theoretical (extended Hückel calculations) studies on the metal complexes indicate that there is no metallocene−metallocene interaction through the alkynyl−platinum bridges.

Introduction

Carbon-rich organometallics containing rigid, π-conjugated chains are of increasing interest due to their uses in the syntheses of unsaturated organic species,[1] organometallic polymers,[2] and π-conjugated bi- or multimetallic systems.[3] These organometallic assemblies are key design targets for the study of electron-transfer processes,[4] the formation of liquid crystalline organometallic polymers,[5] the construction of molecular devices,[6] and the creation of dendrimers containing inorganic or organometallic fragments.[7]

With their importance in the field of materials science, there is currently great interest in the chemistry of ferrocenyl and ferrocenylene oligomers and polymers and their precursors.[8] The introduction of a metal or metallocene unit into "rigid-rod" one-dimensional polymers may introduce a range of properties that differ from those of conventional organic polymers: e.g., redox, magnetic, optical, electrical, and catalytic properties.[9] In addition, alkynyl ligands offer synthetic versatility and structural rigidity and allow electronic communication between redox-active centers through delocalized bonds.[10] Substitution of each of the freely rotating cyclopentadienyl rings is crucial to facilitate linear chain growth, and though alkynylferrocenes and their metal complexes[11] have been well-studied, there has been little scope for further extension due to a lack of useful starting materials. In the quest for new ferrocene-containing materials, 1,1′-diethynylferrocene has proved to be frustratingly elusive due to its spontaneous polymerization, sensitivity to air and moisture, and

(1) (a) Bunz, U. H. F. *Angew. Chem.* **1994**, *106*, 1127; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1073. (b) Diederich, F. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, Germany, 1995; p 443. (c) Diederich, F. *Nature* **1994**, *369*, 149. (d) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107.

(2) For a review on main-group- and transition-metal-based polymers, consult: Manners, I. *Angew. Chem.* **1996**, *108*, 1712; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.

(3) (a) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129. (b) Le Narvor, N.; Lapinte, C. *Organometallics* **1995**, *14*, 634. (c) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411. (d) Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem.* **1994**, *106*, 2272; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199. (e) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (f) Colbert, M. C. B.; Lewis, J.; Long, N. J.; Raithby, P. R.; Younus, M.; White, A. J. P.; Williams, D. J.; Payne, N. N.; Yellowlees, L.; Beljonne, D.; Chawdhury, N.; Friend, R. H. *Organometallics* **1998**, *17*, 3034. (g) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *487*, 139. (h) Whittal, I. R.; Humphrey, M. G.; Hockless, D. C. R.; Skelton, B. W.; White, A. H. *Organometallics* **1995**, *14*, 3970. (i) Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293. (j) Field, L. D.; George, A. V.; Hockless, D. C. R.; Purches, G. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2011. (k) Bunz, U. H. F.; Wiegelmann-Kreiter, J. E. C. *Chem. Ber.* **1996**, *129*, 785 and references therein. (l) Jia, G.; Puddephatt, R. J.; Vittal, J. J.; Payne, N. C. *Organometallics* **1993**, *12*, 263.

(4) Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem.* **1995**, *107*, 1211; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1100.

(5) (a) Altmann, M.; Bunz, U. H. F. *Angew. Chem.* **1995**, *107*, 603; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 569. (b) Oriol, L.; Serrano, J. L. *Adv. Mater.* **1995**, *7*, 348.

(6) (a) Lehn, J.-M. In *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, Germany, 1995. (b) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121. (c) Ward, M. D. *Chem. Ind.* **1996** (August), 568.

(7) (a) Liao, Y. H.; Moss, J. R. *J. Chem. Soc., Chem. Commun.* **1993**, 1774. (b) Achar, S.; Puddephatt, R. J. *Angew. Chem.* **1994**, *106*, 895; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 847. (c) Tzalis, D.; Tor, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1043. (d) Faust, R.; Diederich, F.; Gramlich, V.; Seiler, P. *Chem. Eur. J.* **1995**, *1*, 111. (e) Amoroso, A. J.; Cargill-Thompson, A. M. W.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 4828. (f) Harriman, A.; Hissler, M.; Ziessel, R.; De Cian, A.; Fisher, J. *J. Chem. Soc., Dalton Trans.* **1995**, 4067. (g) Tykwinski, R. R.; Stang, P. J. *Organometallics* **1994**, *13*, 3203. (h) Muller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *127*, 607. (i) Campagna, S.; Denti, G.; Serroni, S.; Juris, A.; Venturi, M.; Riceunto, V.; Balzani, V. *Chem. Eur. J.* **1995**, *1*, 211.

(8) (a) Togni, A., Hayashi,T., Eds. *Ferrocenes: Homogeneous Catalysis-Organic Synthesis-Materials Science*; VCH: Weinheim, Germany, 1995. (b) Long, N. J. In *Metallocenes: An Introduction to Sandwich Complexes*; Blackwell Science: Oxford, U.K., 1998.
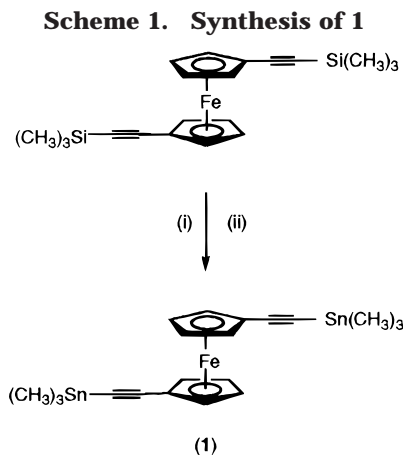
(9) (a) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637. (b) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808.

susceptibility to nucleophilic attack.[12] Disubstituted alkynylferrocene species have only been isolated by incorporation of alkyl, aryl, thioaryl, or trimethylsilyl groups, thus limiting the reactivity and, therefore, synthetic value.[8,13] Organotin exchange reactions are well-known,[14] and stannylalkynes have been involved in a variety of metal-mediated coupling reactions;[15] therefore, disubstituted alkynylferrocenes stabilized by tin moieties are of synthetic value. In contrast to simple ferrocenes, biferrocenyl species are still relatively rare,[8,16] mainly due to the lack of good synthetic routes. However, disubstitution and incorporation into multimetallic systems should prove of great interest due to their electron-delocalized, mixed-valence properties.

Here we report (i) the efficient syntheses of the new disubstituted ethynylferrocenyl and -biferrocenyl ligands $[\{C_5H_4C\equiv CSn(CH_3)_3\}_2Fe]$ (**1**), $[\{C_5H_4FeC_5H_4C\equiv Si(CH_3)_3\}_2]$ (**2**), $[\{C_5H_4FeC_5H_4C\equiv CH\}_2]$ (**3**), and $[\{C_5H_4FeC_5H_4C\equiv CSn(CH_3)_3\}_2]$ (**4**), each featuring rigid, synthetically useful linkages, and (ii) their use in the formation of metallocene−platinum-containing alkynyl species (**5**−**10**).

Results and Discussion

Synthesis. 1 was synthesized in excellent yield (91%) from the trimethylsilyl-protected ethynylferrocene species,[13] by lithiation with 1.5 M methyllithium in diethyl ether at −78 °C under N_2, followed by addition of a THF solution of $(CH_3)_3SnCl$ in situ, also at −78 °C (Scheme

(10) (a) Polin, J.; Schottenberger, H.; Schwarzhans, K. E. *Z. Naturforsch.* **1996**, *51*, 1683. (b) Lavastre, O.; Ollivier, L.; Dixneuf, P. H.; Sibandhit, S. *Tetrahedron* **1996**, *52*, 5495. (c) Khan, M. S.; Kharker, A. K.; Long, N. J.; Lewis, J.; Raithby, P. R.; Nguyen, P.; Marder, T. B.; Wittmann, F.; Friend, R. H. *J. Mater. Chem.* **1994**, *4*, 1227. (d) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920.
(11) (a) Bunz, U. H. F. *J. Organomet. Chem.* **1995**, *494*, C8. (b) Nock, H.; Schottenberger, H. *J. Org. Chem.* **1993**, *58*, 7045. (c) Onitsuko, K.; Tao, X.-Q.; Wang, W.-Q.; Otsuka, Y.; Sonogashira, K.; Adachi, T.; Yoshida, T. *J. Organomet. Chem.* **1994**, *473*, 195. (d) Colbert, M. C. B.; Lewis, J.; Long, N. J.; Raithby, P. R.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 99. (e) Sato, M.; Shintate, H.; Kawata, Y.; Sekino, M.; Katada, M.; Kawata, S. *Organometallics* **1994**, *13*, 1956. (f) Zhu, Y.; Clot, O.; Wolf, M. O.; Yap, G. P. A. *J. Am. Chem. Soc.* **1998**, *120*, 1812. (g) Osella, D.; Gambino, O.; Nervi, C.; Ravera, M.; Vittoria Russo, M.; Infante, G. *Inorg. Chim. Acta* **1994**, *225*, 35. (h) Sato, M.; Hayashi, Y.; Shintate, H.; Katada, M.; Kawata, S. *J. Organomet. Chem.* **1994**, *471*, 179. (i) Sato, M.; Mogi, E.; Kamakura, S. *Organometallics* **1995**, *14*, 3157. (j) Colbert, M. C. B.; Ingham, S. L.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1994**, 2215. (k) Colbert, M. C. B.; Edwards, A. J.; Lewis, J.; Long, N. J.; Page, N. A.; Parker, D. G.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1994**, 2589. (l) Onitsuka, K.; Tao, X.-Q.; Sonogashira, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2611. (m) Wiegand, W.; Robl, C. *Chem. Ber.* **1993**, *126*, 1807. (n) Russo, M. V.; Furlani, A.; Licoccia, S.; Paolesse, R.; Chiesi-Villa, A.; Guastini, C. *J. Organomet. Chem.* **1994**, *469*, 245. (o) Koridze, A. A.; Zdanovich, V. I.; Kizas, O. A.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem.* **1994**, *464*, 197. (p) Sato, M.; Mogi, E.; Katada, M. *Organometallics* **1995**, *14*, 4837. (q) Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *470*, 153. (r) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J.-P. *Organometallics* **1996**, *15*, 1530.
(12) Buchmeiser, M.; Schottenberger, H. *J. Organomet. Chem.* **1992**, *436*, 223.
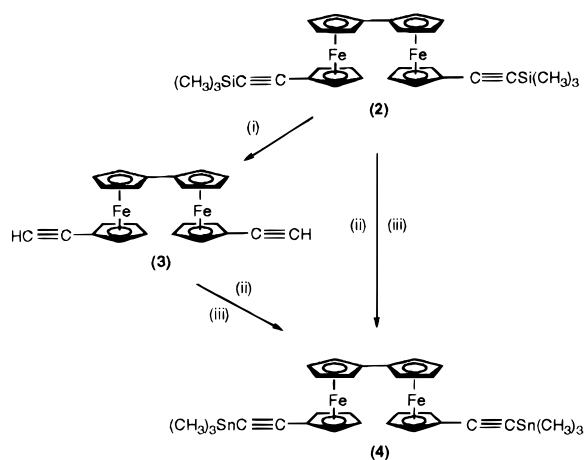(13) Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1992**, *425*, 113.
(14) Butler, I. R.; Wilkes, S. B.; McDonald, S. J.; Hobson, L. J.; Taralp, A.; Wilde, C. P. *Polyhedron* **1993**, *12*, 129.
(15) (a) Lo Sterzo, C.; Stille, J. K. *Organometallics* **1990**, *9*, 687. (b) Bunz, U. H. F.; Enkelmann, V. *Organometallics* **1994**, *13*, 3823. (c) Jones, N. D.; Wolf, M. O.; Giaquinta, D. M. *Organometallics* **1997**, *16*, 1352.
(16) (a) Mueller-Westerhoff, U. T. *Angew. Chem.* **1986**, *98*, 700; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702. (b) Yamamoto, T.; Morikata, T.; Marumaya, T.; Kubota, K.; Katada, M. *Macromolecules* **1997**, *30*, 5390. (c) Lai, L.-L.; Dong, T.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2347.
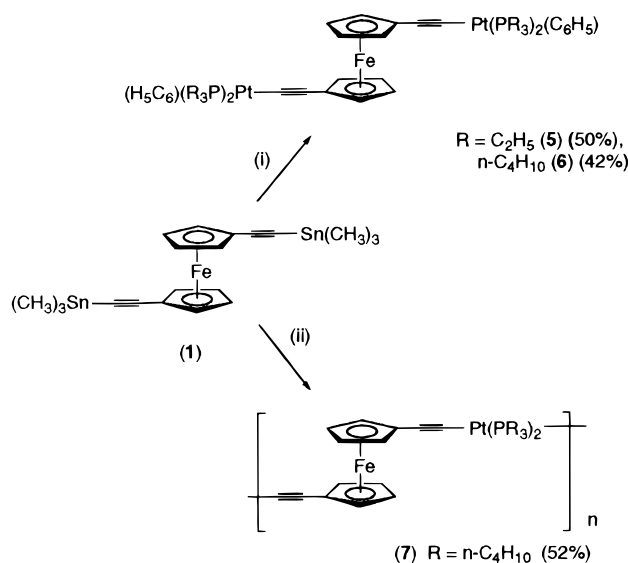
Scheme 1. Synthesis of 1

(i) CH_3Li, $(C_2H_5)_2O$, -78°C; (ii) $(CH_3)_3SnCl$, THF, -78°C

1). After the mixture was stirred at room temperature for several hours and then gently warmed to 40 °C, a crude brown solid was formed. This was subjected to sublimation (0.1 mmHg, 50 °C) to remove any excess trimethyltin chloride, and the product was isolated from the crude mixture by hexane extraction (50 mL). The resultant red-brown solution was evaporated to dryness to leave a brown solid in 91% yield. This 1,1′-disubstituted alkynylferrocene species is moderately air- and moisture-sensitive but can be manipulated using standard inert-atmosphere techniques. It possesses a typical $C\equiv C-Sn$ IR stretching frequency of 2134 cm^{-1}, and the equivalence of the $C\equiv C-Sn(CH_3)_3$ linkages is illustrated by the simple ^1H NMR spectrum.

The alkynylbiferrocene ligands **2** and **3** have been reported previously by our group,[17] but slightly modified preparations were used here to improve yields and ease of purification. In contrast to 1,1′-diethynylferrocene, 1′,1′′′-diethynylbiferrocene (**3**) is an air- and moisture-stable solid (as is **2**) and is thus synthetically useful in its own right, possessing rigid alkynyl ligands that have excellent freedom of motion due to the freely rotating cyclopentadienyl rings to which they are attached. In a fashion similar to that for **1**, the trimethyltin-substituted species **4** can be formed from either **2** or **3** (in ca. 60 and 90% yields, respectively) using 1.5 M methyllithium in diethyl ether at −78 °C, followed by addition of trimethyltin chloride in THF again at −78 °C (Scheme 2). The orange, microcrystalline powder is slightly air- and moisture-sensitive but is stable under inert atmospheres and, once again, shows a single IR $\nu(C\equiv C)$ frequency at 2136 cm^{-1}, indicating equivalence of the alkyne linkages. This was further confirmed by the X-ray crystal structure determination of **3**.

As a guide to the ligands' reactivity we concentrated on −Pt−C≡C− bond formation, as this is currently a topical field of study. Thus, **1** was reacted with *trans*-$[Pt(PR_3)_2(C_6H_5)Cl]$ (2 equiv) (R = C_2H_5, *n*-C_4H_9) using a catalytic amount of CuI (5% mol equiv) in 1,2-dichloroethane (Scheme 3). Purification was effected by column chromatography on neutral grade II alumina (using hexane−ethyl acetate 9:1 as eluent) to give the

(17) Colbert, M. C. B.; Hodgson, D.; Lewis, J.; Raithby, P. R.; Long, N. J. *Polyhedron* **1995**, *14*, 2759.

Scheme 2.　Synthesis of 2−4

(i) $K_2(CO_3)$ / CH_3OH;　(ii) CH_3Li, $(C_2H_5)_2O$, -78°C;　(iii) $(CH_3)_3SnCl$, THF, -78°C.

Scheme 3.　Synthesis of 5−7

(i) 2 equiv. *trans*-Pt(PR$_3$)$_2$(C$_6$H$_5$)Cl, CuI (5% mol), ClCH$_2$CH$_2$Cl, 85°C, 20h;
(ii) 1 equiv. *trans*-Pt(PR$_3$)Cl$_2$, CuI (5% mol), ClCH$_2$CH$_2$Cl, 85°C, 20h.

Scheme 4.　Synthesis of 8−10

(i) 2 equiv. *trans*-Pt(PR$_3$)$_2$(C$_6$H$_5$)Cl, CuI (5% mol), NH(C$_2$H$_5$)$_2$, 25°C, 1h
(ii) 2 equiv. *trans*-Pt(PR$_3$)$_2$(C$_6$H$_5$)Cl, CuI (5% mol), ClCH$_2$CH$_2$Cl, 40°C, 36h
(iii) 1 equiv. *trans*-Pt(P{n-C$_4$H$_{10}$}$_3$)$_2$Cl$_2$, CuI (5% mol), NH(C$_2$H$_5$)$_2$, 25°C, 36h

ation chromatography techniques and illustrated the formation of different sized oligomers with overall weights of $M_w = 4600$ and $M_n = 2800$. The insolubility of these oligomeric materials appears to prevent the formation of polymeric species, but further work is currently underway to incorporate solubilizing moieties. Another factor in the formation of the low-molecular-weight species is the low-yielding reaction itself. The analogous reaction to form the dimeric species gives a 42% yield, probably due to the instability of the tin species; therefore, formation of long-chain polymers is perhaps unlikely, as an almost quantitative reaction would be necessary.

Other new routes to mixed-metal species with ferrocenylethyne units incorporating nickel and palladium metal centers have been reported,[11r] but due to problems of contamination of monomers and starting materials by oligomeric byproducts, direct single-step procedures had to be avoided.

Linear chain growth in two directions from the biferrocenyl species was demonstrated by platinum−alkyne bond formation from either the H (**3**) or Sn(CH$_3$)$_3$ (**4**) terminated ligands to give **8−10** (Scheme 4). In general, reaction yields from **3** (using method i) as opposed to those using **4** (method ii) were higher mainly due to the milder conditions employed in the former pathway. This method involved stirring the reagents at room temperature for 1 h and gave an almost quantitative conversion. However, method ii involved heating the reagents in 1,2-dichloroethane for 36 h, which led to some decomposition and formation of byproducts that could be separated from the desired materials by column chromatography on neutral grade II alumina but reduced reaction yields to 50−60% (X-ray-quality crystals of **8** were grown from a two-layered mixture of methanol and dichloromethane, 1:1). **8** and **9** each exhibit single IR ν(C≡C) stretching frequencies and single ^{31}P{^{1}H} NMR peaks (with Pt satellites), showing a symmetrical geometry. However, the formation of oligomeric **10** was illustrated by a broadening of the IR ν(C≡C) peaks and closely overlapping signals in the ^{31}P{^{1}H} NMR spectrum from species of differing molecular weights. Molecular weight estimations using gel permeation chro-

trimetallic species **5** and **6** in reasonable yields as air- and moisture-stable orange-red microcrystalline powders (X-ray-quality crystals of **5** were obtained from a two-layered mixture of methanol and dichloromethane, 1:1). The simplicity of the IR (one ν(C≡C) stretching frequency at 2098 cm^{-1}) and ^{31}P{^{1}H} NMR (singlet, at δ 10.41 and 2.40 for **5** and **6**, respectively, with associated Pt satellites) data indicates the presence of symmetry around the platinum and metallocene centers.

In preliminary studies to obtain higher molecular weight species, **1** (1 equiv) was reacted with *trans*-[Pt-{P(n-C$_4$H$_{10}$)$_3$}$_2$Cl$_2$] (1 equiv) under conditions similar to those above, to form the brown solid **7** in 52% yield. Evidence for oligomerization was provided by the disappearance of starting material peaks in the IR and NMR spectra, a broadening of signals in the C≡C−Pt stretching region, and a series of resonances in very close proximity within the ^{31}P{^{1}H} NMR spectrum. Molecular weight estimations were carried out using gel perme-

Figure 1. Molecular structure of **3**.

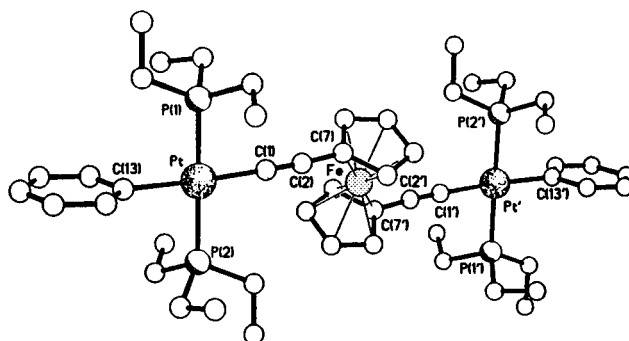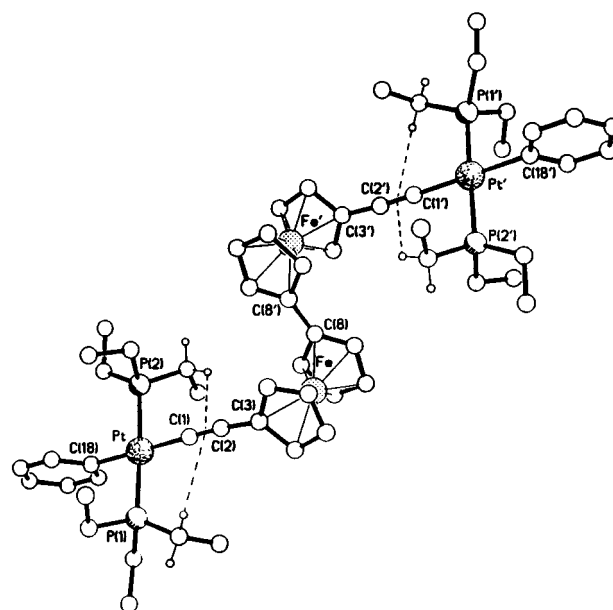**Table 1. Selected Bond Lengths (Å) and Angles
(deg) for 3**

Fe−Cp(3)	1.647(3)	Fe−Cp(8)	1.649(4)
C(1)−C(2)	1.176(5)	C(2)−C(3)	1.436(5)
C(8)−C(8′)	1.464(6)		
C(1)−C(2)−C(3)	178.3(4)		

matographic techniques were made and showed that oligomeric species of up to 12 units had been formed: $M_w = 11\,800$, $M_n = 2640$. Once again, poor solubility of these species brought them out of solution before polymerization could be effected. The greater stability of the biferrocenyl ligands compared to that of the ferrocenyl analogue **4** results in reaction yields of over 90%, which should encourage the formation of higher molecular weight materials, but solubility problems with these biferrocenyl species are more acute.

X-ray Crystallography. The structure of **3** shows the compound to have crystallographic C_i symmetry about the center of the bicyclopentadienyl linkage, its two C_5H_4 rings being coplanar to within 0.01 Å (Figure 1 and Table 1). The Cp rings of each ferrocenyl unit are slightly staggered (ca. 12°), the ethynyl and bicyclopentadienyl substituents being rotated by ca. 60° with respect to each other. The planes of the C(3)- and C(8)-based ring systems are inclined by only ca. 2°. The ethynyl C≡C bond length of 1.176(5) Å is slightly elongated, indicating a degree of delocalization into the adjacent C(2)−C(3) linkage, which is slightly shortened from a normal single bond at 1.436(5) Å. There is only a small departure from linearity within the ethynyl group, the angle at C(2) being 178.3(4)°.

The only intermolecular feature of note is an approach of the C(7) hydrogen atom of one molecule to the center of the ethynyl bond of another—the H···bond-centroid distance is 2.81 Å with an associated C−H···bond-centroid angle of 139°, the H···bond-centroid vector being inclined by 87° to the ethynyl bond.

The X-ray analysis of **5** shows the complex to be centrosymmetric with the iron atom positioned at the inversion center, thus resulting in a perfectly staggered relationship for the substituted Cp rings and an *anti* geometry for the two ethyne linkages (Figure 2 and Table 2). The geometry at platinum is slightly distorted square planar (angles in the ranges 87.6(1)−93.3(1) and 174.4(2)−177.0(1)°), the coordination distances being

Figure 2. Molecular structure of **5**.

Figure 3. Molecular structure of **8** showing the short ethyl···ethynyl contacts.

**Table 2. Selected Bond Lengths (Å) and Angles
(deg) for 5**

Pt−C(1)	2.031(5)	Pt−P(1)	2.300(1)
Pt−P(2)	2.287(1)	Pt−C(13)	2.105(2)
Fe−Cp	1.656(5)	C(1)−C(2)	1.203(7)
C(2)−C(7)	1.439(7)		
C(1)−Pt−P(1)	88.7(1)	C(1)−Pt−P(2)	93.3(1)
P(1)−Pt−C(13)	90.7(1)	P(2)−Pt−C(13)	87.6(1)
C(1)−Pt−C(13)	174.4(2)	P(1)−Pt−P(2)	177.0(1)
Pt−C(1)−C(2)	173.0(4)	C(1)−C(2)−C(7)	175.8(6)

unexceptional. The plane of the substituted Cp ring is rotated by ca. 60° out of the platinum coordination plane, the phenyl ring being oriented orthogonally (ca. 90°). There is a slight nonlinearity in the alkynyl linkage with angles of 173.0(4) and 175.8(6)° at C(1) and C(2), respectively. There are no intermolecular interactions of note.

The X-ray structure of **8** has an inversion center at the middle of the bicyclopentadienyl unit which is coplanar to within 0.05 Å (Figure 3 and Table 3). Within each ferrocenyl unit the C_5H_4 rings have a slightly staggered (ca. 8°) conformation, the rings being parallel to within 1°. In contrast to the ligand **3**, here the ethynyl and bicyclopentadienyl substituents are rotated by ca. 81° with respect to each other (cf. 60° in **3**). As in **5**, the ethynyl linkage is essentially linear with angles at C(1) and C(2) of 177.4(9) and 174.1(11)°, respectively: cf.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 8

Pt−C(1)	2.011(9)	Pt−P(1)	2.291(3)
Pt−P(2)	2.281(3)	Pt−C(18)	2.096(5)
Fe−Cp(3)	1.63(2)	Fe−Cp(8)	1.63(2)
C(1)−C(2)	1.206(14)	C(2)−C(3)	1.437(14)
C(8)−C(8′)	1.42(3)		

C(1)−Pt−P(1)	91.8(3)	C(1)−Pt−P(2)	87.1(3)
P(1)−Pt−C(18)	89.3(2)	P(2)−Pt−C(18)	91.9(2)
C(1)−Pt−C(18)	178.3(4)	P(1)−Pt−P(2)	174.1(1)
Pt−C(1)−C(2)	177.4(9)	C(1)−C(2)−C(3)	174.1(11)

173.0(4) and 175.8(6)° in **5**. The geometry at platinum is slightly distorted square planar with angles in the ranges 87.1(3)−91.9(2) and 174.1(1)−178.3(4)°, the coordination distances not differing significantly from those in **5**. As in **5**, the phenyl ring is oriented orthogonally (ca. 90°) to the coordination plane, but the proximal cyclopentadienyl ring is inclined by 47° to this plane (cf. 60° in **5**). A possible intramolecular stabilizing feature is a pair of C−H···π interactions between a methylene proton on each of the triethylphosphine groups and the center of the ethynyl bond—the H···centroid distances are 2.88 and 2.91 Å, and the H···π vectors are inclined by 79 and 80°, respectively, to the triple bond. The analogous contacts in **5** are both significantly longer at 3 Å. There are no intermolecular contacts of note.

Electrochemistry. The redox properties of ferrocene can be "fine-tuned" by coordinating different metal fragments to alkynyl linkages attached to the cyclopentadienyl rings, and recently our group[11d,j,k,17] and others[15c,18−20] have studied the electrochemical properties of metallo−C≡C−ferrocenyl systems where the metals can act as donors or acceptors. Electrochemical measurements of all complexes were carried out in a solution of 0.1 M [Bu₄N][BF₄] in CH₂Cl₂ with a sweep rate of 100 mV s⁻¹ (for more details see the Experimental Section). Complexes **5** and **6** were reversibly oxidized at −0.24 and −0.32 V vs Fc/Fc⁻, respectively ($E_{1/2}$ of Fc is +0.47 vs Ag/Ag⁻), which is due to the oxidation of ferrocenyl fragments. The redox potentials are more cathodic than that of ferrocene, suggesting that platinum fragments act as electron donors toward the ferrocenyl moiety. Changing the auxiliary ligands from ethyl to butyl phosphines on the platinum does not significantly ease the oxidation of the ferrocenyl center, as is evident by the oxidation potentials of **5** and **6**. In contrast to the electron-donating nature of platinum moieties, when group 8 metals are bonded to ferrocene through an ethynyl bridge as in *trans*-[(dppm)₂ClMC≡CC₅H₄FeC₅H₅] (M = Ru, Os),[11j] the redox potential of the ferrocene moieties becomes more anodic than ferrocene (cyclic voltammograms were obtained under same experimental conditions). Sato et al.[19] studied the cyclic voltammetry of the similar series of complexes *trans*-[Ph(PPh₃)₂PtC≡CC₅H₄FeC₅H₅] in CH₂Cl₂ and observed the cathodic shift of the redox potentials of the ferrocenyl moiety compared to ferrocene. The cyclic voltammogram of the ferrocene−platinum oligomeric

species **7** showed a single irreversible oxidation peaking at +0.06 V vs Fc/Fc⁺ due to the oxidation of the iron center of ferrocenyl fragments. Osella et al.[18] have studied the cyclic voltammetry of a series of complexes of the type [C₅H₅FeC₅H₄C≡CPt{PR₃}₂C≡CC₅H₄FeC₅H₅] in tetrahydrofuran as solvent and found that there is very little electronic interaction between the redox-active iron cores through the platinum ethynyl bridge. In contrast, our group and Zhu et al. have shown that the group 8 metal ethynyl-bridged ferrocenes [C₅H₅FeC₅H₄C≡CM{dppm}₂C≡CC₅H₄FeC₅H₅] (M = Ru, Os) in CH₂Cl₂ exhibit moderate metal−metal interactions of the ferrocenyl moieties through the metal ethynyl linkages.[11d,f] It is interesting to compare our findings with electrochemical investigations of some other ferrocene-based polymer systems, namely poly(ferrocenylsilane)[21] and poly(ferrocenylene persulfides),[22] where two reversible oxidation waves of equal intensity were observed, indicating the existence of interactions through the polymer chain. These studies also suggested that the interaction between the ferrocenyl units decreases as the length of the bridge between them increases; therefore, this may be a factor in our findings along with orbital overlap within the system (see Theoretical Studies). It should also be noted that electrostatic ("through space") interactions (mediated by solvent) can also contribute to low intermetallic separations and dominate in the absence of electronic coupling.

The biferrocenylplatinum complex **8** showed two successive irreversible oxidations (−0.20 and 0.18 V vs Fc/Fc⁺) due to the oxidation of the first and second iron centers of the biferrocene fragment. Similar irreversible oxidations were also observed in our previously reported complex *trans*-[(dppm)₂ClRuC≡C{C₅H₄Fe(C₅H₄)₂FeC₅H₄}₂C≡CRuCl(dppm)₂] and suggested that mixed-valence species are not stable when platinum or ruthenium centers are bound to biferrocene through C≡C bridges.[17] However, for **9**, one irreversible and one reversible oxidation at −0.24 and 0.14 V vs Fc/Fc⁺, respectively, were observed, while for the oligomeric species **10** two reversible oxidations were apparent. These arose at −0.09 and 0.18 V vs Fc/Fc⁺ and may be due to the oxidations of iron centers in the same molecular fragments or possibly different iron centers of different oligomers.

Theoretical Studies. To gain a better understanding of the electronic behavior of **5**, extended Hückel calculations were performed using the CACAO program developed by Mealli and Proserpio.[23,24] The input geometries were obtained from the crystallographic data of **5**, and the calculations were performed in a C_{2h} symmetry. To reduce the computational efforts, PH₃ was used instead of the actual phosphines and H instead of the C₆H₅ rings attached to the platinum centers.

A fragment calculation shows the main interactions between the ferrocene-containing fragment and the

(18) Osella, D.; Milone, L.; Nervi, C.; Ravera, M. *J. Organomet. Chem.* **1994**, *488*, 1. Osello, D.; Gobetto, R.; Nervi, C.; Ravera, M.; D'Amato, R.; Russo, M. V. *Inorg. Chem. Commun.* **1998**, *1*, 239.

(19) Sato, M.; Hayashi, Y.; Kumakura, S.; Shimizu, N.; Katada, M.; Kawata, S. *Organometallics* **1996**, *15*, 721.

(20) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184.

(21) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131.

(22) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926.

(23) Mealli, C.; Proserpio, D. M. CACAO 4.0; Instituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, Florence, Italy, 1994.

(24) Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.
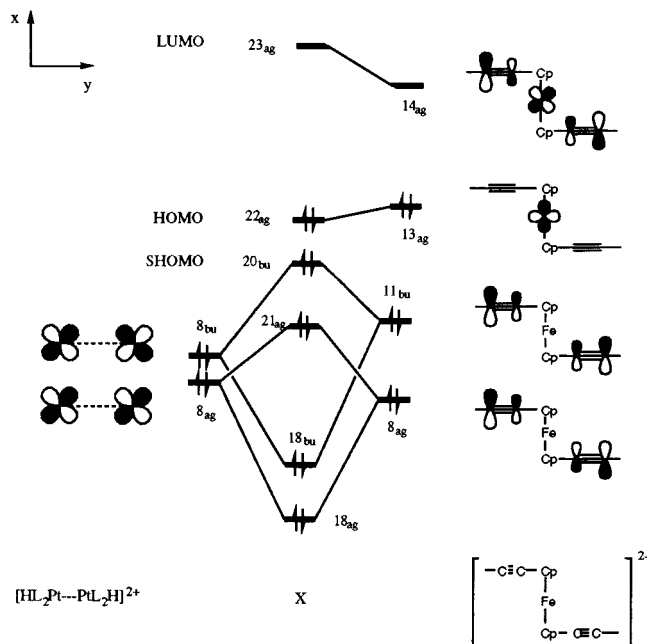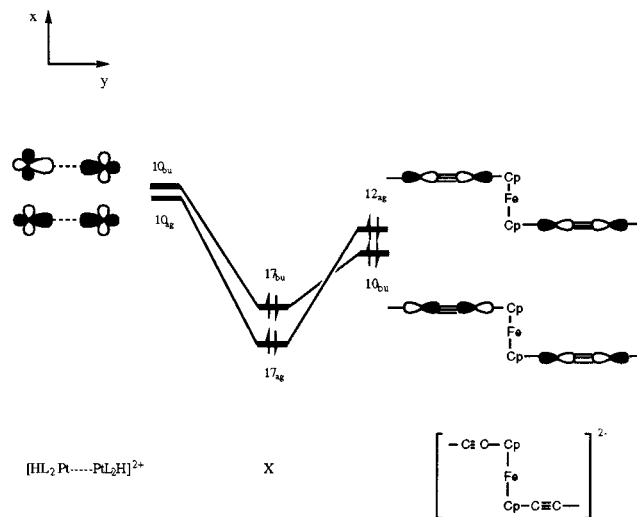
Figure 4. Interaction diagram showing the main contributions to the LUMO, HOMO, and SHOMO in **5**. For clarity the contributions from the Cp rings (which are small in these MOs) have been omitted.
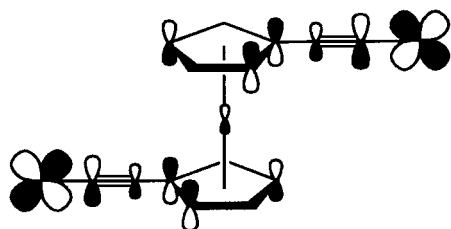
Figure 5. Representation of the most important contributions to the SHOMO in **5**.

platinum centers (Figure 4). The HOMO in **5** is mainly located on the d orbitals ($d_{x^2-y^2}$ and d_{z^2}) of the iron atom. In this molecular orbital there are no important contributions from the connecting ligands or from the platinum centers. The next occupied molecular orbital (the SHOMO) arises from a π interaction between the 8_{bu} orbitals of the platinum centers (which are mainly of d_{xy} character) and the 11_{bu} orbital of the ferrocene fragment. This generates a bonding (18_{bu}) and an antibonding (20_{bu}) orbital; the latter corresponds to the SHOMO (a full representation of this MO is shown in Figure 5). This is a four-electron destabilizing interaction which is analogous to the one that has been previously reported for more simple platinum alkynyl complexes.[25] A second linear combination of the d_{xy} orbitals from the platinum centers is possible, giving another π interaction between the ferrocene fragment and the platinum centers. The LUMO in **5** has, mainly, the same character as in the ferrocene-derivative fragment (Figure 4).

From the fragment calculation it is also possible to assign the orbitals which have major contributions to the Pt–alkynyl σ bond. The stabilizing interaction between the empty (degenerate) 10_{ag} and 10_{bu} orbitals located on the platinum fragment and the 12_{ag} and 10_{bu}

(25) Frapper, G.; Kertesz, M. *Inorg. Chem.* **1993**, *32*, 732.

Figure 6. Interaction diagram showing the main contributions to the Pt–alkynyl σ bonding.

orbitals located on the ferrocene derivative gives rise to two bonding molecular orbitals (Figure 6). This is analogous to what has been previously reported for more simple platinum–alkynyl bonds.[25]

It has been discussed elsewhere[26] that, in bridged polynuclear systems, the coupling between two metals (i.e. the M–M communication) is mediated by the extent to which the ligand orbitals overlap with the orbitals from the metal. In an ideal situation, M–M communication is achieved if there is conjugation of the metals through the bridging ligand. We have taken a simplified approach in which only the frontier orbitals are analyzed. In particular, the HOMO and SHOMO are of great importance in deciding whether there is an appropriate route for conjugation between the metal centers. From the results discussed above, it is clear that the HOMO does not provide a good *route* for Pt–Fe–Pt communication. It is located on the Fe atom, and there are no contributions from the other atoms. On the other hand, the SHOMO shows a good π-conjugation between the d_{xy} orbitals of the platinum atoms, the p_x orbitals of the alkynyl carbon atoms, and the p_x orbital of the linking carbon on the Cp ring. However, this conjugation is not *continued* through the Cp–Fe–Cp ring, suggesting that appropriate Pt–Fe–Pt communication cannot be achieved through this molecular orbital. This is consistent with the electrochemical measurements discussed in this paper.

Similar calculations have been performed on the biferrocene derivative **8**. The fragment calculations have shown that the σ- and π-interactions in this system are analogous to the ones described in **5**. The HOMO in **8** is again located on the iron atoms. The main difference between **8** and **5** is that the SHOMO in **8** is also located on the iron atoms (the maximum contributions come from their d_{z^2} orbitals). The fact that there is not an appropriate route for conjugation between the platinum centers and the central biferrocene fragment again suggests that M–M communication will not be observed. The electrochemical results are consistent with this prediction.

(26) Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Bensiman, C.; Greedan, J. E.; Crutchley, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5130.

Experimental Section

All preparations were carried out using standard Schlenk techniques.[27] All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (neutral, grade II) was used for chromatographic separations.

All NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 250.1 MHz (^{1}H), 62.9 MHz (^{13}C{^{1}H}), and 101.3 MHz (^{31}P{^{1}H}), respectively. Chemical shifts are reported in δ using CDCl$_3$ (^{1}H, δ 7.25 ppm; ^{13}C, δ 77.0 ppm) as the reference for ^{1}H and ^{13}C{^{1}H} spectra, while the ^{31}P{^{1}H} spectra were referenced to H$_3$PO$_4$. Infrared spectra were recorded using NaCl solution cells (CH$_2$Cl$_2$) using a Mattson Polaris Fourier transform IR spectrometer. Mass spectra were recorded using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out in the Department of Chemistry, Imperial College of Science, Technology and Medicine. The electrochemical responses were recorded using an Autolab PGSTAT 20 potentiostat with a standard three-electrode system (platinum working/auxiliary electrodes and silver-wire pseudo reference electrode) with a sweep rate of 100 mV s^{-1}. The electrochemical measurements were conducted at 298 K using a 0.1 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ (solvent dried over CaH$_2$) solution as supporting electrolyte, and all solutions were N$_2$-purged. All electrochemical measurements were referenced against the ferrocene/ferrocenium redox couple ($E_{1/2}$ = 0.47 V vs Ag/Ag$^+$ at 298 K in 0.1 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$).

The EH-MO calculations were performed using the program CACAO, version 4.0, developed by Mealli and Proserpio[23,24] on a DOS-PC (80486, 8 MB RAM). Standard atomic parameters were used for the calculations.[28]

The molecular weights were estimated by gel permeation chromatography.[29]

Starting Materials. Literature preparations were followed to form the compounds Pt{P(n-C$_4$H$_{10}$)$_3$}$_2$(C$_6$H$_5$)Cl,[30] Pt{P(C$_2$H$_5$)$_3$}$_2$(C$_6$H$_5$)Cl,[31] Pt{P(n-C$_4$H$_{10}$)$_3$}$_2$Cl$_2$,[30] and [{C$_5$H$_4$C≡CSi(CH$_3$)$_3$}$_2$Fe].[13]

Synthesis and Data for [{C$_5$H$_4$C≡CSn(CH$_3$)$_3$}$_2$Fe] (1). [{C$_5$H$_4$C≡CSi(CH$_3$)$_3$}$_2$Fe] (0.4 g, 1.05 mmol) was dissolved in freshly distilled THF (40 mL) and treated with 1.5 M methyllithium in diethyl ether (2.0 mL, 3.0 mmol) at −78 °C under N$_2$. The mixture was warmed to room temperature and stirred for 20 h, after which trimethyltin chloride (1.05 g, 5.25 mmol) dissolved in THF (10 mL) was added dropwise at −78 °C. The reaction mixture was again warmed to room temperature and stirred for a further 4 h, after which it was heated at 40 °C for 30 min, followed by evaporation of the solvent in vacuo. The crude solid was heated under vacuum (0.1 mmHg) at 50 °C to remove excess trimethyltin chloride by sublimation. Hexane (50 mL) was added to the residue, and while the inert atmosphere was maintained, the product was extracted via cannula filtration as a red solution, which after evaporation of the solvent afforded a brown powder (**1**) in 91% yield. IR (CH$_2$Cl$_2$); ν(C≡C) 2134 cm^{-1}. ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 0.31 (s, 18H, CH_3), 4.16 (t, 4H, C$_5H_4$), 4.38 (t, 4H, C$_5H_4$). MS (FAB +ve): m/z 560 (calcd M$^+$ 559).

Synthesis and Data for [{C$_5$H$_4$FeC$_5$H$_4$C≡CSi(CH$_3$)$_3$}$_2$] (2). 1′,1′′′-Diiodobiferrocene[32] (3.2 g, 5.10 mmol), trimethylsi-

lylethyne (2.2 mL, 15.8 mmol), and diisopropylamine (100 mL) were stirred at 0 °C for 15 min. Catalytic amounts of CuI (15 mg), Pd(OAc)$_2$ (15 mg), and PPh$_3$ (30 mg) were then added, and the stirring was continued at 0 °C for 1 h. The reaction mixture was then warmed to room temperature and heated to reflux for 16 h. After it was cooled, the suspension was filtered to remove diisopropylamine iodide, the filtrate was reduced to dryness in vacuo and redissolved in diethyl ether (100 mL), and the resulting solution washed with 10% HCl solution (3 × 100 mL), water (2 × 100 mL), aqueous sodium bicarbonate solution (3 × 100 mL), water (2 × 100 mL) and dried over MgSO$_4$ (the crude product could be used in the subsequent deprotection step without further purification, but an analytically pure sample was obtained by recrystallization from a hexane:diethyl ether (1:1) solution); yield 1.77 g, 62%. Mp: 145−147 °C. Anal. Found: C, 63.95; H, 6.58. Calcd for [C$_{30}$H$_{34}$Fe$_2$Si$_2$]: C, 63.83; H, 6.43. IR (Nujol): ν(C≡C) 2144 cm^{-1}. ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 0.22 (s, 18H, CH_3), 4.00 (t, 4H, C$_5H_4$), 4.18 (t, 4H, C$_5H_4$), 4.21 (t, 4H, C$_5H_4$), 4.36 (t, 4H, C$_5H_4$); ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ 0.26 (s, CH$_3$), 65.21 (s, C≡C−Si−), 68.79 (s, C_5H$_4$-α), 70.06 (s, C_5H$_4$-β′), 70.10 (s, C_5H$_4$-β), 73.06 (s, C_5H$_4$-α′), 84.34 (s, C_5H$_4$-ipso), 90.56 (s, C_5H$_4$-ipso′), 104.15 (s, C≡C−Si−). MS (FAB + ve): m/z 562 (calcd M$^+$ 562).

Synthesis and Data for [{C$_5$H$_4$FeC$_5$H$_4$C≡CH}$_2$] (3). 2 (500 mg, 0.9 mmol) was suspended in a diethyl ether−methanol mixture (100 mL−100 mL), and potassium carbonate (344 mg, 2.5 mmol) was added. The mixture was stirred under a nitrogen atmosphere in the absence of light for 16 h. The mixture was then filtered, reduced to dryness in vacuo, redissolved in diethyl ether (80 mL), washed with water (2 × 100 mL), and dried over MgSO$_4$. The product was further purified by column chromatography on alumina using hexane−dichloromethane (1:1) as eluent and collected as the first band (274 mg, 74%). Mp: 118−120 °C. Anal. Found: C, 68.84; H, 4.42. Calcd for [C$_{24}$H$_{18}$Fe$_2$]: C, 68.94; H, 4.34. IR (Nujol): ν-(C≡C) 2109, ν(C≡C−H) 3305 cm^{-1}. ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 2.66 (s, 2H, C≡C−H), 4.00 (t, 4H, C$_5H_4$), 4.23 (t, 4H, C$_5H_4$), 4.26 (t, 4H, C$_5H_4$), 4.40 (t, 4H, C$_5H_4$). ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ 64.46 (s, C≡CH), 68.47 (s, C_5H$_4$-α), 70.03 (s, C_5H$_4$-β), 70.15 (s, C_5H$_4$-β′), 73.07 (s, C_5H$_4$-α′), 73.86 (s, C_5H$_4$-ipso′), 82.46 (s, C≡CH), 84.35 (s, C_5H$_4$-ipso). MS (EI): m/z 418 (calcd M$^+$ 418).

Synthesis and Data for [{C$_5$H$_4$FeC$_5$H$_4$C≡CSn(CH$_3$)$_3$}$_2$] (4). A portion of 1.5 M methyllithium in diethyl ether (1.6 mL, 2.40 mmol) was added dropwise to a solution of [{C$_5$H$_4$-FeC$_5$H$_4$C≡CH}$_2$] (**3**; 0.33 g, 0.77 mmol) in dry THF (20 mL) at −78 °C. The solution was stirred at this temperature for 1 h and then warmed to room temperature. The orange-red solution was cooled again to −78 °C, at which temperature trimethyltin chloride (0.70 g, 3.50 mmol) was added dropwise as a solution in dry THF (15 mL). Stirring was continued at this temperature for 30 min, at room temperature for 2 h, and at 60 °C for 3 h. The reaction mixture was reduced to dryness and subjected to sublimation (0.1 mmHg, 50 °C) to remove the excess trimethyltin chloride. The crude reaction mixture was extracted with dry hexane (2 × 20 mL), and the resulting orange solution was collected by cannula filtration and reduced to dryness. This resulted in the isolation of an orange powder (**4**) in 90% yield. Mp: 98−102 °C. Anal. Found: C ,48.89; H, 4.14. Calcd for [C$_{30}$H$_{34}$Fe$_2$Sn$_2$]: C, 48.45; H, 4.14. IR (Nujol): ν(C≡C) 2136 cm^{-1}.; ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 0.32 (s, 18H, CH_3), 3.97 (t, 4H, C$_5H_4$), 4.19 (m, 8H, C$_5H_4$), 4.34 (t, 4H, C$_5H_4$). MS (FAB + ve): m/z 743 (calcd M$^+$ 744).

N.B.: **4** can be formed from **2** in a reaction analogous to the above, but in yields of ca. 60%.

Synthesis and Data for *trans*-[C$_6$H$_5${(C$_2$H$_5$)$_3$P}$_2$PtC≡CC$_5$H$_4$FeC$_5$H$_4$C≡CPt{P(C$_2$H$_5$)$_3$}$_2$C$_6$H$_5$] (5). A mixture of *trans*-[Pt{P(C$_2$H$_5$)$_3$}$_2$(C$_6$H$_5$)Cl] (0.22 g, 0.4 mmol), freshly prepared (CH$_3$)$_3$SnC≡CC$_5$H$_4$FeC$_5$H$_4$−C≡C−Sn(CH$_3$)$_3$ (0.11 g, 0.2

(27) Errington, R. J. In *Advanced Practical Inorganic and Metalorganic Chemistry*; Blackie: London, 1997.
(28) Alvarez, S. In *Tables of Parameters for EH Calculations*; Universitat de Barcelona: Barcelona, Spain, 1989.
(29) For GPC procedural details see: Takahashi, S.; Kariya, M.; Yatake, T.; Sonogashira, K.; Hagihara, N. *Macromolecules* **1978**, *11*, 1060.
(30) Muller, W.; Schmidtberg, G.; Brune, H. *Chem. Ber.* **1985**, *118*, 4653.
(31) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1960**, 4020.
(32) Kovar, R. F.; Rausch, M. D.; Rosenberg, H. *Organomet. Chem. Synth.* **1970−71**, *1*, 173.

mmol), and CuI (5 mol equiv) in freshly dried ClCH$_2$CH$_2$Cl (20 mL) was refluxed for 20 h under N$_2$. The reaction mixture was cooled to room temperature and solvent removed in vacuo. The crude brown residue was subjected to column chromatography on neutral grade II alumina using 9:1 hexane−ethyl acetate as eluent. The first band descending the column contained the product, which was isolated as a brown-red solid in 50% yield (0.13 g). Mp: 142−144 °C. Anal. Found: C, 47.89; H, 5.84. Calcd for [C$_{50}$H$_{78}$FeP$_4$Pt$_2$]: C, 48.08; H, 6.25. IR (CH$_2$-Cl$_2$): ν(C≡C) 2098 cm^{-1}. ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 1.08 (m, 36H, CH_3), 1.76 (m, 24H, CH_2), 4.02 (br, 4H, C$_5$H$_4$), 4.21 (br, 4H, C$_5$H$_4$), 6.76 (t, 2H, C$_6$H$_5$), 6.92 (t, 4H, C$_6$H$_5$), 7.31 (d, 4H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ 8.03 (t, CH$_3$, $^2J_{P-C}$ 12.6 Hz), 15.13 (p, CH_2, $^1J_{P-C}$ 17.3 Hz, $^2J_{Pt-C}$ 72.1 Hz), 69.61 (s, C$_5$H$_4$-α), 70.81 (s, C$_5$H$_4$-β), 73.39 (s, C$_5$H$_4$-$ipso$), 105.47 (s, C≡C−Pt-), 107.95 (t, C≡C-Pt-, $^2J_{P-C}$ 14.8 Hz), 121.02 (s, p-C$_6$H$_5$), 127.16 (s, o-C$_6$H$_5$), 139.34 (s, m-C$_6$H$_5$), 157.21 (t, C$_6$H$_5$-$ipso$, $^2J_{P-C}$ 10.2 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.3 MHz): δ 10.41, $^1J_{Pt-P}$ 2651 Hz. MS (FAB + ve): m/z 1248 (calcd M$^+$ 1249).

Synthesis and Data for *trans*-[C$_6$H$_5${(*n*-C$_4$H$_{10}$)$_3$P}$_2$PtC≡CC$_5$H$_4$FeC$_5$H$_4$C≡CPt{P(*n*-C$_4$H$_{10}$)$_3$}$_2$C$_6$H$_5$] (6). This was prepared under conditions similar to those described for **5**, in 42% yield. Mp: 70−72 °C. Anal. Found: C, 55.78; H, 7.87. Calcd for [C$_{74}$H$_{126}$FeP$_4$Pt$_2$]: C, 56.06; H, 7.95. IR (CH$_2$Cl$_2$) ν(C≡C) 2098 cm^{-1}. ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 0.88 (m, 36H, CH_3), 1.33 (m, 24H, CH_2), 1.38 (br, 24H, CH_2), 1.67 (br, 24H, CH_2), 3.99 (br, 4H, C$_5$H$_4$), 4.23 (br, 4H, C$_5$H$_4$), 6.74 (t, 2H, C$_6$H$_5$), 6.90 (t, 4H, C$_6$H$_5$), 7.27 (d, 4H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ 13.81 (s, CH_3), 22.71 (t, α-CH_2, $^3J_{P-C}$ 16.4 Hz), 24.42 (t, β-CH_2, $^3J_{P-C}$ 5.9 Hz), 26.19 (s, γ-CH_2), 69.15 (s, C$_5$H$_4$-α), 69.90 (s, C$_5$H$_4$-β), 84.20 (s, C$_5$H$_4$-$ipso$), 105.25 (s, C≡C−Pt-−, 121.85 (s, p-C$_6$H$_5$), 128.35 (s, o-C$_6$H$_5$), 139.40 (s, m-C$_6$H$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.3 MHz): δ 2.4, $^1J_{Pt-P}$ 2633 Hz. MS (FAB + ve): m/z 1586 (calcd M$^+$ 1584).

Synthesis and Data for *trans*-[{(*n*-C$_4$H$_{10}$)$_3$P}$_2$PtC≡CC$_5$H$_4$FeC$_5$H$_4$C≡C−]$_n$ (7). Under similar conditions, equimolar quantities of *trans*-[{(*n*-C$_4$H$_{10}$)$_3$P}$_2$PtCl$_2$] and (CH$_3$)$_3$SnC≡CC$_5$H$_4$FeC$_5$H$_4$C≡CSn(CH$_3$)$_3$ were reacted to give a brown solid (52%) comprising a number of oligomers. Mp: 156−158 °C. Anal. Found: C, 49.67; H, 7.46. Calcd for [C$_{38}$H$_{68}$FeP$_2$Pt: C, 54.49; H, 8.12. IR (CH$_2$Cl$_2$): ν(C≡C) 2117 (very broad) cm^{-1}. ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 0.97 (br t, 18H, CH_3), 1.49 (br m, 24H, CH_2), 2.11 (br s, 12H, CH_2), 3.99 (br s, 4H, C$_5$H$_4$), 4.23 (br s, 4H, C$_5$H$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ 13.97 (s, CH_3), 23.73 (m, α-CH_2), 24.44 (m, β-CH_2), 26.37 (m, γ-CH_2), 70.31 (s, C$_5$H$_4$-α), 70.65 (s, C$_5$H$_4$-β), 72.95 (s, C$_5$H$_4$-$ipso$), 103.63 (s, C≡C-Pt-), 104.31 (s, C≡C−Pt-). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.3 MHz): a series of singlets with ^{195}Pt satellites between δ 16 and −12. M_w = 4600, M_n = 2800.

N.B.: Microanalyses obtained for the ferrocenyl polymers were unsatisfactory. However, this is a common occurrence,[33] with the carbon values being notoriously low due to incomplete oxidation and formation of carbides and ceramics in the analytical process.

Synthesis and Data for [(C$_6$H$_5$Pt{P(C$_2$H$_5$)$_3$}$_2$C≡C-{C$_5$H$_4$Fe(C$_5$H$_4$)$_2$FeC$_5$H$_4$}C≡CPt{P(C$_2$H$_5$)$_3$}$_2$C$_6$H$_5$] (8).
Method i. 3 (0.12 g, 0.17 mmol), [PtCl{P(C$_2$H$_5$)$_3$}$_2$C$_6$H$_5$] (0.18 g, 0.34 mmol), and copper iodide (0.003 g) were all charged into a Schlenk tube under an atmosphere of nitrogen, and diethylamine (15 mL) was added. The reaction mixture was stirred for 1 h, following which it was reduced to dryness in vacuo. The crude product was washed with water (20 mL), extracted with benzene, and recrystallized from methanol−dichloromethane (1:1). The product was isolated as an orange-brown microcrystalline product in 94% yield (0.15 g). Mp: 134 °C. Anal. Found: C, 49.95; H, 5.67. Calcd for [C$_{60}$H$_{86}$Fe$_2$P$_4$-Pt$_2$]: C, 50.29; H, 6.05. IR (Nujol): ν(C≡C) 2100 cm^{-1}. ^{1}H NMR

(CDCl$_3$, 250.1 MHz): δ 1.13 (t, 36H, CH_3), 1.78 (q, 24H, CH_2), 3.89 (t, 4H, C$_5$H$_4$), 4.05 (t, 4H, C$_5$H$_4$), 4.18 (t, 4H, C$_5$H$_4$), 4.36 (t, 4H, C$_5$H$_4$), 6.82 (m, 4H, C$_6$H$_5$), 6.98 (t, 6H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ 8.08 (t, CH_3, $^2J_{P-C}$ 12.5 Hz), 15.06 (m, CH_2, $^1J_{P-C}$ 17.4 Hz, $^2J_{Pt-C}$ 71.1 Hz), 68.37 (s, C$_5$H$_4$-α), 69.60 (s, C$_5$H$_4$-β), 70.15 (s, C$_5$H$_4$-β'), 72.84 (s, C$_5$H$_4$-α'), 73.80 (s, C$_5$H$_4$-$ipso$), 82.36 (s, C$_5$H$_4$-$ipso'$), 105.25 (s, C≡C−Pt−), 107.77 (t, C≡C−Pt−, $^2J_{P-C}$ 14.7 Hz), 121.05 (s, p-C$_6$H$_5$), 127.19 (s, o-C$_6$H$_5$), 139.28 (s, m-C$_6$H$_5$), 156.58 (t, C$_6$H$_5$-$ipso$, $^2J_{P-C}$ 10.3 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.3 MHz): δ 10.46, $^1J_{Pt-P}$ 2653 Hz. MS (FAB + ve): m/z 1433, 925, 718 (calcd. M$^+$ 1433).

Method ii. 4 (0.12 g, 0.17 mmol), [PtCl{P(C$_2$H$_5$)$_3$}$_2$C$_6$H$_5$] (0.18 g, 0.34 mmol), and copper iodide (0.003 g) were all charged into a Schlenk tube under an atmosphere of nitrogen, and 1,2-dichloroethane (15 mL) was added. The reaction mixture was heated to reflux for 36 h, at which time it was then reduced to dryness in vacuo. The crude product was subjected to column chromatography on neutral grade II alumina using a mixture of hexane and dichloromethane (1:1) as eluent. The first band to descend the column contained unreacted ligand, but this was followed by a brown band that contained the product which, after evaporation of the solution in vacuo, left an orange-brown solid (0.14 g, 60%).

Synthesis and Data for [(C$_6$H$_5${(*n*-C$_4$H$_{10}$)$_3$P}$_2$PtC≡C-{C$_5$H$_4$Fe(C$_5$H$_4$)$_2$FeC$_5$H$_4$}C≡CPt{P(*n*-C$_4$H$_{10}$)$_3$}$_2$C$_6$H$_5$}] (9). 9 was synthesized by following the procedure as for **8**.

Method i. Yield: 90%. Mp: 111 °C. Anal. Found: C, 55.54; H, 7.40. Calcd for [C$_{84}$H$_{134}$Fe$_2$P$_4$Pt$_2$]: C, 56.01; H, 7.63. IR (Nujol): ν(C≡C) 2102 cm^{-1}. ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 0.68−1.70 (m, 108H, CH_2, CH_3), 3.85 (t, 4H, C$_5$H$_4$), 4.06 (t, 4H, C$_5$H$_4$), 4.17 (t, 4H, C$_5$H$_4$), 4.35 (t, 4H, C$_5$H$_4$), 6.79−7.29 (m, 10H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ 13.88 (s, CH_3), 22.74 (t, α-CH_2, $^3J_{P-C}$ 16.5 Hz), 24.36 (t, β-CH_2, $^3J_{P-C}$ 5.9 Hz), 26.10 (s, γ-CH_2), 67.81 (s, C$_5$H$_4$-α), 68.79 (s, C$_5$H$_4$-β), 69.97 (s, C$_5$H$_4$-β'), 71.05 (s, C$_5$H$_4$-α'), 84.10 (s, C$_5$H$_4$-$ipso$), 105.16 (s, C≡C−Pt−), 121.10 (s, p-C$_6$H$_5$), 128.32 (s, o-C$_6$H$_5$), 139.30 (s, m-C$_6$H$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.3 MHz): δ 3.72, $^1J_{Pt-P}$ 2662 Hz. MS (FAB + ve): m/z 1768, 1170, 1094, 676 (calcd M$^+$ 1768).

Method ii. Yield: 52%.

Synthesis and Data for [{(*n*-C$_4$H$_{10}$)$_3$P}$_2$PtC≡C{C$_5$H$_4$Fe-(C$_5$H$_4$)$_2$FeC$_5$H$_4$}C≡C−]$_n$ (10). 3 (0.05 g, 0.12 mmol), [Pt{P(*n*-C$_4$H$_{10}$)$_3$}$_2$Cl$_2$] (0.08 g, 0.12 mmol), and copper iodide (0.003 g) were all charged into a Schlenk tube under an atmosphere of nitrogen, and diethylamine (20 mL) was added. The reaction mixture was stirred for 36 h at room temperature, at which time ^{31}P{^{1}H} NMR confirmed that the platinum starting material was spent. The product was isolated as an orange-brown solid by reprecipitation from a methanol−dichloromethane mixture (yield 0.09 g, 41%). Mp: 90−92 °C. Anal. Found:[33] C, 54.14; H, 7.01. Calcd for [C$_{48}$H$_{76}$Fe$_2$P$_2$Pt]: C, 56.42; H, 7.44. IR (Nujol): ν(C≡C) 2211 cm^{-1} (broad). ^{1}H NMR (CDCl$_3$, 250.1 MHz): δ 0.98 (br t, 18H, CH_3), 1.51 (br m, 24H, CH_2), 2.12 (br s, 12H, CH_2), 3.83 (br s, 4H, C$_5$H$_4$), 4.01 (br s, 4H, C$_5$H$_4$), 4.13 (br s, 4H, C$_5$H$_4$), 4.30 (br s, 4H, C$_5$H$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ 14.03 (s, CH_3), 23.70 (br m, α-CH_2), 24.45 (br m, β-CH_2), 26.37 (br m, γ-CH_2), 67.84 (s, C$_5$H$_4$-α), 69.07 (s, C$_5$H$_4$-β), 70.26 (s, C$_5$H$_4$-β'), 71.18 (s, C$_5$H$_4$-α'), 73.14 (s, C$_5$H$_4$-$ipso'$), 84.08 (s, C$_5$H$_4$-$ipso$), 103.03 (s, C≡C−Pt−), 103.88 (s, C≡C−Pt−). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.3 MHz): a series of singlets with^{195}Pt satellites between δ 17 and −10. MS (FAB + ve): m/z 3045 [3M$^+$], 2290, 2212, 2031, [2M$^+$], 1871, 1777, 1304, 1205, 1079 [M$^+$]. M_w = 11 800, M_n = 2640.

X-ray Crystallography. Table 4 provides a summary of the crystal data and data collection and refinement parameters for compounds **3**, **5**, and **8**. All three structures were solved by direct methods, and all the non-hydrogen atoms were refined anisotropically by full-matrix least squares based on F^2. In **5** and **8** the unique pendant phenyl ring was refined as

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(33) Manners, I. R. Personal communication.

Table 4. Crystal Data and Data Collection and Refinement Parameters for 3, 5, and 8[a]

	3	5	8
formula	$C_{24}H_{18}Fe_2$	$C_{50}H_{78}P_4FePt_2$	$C_{60}H_{86}P_4Fe_2Pt_2$
solvent		$2CH_2Cl_2$	
fw	418.1	1418.9	1433.1
color, habit	orange-red rhombs	orange platelike needles	orange prisms
cryst size/mm	$0.37 \times 0.33 \times 0.23$	$0.83 \times 0.48 \times 0.14$	$0.60 \times 0.53 \times 0.53$
cryst syst	monoclinic	triclinic	monoclinic
space group (No.)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P2_1/c$ (14)
cell dimens			
a/Å	10.568(1)	9.073(2)	9.240(3)
b/Å	9.245(1)	11.401(2)	9.336(1)
c/Å	10.264(1)	14.753(3)	34.801(6)
α/deg		87.86(1)	
β/deg	116.01(1)	75.60(2)	93.55(2)
γ/deg		81.41(2)	
V/Å^3	901.3(1)	1461.6(5)	2996.2(10)
Z	2[b]	1[b]	2[b]
D_c/g cm^{-3}	1.541	1.612	1.588
F(000)	428	704	1428
μ/mm^{-1}	1.61	5.34	5.27
θ range/deg	2.1−25.0	1.8−30.0	2.2−25.0
no. of unique rflns			
measd	1586	8512	5267
obsd, $|F_o| > 4\sigma(|F_o|)$	1294	7113	3829
abs cor	semiempirical	Gaussian	semiempirical
max, min transmissn	0.75, 0.60	0.48, 0.10	0.06, 0.03
no. of variables	119	274	296
R_1[c]	0.036	0.038	0.052
wR_2[d]	0.078	0.081	0.121
weighting factors a, b[e]	0.034, 0.125	0.042, 0.000	0.070, 0.811
largest diff peak, hole/e Å^{-3}	0.27−0.28	1.75, −1.27	1.90, −1.24

[a] Details in common: graphite-monochromated Mo Kα radiation, ω-scans, Siemens P4/PC diffractometer, 203 K, refinement based on F^2. [b] The molecule has crystallographic C_i symmetry. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [e] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

an idealized rigid body. The C−H hydrogen atoms in each structure were placed in calculated positions, assigned isotropic thermal parameters (U(H) = 1.2 U_{eq}(C) [U(H) = 1.5 U_{eq}(C−Me)]), and allowed to ride on their parent atoms. The ethynyl hydrogen atom in **3** was located from a ΔF map, optimized, and allowed to ride on its parent atom. Computations were carried out using the SHELXTL PC program system.[34]

The crystallographic data (excluding structure factors) for the structures reported in Table 4 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-134581, -134582, -134583. Copies of the data can be obtained free of charge on application to

The Director, CCDC, 12 Union Road, Cambridge CB12 1EZ, U.K. (fax, Int. code+(1223)336-033; e-mail, teched@chemcrys.cam.ac.uk).

Supporting Information Available: Figures and tables giving X-ray crystallographic data for **3**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980986+

(34) SHELXTL PC, version 5.03; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.