Experimental Section

Reagents. Dichloromethane was freshly distilled under nitrogen from calcium hydride before use. Cyanogen bromide, cyanogen iodide, and iodine monochloride were purchased from Aldrich and used without further purification. Literature methods were used to prepare $[PtCl_2(COD)]$,[25] $[PtClPh(COD)]$,[26] $[Pt(COD)Cl(PhCO)]$,[27] and $[Pt(dppe)Cl(PhCO)]$.[27] The acyl compounds *trans*-$[Pt(PPh_3)_2(RCO)X]$ were synthesized from the reactions of the corresponding acid halides RCOX and $[Pt(PPh_3)_2(C_2H_4)]$ as previously described.[9,28] The palladium acyl compounds were prepared from the reactions of the acyl halides and $[Pd(PPh_3)_4]$.[29] Anal. Calcd for $[Pd(CH_3CO)Cl(PPh_3)_2]$ ($C_{38}H_{33}OClP_2Pd$): C, 64.33; H, 4.69. Found: C, 64.23; H, 4.77. Anal. Calcd for $[Pd(PPh_3)_2Cl(PhCH_2CO)]$ ($C_{44}H_{37}OClP_2Pd$): C, 67.27; H, 4.75. Found: C, 67.30; H, 4.90. The purity of the acyl complexes was established by satisfactory elemental analysis as previously described, IR spectra data, and thin-layer chromatography on silica plates with elution with chloroform. Microanalyses were performed by the Galbraith Laboratories Inc., Knoxville, TN.

Isolation of Chlorinated Platinum Product. A suspension of 100 mg of *trans*-$[Pt(PPh_3)_2Cl(PhCH_2CO)]$ was treated with a stream of chlorine gas for 30 s. The yellow solution was stirred for 30 min, and the solvent was removed in vacuo. The yellow product was recrystallized from dichloromethane–ethanol (58 mg, 55%). Anal. Calcd for $[Pt(PPh_3)_2Cl_4]$ ($C_{36}H_{30}Cl_4P_2Pt$): C, 50.20; H, 3.50; Cl, 16.45. Found: C, 49.50; H, 3.51; Cl, 16.74.

IR Spectral Studies of the Halogenation Reactions. The IR spectrum of a stock solution of 70 mg of bromine in 10 mL of dichloromethane in a 0.5-mm sodium chloride cell was stored in the memory of a Perkin-Elmer 983 infrared spectrometer. This spectrum was subtracted from the spectrum of a solution prepared by the addition of 1 mL of the bromine stock solution to 5 mg of *trans*-$[Pt(PPh_3)_2(PhCO)Cl]$. The spectra such as shown in Figures 1 and 2 were recorded a few seconds after the addition of the solution containing the halogen. Similar data were obtained for solutions of chlorine, bromine, iodine, ICl, ICN, and BrCN added to the acylplatinum or -palladium complexes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported by the National Science Foundation (CHE-8410454 and CHE-8712409). We thank the Perkin-Elmer Corp. for providing the Perkin-Elmer Model 983 infrared spectrophotometer. We thank P. J. Hanson, K. A. Hall, T. J. Anderson, and H. Silva for syntheses of some of the compounds.

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(25) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(26) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978**, 357.

(27) Anderson, G. K.; Lumetta, G. J. *Organometallics* **1985**, *4*, 1542.

(28) Kubota, M.; Rothrock, R. K.; Geibel, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1267.

(29) Coulson, D. R. *Inorg. Synth.* **1970**, *13*, 121.

A Metal Pentadienyl Prepared by Reacting a Metal Carbyne with an Enyne

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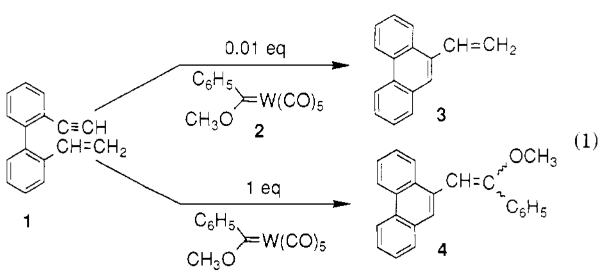
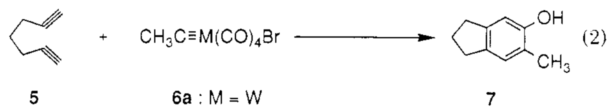
Received August 19, 1988

Unlike essentially all isolable metal pentadienyls, the tungsten pentadienyl 8 has a sickle shape. This material is produced in a novel reaction when bromotetracarbonyl(ethylidyne)tungsten is combined with 2-ethenyl-2′-ethynyl-1,1′-biphenyl. The structure, analyzed by X-ray diffraction, appears to consist of vinyl and distorted allyl moieties bonded to the metal. The chromium analogue of the metal carbyne forms not the chromium analogue of 8 but two hydrocarbons, one a protonation product of a metal pentadienyl and the other an indene. Mechanisms are suggested for the transformations.

Among a variety of transformations that occur when metal carbenes or metal carbynes combine with alkenes,[1] alkynes,[2] enynes,[3] and diynes[4] are those illustrated in eq 1 and 2. The enyne 1 is transformed by small amounts





5 6a : M = W 7
b : M = Cr

of metal carbene 2 into structure 3 and by stoichiometric amounts into structure 4 (eq 1).[3a] Diyne 5 is transformed by stoichiometric amounts of metal carbynes 6a and 6b into phenol 7 (eq 2).[4b] However, the combination of 1 with 6 represents a permutation of which no example has previously been reported.

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(1) (a) Katz, T. J.; Lee, S. J.; Acton, N. *Tetrahedron Lett.* **1976**, 4247. (b) Katz, T. J.; Acton, N. *Tetrahedron Lett.* **1976**, 4251. (c) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983. (d) Casey, C. P. in *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York: 1981; Vol. 2, Chapter 4; 1985; Vol. 3, Chapter 4. (e) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373 and references therein. (f) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (g) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2162. (h) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (i) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

(2) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. D.; Tang, P.-C.; Chan, K.-S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (c) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (d) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342 and references therein. (e) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

(3) (a) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (b) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461. (c) Xu, Y.-C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.

(4) (a) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P.-C. *J. Am. Chem. Soc.* **1985**, *107*, 1060. (b) Sivavec, T. M.; Katz, T. J. *Tetrahedron Lett.* **1985**, *26*, 2159.

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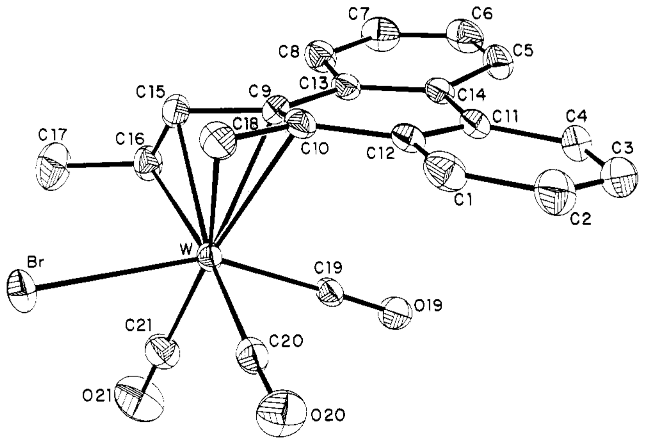


Figure 1. The structure of 8 as analyzed by X-ray diffraction. Hydrogens have been omitted for clarity. Ellipsoids are at the 30% probability level.

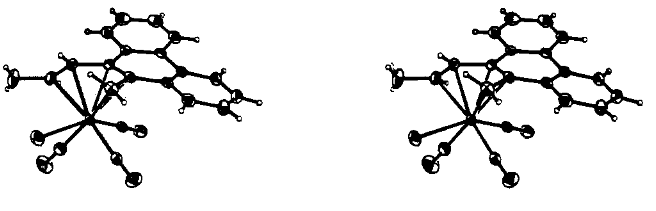
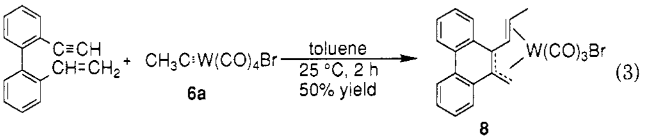
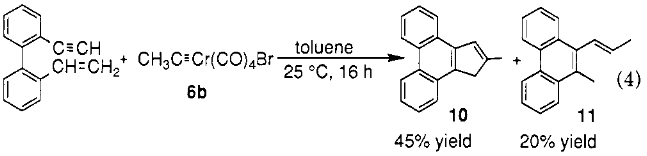


Figure 2. A stereoscopic view of structure 8.

This combination gives a metal pentadienyl,[5] a type of structure that has not previously been observed in reactions of metal carbenes or carbynes (eq 3). The reaction is significant because this transformation represents a new way to make metal pentadienyls and because 8 has a rare sickle shape (9), not the U shape characteristic of most.[5] In addition, the structures of the products in eq 3 and 4 suggest mechanistic pathways that other reactions mediated by metal carbenes may follow.

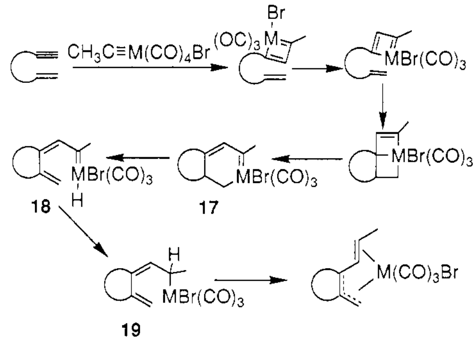




Results

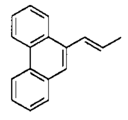
Combining enyne 1 as a 0.2 M solution in toluene for 2 h at room temperature with metal carbyne 6a[6] gives, after chromatography on silica gel and crystallization from pentane–methylene chloride (4:1), a deep red crystalline material in 50% yield. Its structure (8), analyzed by X-ray diffraction, is shown in Figure 1 without hydrogens so as not to obscure the basic skeleton and in stereoscopic projection in Figure 2 with the hydrogens. Its proton NMR and mass spectra are recorded in the supplementary material.

Scheme I



When chromium carbene 6b,[6] rather than tungsten carbene 6a, was combined with 1, no pentadienyl–chromium compound was recognized in the product, but two hydrocarbons, 10 and 11, were isolated by chromatography. The latter was also obtained from a solution of 1 in chloroform containing small amounts of water. (After 2 days at room temperature the solution of 1 deposited a blue precipitate, presumably tungsten salts, and faded from maroon to colorless.) The structure 11 was assigned on the basis of the hydrocarbon's mass spectrum and the similarities between its proton NMR spectrum and that of 12, which had been synthesized and characterized previously.[7] In particular, their vinylic, methyl, and aromatic proton resonances and their vinylic proton couplings are essentially identical, but the spectrum of 11 also includes a required three-proton singlet. The structure was assigned to 10 on the basis of its mass spectrum and the similarities of its proton NMR chemical shifts to those of the phenanthrene protons in 11 and to the methyl, vinyl, and methylene resonances in 13. (The vinyl and methylene protons are less shielded in 10 than in 13, by ca. 0.65 ppm, and they display characteristic long-range couplings.[4b,8])

9



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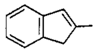

13

Attempts to obtain similar products by replacing 1 with the acyclic analogues 6-octen-1-yne[9,10] and 7-nonen-1-yne[11] seem to give only oligomers of the hydrocarbons and no recognizable pentadienylmetals. Similarly, the analogues of 6a in which the methyl was replaced by phenyl[6,12] or Br(CO)$_2$ by η^5-C_5H_5[13] failed to bring about significant re-

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[5] (a) Ernst, R. D. *Struct. Bonding Berlin* **1984**, *57*, 1. (b) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125. (c) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56.

[6] Fischer, E. O.; Kreis, G. *Chem. Ber.* **1976**, *109*, 1673. The purification by chromatography at −25 °C was replaced by repeated washing with pentane at −78 °C and drying at −20 °C for several hours.

[7] Previously characterized by: Matsumoto, M.; Dobashi, S.; Kondo, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 185. It was prepared by isomerizing a mixture of cis and trans isomers (86% cis, from a Wittig reaction) by refluxing in xylenes for 4 h with a trace of I_2.

[8] (a) Ohtsuru, M.; Tori, K.; Watanabe, H. *Chem. Pharm. Bull.* **1967**, *15*, 1015. (b) Elvidge, J. A.; Foster, R. G. *J. Chem. Soc.* **1963**, 590. (c) Banks, H.; Ziffer, H. *J. Org. Chem.* **1982**, *47*, 3743.

[9] Prepared from THF + BBr_3, followed by oxidation using pyridinium chlorochromate [Kulkarni, S. U.; Patil, V. D. *Heterocycles* **1982**, *18*, 163]. Ethylene glycol + $(CH_3)_3SiCl$ gave the acetal [Chan, T. H.; Brook, M. A.; Chaly, T. *Synthesis* **1983**, 203], $LiC_2H{\cdot}(H_2NCH_2)_2$ the acetylene [Smith, W. N.; Beumel, O. F., Jr. *Synthesis* **1974**, 441], and 5% HCl in water–THF (1:2) at 50 °C the aldehyde. Ethyltriphenylphosphonium bromide and sodamide in THF [Schlosser, M.; Schaub, B. *Chimia* **1982**, *36*, 396] converted this into the enyne (96% cis according to VPC analysis). See ref 10.

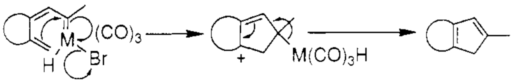
[10] Sivavec, T. M. Ph.D. Dissertation, Columbia University, 1986.

[11] Prepared 88% cis from tetrahydropyran by the procedure used to make the 6-octen-1-yne (ref 9), except that the acetal was prepared by using *p*-toluenesulfonic acid in refluxing benzene from which water was continuously removed.

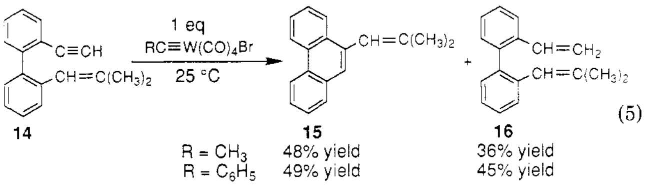
[12] Fischer, E. O.; Schubert, U.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 172.

[13] Uedelhoven, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* **1979**, *112*, 3376.

Scheme II



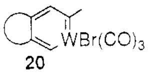
actions when they were combined with 1. And when the terminal CH_2 in 1 was replaced by $C(CH_3)_2$,[3a] the products formed either by **6a** or by its phenyl analogue [$C_6H_5C{\equiv}W(CO)_4Br$, eq 5] were **15**, the analogue of **3** in eq 1,[3a] and **16**, the structure in which the triple bond of the starting hydrocarbon has been reduced.[14]



Discussion

To account for the formation of the pentadienyl **8**, plausible steps[15] are summarized in Scheme I. Structure **17** in particular appears attractive as an intermediate because of the expectation that a diyne should then yield structure **20**, which itself is a plausible intermediate[16] on the path diynes follow when they yield phenols, as for example when **5** yields **7** in eq 2.[4b]

Pathways similar to those in Scheme I also account for the minor product **11**, formed in eq 4 by the chromium carbyne, for it seems to be the product expected when organometallics like **8** or **19** combine with protons. It is not obvious, however, why the organochromium analogue of **8** is not isolable.



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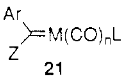

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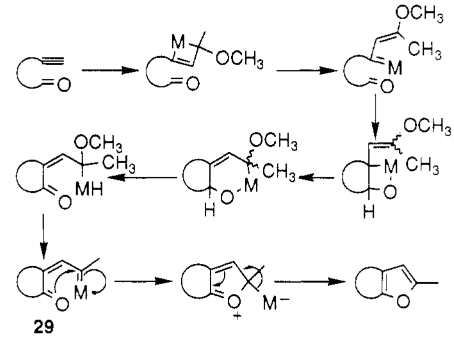
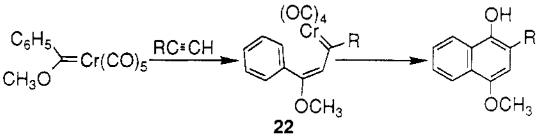
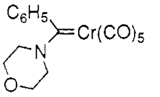
Accounting for the major product of eq 4, the indene **10**, is more interesting. Indenes have been observed to form in a number of reactions of acetylenes with metal carbenes like **21** (here Ar is an aromatic ring, Z is O or N, L is CO or a phosphine, and M is Cr or W).[17] However, it is not clear what determines whether such reactions yield indenes rather than the most common products, phenols,[2a,b] or whether they give other products like furans,[3b,17a,18] cyclobutenones,[17a,f,19] or pentadienyls. Why, in other words, do eq 3 and 4 give pentadienyls and indenes rather than, for example, phenols considering that **18** looks very much like **22**, the precursor of the phenols that form in the Dötz reaction (eq 6)?[2a,b]

Scheme III





One possibility is that coordination of acids with the metal, as in **18**,[15k] which increases the metal's formal oxidation state, increases the electrophilicity of the adjacent carbon and thereby facilitates the path to the indene depicted in Scheme II. This could account for why metal carbenes that should enjoy enhanced basicity at the metal (aminocarbenes like **23**,[17e] (*o*-methoxyphenyl)carbenes like **24**,[17f] phosphine-substituted metal carbenes like **25**,[3c,17b] and tungsten carbenes like **2**[17c,20] give in their reactions with acetylenes indenes exclusively, or at least in notably large amounts.



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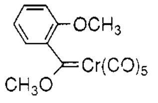

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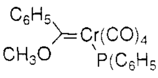

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[14] Other metal derivatives also bring about this reduction. The product was identified with one prepared by reducing the enyne in methanol containing pyridine with hydrogen and minute amounts of $Pd/BaSO_4$. See ref 10.

[15] Metal carbynes add to acetylenes, giving metallacyclobutadienes [(a) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808. (b) Churchill, M. R.; Wasserman, H. J. *J. Organomet. Chem.* **1984**, *270*, 201. (c) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (d) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (e) Churchill, M. R.; Ziller, J. W. *J. Organomet. Chem.* **1985**, *286*, 27]. More oxidized d^2 metal alkyls interconvert with d^0 metal alkylidene hydrides [(f) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121. (g) Canestrari, M.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1979**, 913. (h) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648], as do d^2 metal alkylidenes with d^0 metal alkylidyne hydrides [(i) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710. (j) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739. (k) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322].

[16] The intermediacy of metallabenzenes accounts for the formation of cyclopentadienylmetals in other reactions of metal carbynes with acetylenes [Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574] as well as in a reaction of a dilithiobutadiene with cyclopentadienyliodoiron carbonyl [Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463]. Two metallabenzenes prepared in other ways have been isolated [Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811. Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612].

[17] (a) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177. (b) Dötz, K. H.; Dietz, R.; Kappenstein, C.; Neugebauer, D.; Schubert, U. *Chem. Ber.* **1979**, *112*, 3682. (c) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (d) Tang, P.-C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132. (e) Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915. (f) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

[18] (a) Dötz, K. H.; Dietz, R.; Neugebauer, D. *Chem. Ber.* **1979**, *112*, 1486. (b) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550. (c) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520. (d) McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.

[19] (a) Dötz, K. H.; Dietz, R. *J. Organomet. Chem.* **1978**, *157*, C55. (b) Yamashita, A.; Scahill, T. A.; Toy, A. *Tetrahedron Lett.* **1985**, *26*, 2969. (c) Dötz, K. H.; Sturm, W. *J. Organomet. Chem.* **1986**, *310*, C22. (d) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471.

[20] That the polarization of tungsten carbenes, compared to other group VIB metal carbenes, is enhanced in the direction indicated is implied by these very different kinds of observations [(a) diminished regioselectivity in olefin metatheses;[21] (b) diminished stereoselectivity in olefin metatheses;[22] (c) enhanced trapping of intermediates by nucleophiles during additions to alkoxyl-substituted dienes].[23]

[21] (a) McGinnis, J.; Katz, T. J.; Hurwitz, S. *J. Am. Chem. Soc.* **1976**, *98*, 605. (b) Katz, T. J.; McGinnis, J.; Altus, C. *J. Am. Chem. Soc.* **1976**, *98*, 606. (c) Lee, S. J.; McGinnis, J.; Katz, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 7818.

[22] Katz, T. J.; Hersh, W. H. *Tetrahedron Lett.* **1977**, 585.

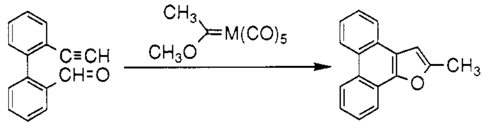
[23] Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653.

Table I. Selected Bond Lengths (Å) in 8 with the Analogous Data for 30[a] Shown for Comparison

	8	30
C(16)-C(15)	1.377 (7)	1.366 (23)
C(15)-C(9)	1.475 (7)	1.481 (22)
C(9)-C(10)	1.438 (8)	1.327 (26)
C(10)-C(18)	1.394 (9)	1.380 (22)
M-C(16)	2.530 (8)	2.285 (19)
M-C(15)	2.275 (7)	2.164 (14)
M-C(9)	2.317 (7)	2.208 (16)
M-C(10)	2.369 (6)	2.390 (15)
M-C(18)	2.330 (6)	2.349 (16)

[a] Reference 25.

The mechanisms in Schemes I and II need little modification to account for why the alkyne aldehyde **26**, related to **1**, combines with metal carbenes **27a** and **27b** to give furan **28** (eq 7). This transformation, described in the Experimental Section, presumably involves a novel way to create the metal carbene enone (**29** in Scheme III), for whose subsequent conversion to the furan there are now a few precedents.[3b,17a,18]



(7)

26

27a: M = W
b: M = Cr

28
72% yield
85% yield

Molecular Structure of Tungsten Pentadienyl 8. The pentadienyls in almost all their transition-metal complexes adopt a U shape.[5,24] There appear to be three exceptions: a bis(2,4-dimethylpentadienyl)(triethylphosphine)molybdenum, whose structure (**30**), determined by X-ray diffraction, shows one of the pentadienyls in a bent sickle shape;[25] a cyclopentadienylpentadienylmolybdenum carbonyl, whose proton NMR spectrum indicates that the molecule has lower symmetry than expected for the U conformation;[26] and molecule **8** reported here. It is interesting that all three exceptions are derivatives of the higher group VIB metals. Pentadienyls bonded to chromium, however, as in bis(2,4-dimethylpentadienyl)chromium and chloro(2,4-dimethylpentadienyl)[bis(dimethylphosphino)ethane]chromium, have the usual U shape.[27]

Table II. Coordinates (×10⁴) and Temperature Factors (Å² × 10³) of Hydrogen Atoms

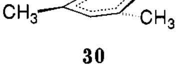
atom	x	y	z	U
H(18a)	752 (63)	1672 (65)	−205 (62)	50
H(18b)	2471 (63)	1796 (65)	−271 (62)	50
H(1)	−1524 (63)	2801 (65)	92 (63)	50
H(2)	−3825 (60)	3945 (63)	217 (64)	50
H(3)	−4330 (66)	5264 (66)	1904 (64)	50
H(4)	−2343 (65)	5653 (63)	2907 (64)	50
H(5)	−719 (67)	6200 (67)	3279 (65)	50
H(6)	1287 (63)	6388 (65)	4287 (63)	50
H(7)	3459 (63)	5152 (63)	4021 (62)	50
H(8)	3957 (64)	3589 (66)	3159 (64)	50
H(15)	4153 (63)	1795 (65)	813 (63)	50
H(16)	4349 (63)	1029 (63)	3799 (63)	50
H(17a)	6342 (68)	100 (69)	1821 (69)	50
H(17b)	6304 (64)	−551 (66)	3500 (67)	50
H(17c)	6679 (67)	215 (70)	2953 (67)	50

Table III. Coordinates (×10⁴) and Temperature Factors (Å² × 10³) of Non-Hydrogen Atoms

atom	x	y	z	U[a]
W	2243 (1)	427 (1)	2435 (1)	26 (1)
Br	3772 (1)	−1533 (1)	1330 (1)	54 (1)
C(19)	1034 (5)	1098 (5)	3833 (5)	32 (2)
O(19)	332 (5)	1462 (4)	4662 (4)	54 (2)
C(20)	531 (5)	−232 (5)	2213 (5)	36 (2)
O(20)	−483 (5)	−534 (5)	2012 (5)	61 (2)
C(21)	3233 (6)	−1262 (6)	4110 (7)	46 (2)
O(21)	3780 (6)	−2178 (5)	5043 (5)	78 (2)
C(18)	1521 (6)	1859 (6)	193 (5)	40 (2)
C(10)	1111 (5)	2791 (5)	966 (5)	33 (2)
C(12)	−428 (5)	3556 (5)	1169 (5)	33 (2)
C(1)	−1596 (6)	3390 (6)	545 (6)	46 (2)
C(2)	−3037 (6)	4031 (7)	773 (7)	55 (2)
C(3)	−3328 (7)	4859 (7)	1643 (7)	55 (2)
C(4)	−2208 (6)	5063 (6)	2241 (6)	45 (2)
C(11)	−728 (5)	4420 (5)	2017 (5)	36 (2)
C(14)	493 (5)	4645 (5)	2642 (5)	34 (2)
C(5)	257 (7)	5705 (6)	3282 (6)	46 (2)
C(6)	1413 (8)	5903 (6)	3837 (7)	53 (3)
C(7)	2820 (7)	5087 (7)	3753 (7)	52 (3)
C(8)	3119 (6)	4068 (6)	3114 (6)	42 (2)
C(13)	1954 (5)	3823 (5)	2557 (5)	32 (2)
C(9)	2252 (5)	2804 (5)	1802 (5)	31 (2)
C(15)	3739 (5)	1856 (5)	1710 (6)	37 (2)
C(16)	4578 (5)	935 (6)	2863 (6)	42 (2)
C(17)	6074 (7)	−53 (9)	2807 (8)	70 (3)

[a] Equivalent isotropic U is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Both the structure reported here, of **8**, and that of **30** seem best described as combinations of vinyl and allyl units bonded to the transition metal and electronically isolated from one another by substantial rotation about the single bond linking them. Thus in **8**, carbons 17, 16, 15, and 9 all lie in one plane. This is demonstrated by the average deviation from their mean plane being only 0.0054 Å and by the sum of the angles at the two ends of the double bond being 360°. [The measured angles sum to 359.8° around C(15) and to 358.6° around C(16).] The angle between the planes defined by carbon atoms 9, 15, and 16 (and 17 for that matter) and that defined by carbon atoms 15, 9, 10, and 18 is 50°, essentially the same as the 52° angle reported for **30**. The length of the carbon-carbon bond between atoms 15 and 16 (1.38 Å) is the shortest of all in the molecule and is similar to that in related alkene–metal complexes.[28] The length of the bond between carbons 9 and 15, in contrast, is the largest in the molecule, indicative of a single bond between adjacent sp²



30

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(24) Pentadienyliron carbonyl cations have been made in the sickle conformation **9**, but unless sterically encumbering substituents destabilize the U form, the sickles quickly isomerize. See (a) ref 5b, p 143 ff. (b) Sorenson, T. S.; Jablonski, C. R. *J. Organomet. Chem.* **1970**, *25*, C62. (c) Brookhart, M.; Harris, D. L. *J. Organomet. Chem.* **1972**, *42*, 441.

(25) Stahl, L.; Hutchinson, J. P.; Wilson, D. R.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 5016.

(26) Lee, G.-H.; Peng, S.-M.; Lee, T.-W.; Liu, R.-S. *Organometallics* **1986**, *5*, 2378.

(27) Newbound, T. D.; Freeman, J. W.; Wilson, D. R.; Kralik, M. S.; Patton, A. T.; Campana, C. F.; Ernst, R. D. *Organometallics* **1987**, *6*, 2432.

(28) In a tungsten carbene–olefin complex, it is 1.383 (13) Å [Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417]. In an oxo–W(IV)–dichloro–ethene complex it is 1.404 (17) Å [Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545]. In a Pt(II)–2-butene complex it is 1.36 (6) Å [Benedetti, E.; Corradini, P.; Pedone, C. *J. Organomet. Chem.* **1969**, *18*, 203] and in a Pt(II) complex of ethene, 1.375 (4) Å [Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653]. Data for other transition-metal complexes of olefins are in tables in: Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. In: Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

Table IV. Bond Lengths (Å) Other Than Those in Table I

W–Br	2.645 (5)	C(14)–C(5)	1.406 (9)
W–C(19)	1.967 (6)	C(5)–C(6)	1.371 (11)
W–C(20)	1.998 (7)	C(6)–C(7)	1.365 (9)
W–C(21)	2.047 (6)	C(7)–C(8)	1.363 (11)
C(19)–O(19)	1.146 (7)	C(8)–C(13)	1.405 (9)
C(20)–O(20)	1.150 (9)	C(13)–C(9)	1.453 (8)
C(21)–O(21)	1.128 (7)	C(10)–C(12)	1.478 (7)
C(1)–C(2)	1.376 (8)	C(12)–C(1)	1.402 (9)
C(2)–C(3)	1.391 (12)	C(16)–C(17)	1.490 (8)
C(3)–C(4)	1.368 (11)	C(13)–C(14)	1.408 (7)
C(4)–C(11)	1.406 (7)	C(14)–C(11)	1.476 (9)
C(11)–C(12)	1.401 (9)		

Table V. Bond Angles (deg)

Br–W–C(19)	154.9 (2)	Br–W–C(20)	85.3 (2)
C(19)–W–C(20)	83.0 (3)	Br–W–C(21)	77.9 (2)
C(19)–W–C(21)	81.7 (2)	C(20)–W–C(21)	97.6 (3)
Br–W–C(18)	84.6 (2)	C(19)–W–C(18)	115.2 (2)
C(20)–W–C(18)	81.1 (2)	C(21)–W–C(18)	162.5 (3)
Br–W–C(10)	118.1 (2)	C(19)–W–C(10)	84.5 (2)
C(20)–W–C(10)	92.3 (2)	C(21)–W–C(10)	161.9 (3)
C(18)–W–C(10)	34.5 (2)	Br–W–C(9)	126.1 (2)
C(19)–W–C(9)	78.4 (2)	C(20)–W–C(9)	125.6 (2)
C(21)–W–C(9)	128.9 (3)	C(18)–W–C(9)	62.5 (2)
C(10)–W–C(9)	35.7 (2)	Br–W–C(15)	94.3 (2)
C(19)–W–C(15)	106.1 (2)	C(20)–W–C(15)	153.2 (2)
C(21)–W–C(15)	108.6 (2)	C(18)–W–C(15)	72.1 (2)
C(10)–W–C(15)	64.2 (2)	C(9)–W–C(15)	37.5 (2)
Br–W–C(16)	90.3 (2)	C(19)–W–C(16)	98.9 (2)
C(20)–W–C(16)	172.9 (2)	C(21)–W–C(16)	75.9 (2)
C(18)–W–C(16)	104.1 (2)	C(10)–W–C(16)	94.7 (2)
C(9)–W–C(16)	61.5 (2)	C(15)–W–C(16)	32.8 (2)
W–C(19)–O(19)	178.7 (4)	W–C(20)–O(20)	175.6 (4)
W–C(21)–O(21)	179.0 (7)	W–C(18)–C(10)	74.3 (3)
W–C(10)–C(18)	71.2 (3)	W–C(10)–C(12)	119.8 (3)
C(18)–C(10)–C(12)	124.5 (5)	W–C(10)–C(9)	70.2 (3)
C(18)–C(10)–C(9)	116.7 (4)	C(12)–C(10)–C(9)	117.9 (5)
C(10)–C(12)–C(1)	120.2 (5)	C(10)–C(12)–C(11)	120.2 (5)
C(1)–C(12)–C(11)	119.6 (5)	C(12)–C(1)–C(2)	121.3 (7)
C(1)–C(2)–C(3)	118.8 (7)	C(2)–C(3)–C(4)	121.0 (6)
C(3)–C(4)–C(11)	121.0 (7)	C(12)–C(11)–C(4)	118.2 (6)
C(12)–C(1)–C(14)	120.1 (4)	C(4)–C(11)–C(14)	121.7 (6)
C(11)—C(14)–C(5)	122.1 (5)	C(11)–C(14)–C(13)	119.9 (5)
C(5)–C(14)–C(13)	118.0 (6)	C(14)–C(5)–C(6)	120.9 (5)
C(5)–C(6)–C(7)	120.2 (7)	C(6)–C(7)–C(8)	121.5 (7)
C(7)–C(8)–C(13)	119.5 (5)	C(14)–C(13)–C(8)	119.9 (5)
C(14)–C(13)–C(9)	119.5 (5)	C(8)–C(13)–C(9)	120.4 (5)
W–C(9)–C(10)	74.1 (3)	W–C(9)–C(13)	131.6 (3)
C(10)–C(9)–C(13)	120.5 (4)	W–C(9)–C(15)	69.7 (3)
C(10)–C(9)–C(15)	116.0 (5)	C(13)–C(9)–C(15)	123.1 (5)
W–C(15)–C(9)	72.8 (3)	W–C(15)–C(16)	83.8 (4)
C(9)–C(15)–C(16)	121.2 (5)	W–C(16)–C(15)	63.4 (3)
W–C(16)–C(17)	122.7 (6)	C(15)–C(16)–C(17)	122.6 (6)

centers.[29] Selected bond distances measured for **8** are shown in Table I, along with related data for structure **30**.[25] Carbon–hydrogen bond distances, tabulated in the supplementary material, average to 0.90 ± 0.1 Å.

The remainder of the pentadienyl carbons in **8** are bonded to the metal as in a distorted metal allyl. The lengths of the bonds between these carbons are neither as short as in the double bond of the vinyl group nor as long as in the single bond to the vinyl group. Nor are they equal. The bond between atoms 9 and 10 is larger than that between atoms 10 and 18, a distortion to be expected considering that for the corresponding pentadienyl radical, 10 of the 14 resonance structures with seven double bonds have single bonds between atoms 9 and 10 and double bonds between atoms 10 and 18.

In **30** the lengths of the bonds corresponding to those identified here as belonging to the vinyl group and from the vinyl to the allyl group [C(15)–C(16) and C(15)–C(9)] are similar to the lengths in **8**. However the lengths of the carbon–carbon bonds in the "allyl" portion are more similar in **30** than in **8**, which, considering the simpler substitution, appears reasonable.

Experimental Section

Preparation of Pentadienyl–Tungsten Complex 8. 2-Ethenyl-2′-ethynyl-1,1′-biphenyl (**1**)[3a] (204 mg, 1.00 mmol) diluted with 5.0 mL of toluene was added to a Pyrex ampule containing *trans*-bromotetracarbonyl(ethylidyne)tungsten[6] (**6a**, 403 mg, 1.00 mmol). The ampule, degassed at high vacuum (10^{-5} mm), was sealed, allowed to warm to room temperature, and after 2 h opened. The solvent was evaporated in a high vacuum and the residue chromatographed on silica gel, CH_2Cl_2 eluting a red band, $R_f = 0.69$. Evaporation of the CH_2Cl_2 and recrystallization from pentane–CH_2Cl_2 (4:1) gave 335 mg (58% yield) of **8** as deep red needles. Two similar experiments carried out with 0.59 and 0.78 mmol of **1** gave yields of 48 and 44%, respectively. IR ($\tilde{\nu}_{CO}$, in KBr): 2035, 1974, 1917 cm^{-1}. IR (in toluene): 2041, 1985, 1927 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.41 (d, J = 6 Hz, 3 H), 2.76 (d, J = 4 Hz, 1 H), 3.02 (d, J = 14 Hz, 1 H), 5.03 (d, J = 4 Hz‡, 1 H), 5.19 (dq, J = 13$^{\#}$, 6 Hz*, 1 H), 7.40 (t, J = 8 Hz, 1 H), 7.57 (m, 4 H), 7.87 (dd, J = 8, 1.4 Hz, 1 H), 8.41 (t, J = 8 Hz, 2 H). The splittings marked by a *, ‡, and # were removed by irradiation at δ 2.4, 2.8, and 3.0, respectively. MS (EI): no parent peak; prominent are m/e 232 [H + 1, where H is $C_{21}H_{15}$, the hydrocarbon portion of the molecule], 217 [$H - CH_2$], 215 [$H - CH_4$], 202 [$H - C_2H_5$]. The FAB positive-ion mass spectrum of the sample in a matrix of 3-nitrobenzyl alcohol showed the eight parent peaks, m/e 576–583, with intensities approximately those calculated. Anal. Calcd for $C_{21}H_{15}BrO_3W$ (579.11): C, 43.56; H, 2.61; Br, 13.81; W, 31.75. Found: C, 43.48; H, 2.63; Br, 13.96; W, 29.62, 27.31.[30]

Reaction of 1 with 6b. **1** (120 mg, 0.59 mmol) diluted with 3.0 mL of toluene was added to a Pyrex ampule containing *trans*-bromotetracarbonyl(ethylidyne)chromium[6] (**6b**, 160 mg, 0.59 mmol). The ampule, degassed at high vacuum (10^{-5} mm), was sealed, allowed to warm to room temperature, and after 16 h opened. The solvent was evaporated in a high vacuum and the residue chromatographed on silica gel, methylene chloride–pentane (4:1) eluting a 90-mg fraction of colorless oil. The ^{1}H NMR ($CDCl_3$) spectrum showed this oil to be a 70:30 mixture of **10** and **11**. These were separated by preparative TLC [silica gel, pentane–CH_2Cl_2 (4:1)].

9-Methyl-10-[1(*E*)-propenyl]phenanthrene (11). ^{1}H NMR ($CDCl_3$): δ 2.07 (dd, J = 6.5$^{\#}$, 1.7 Hz, 3 H), 2.73 (s, 3 H), 5.78 (dq, J = 16, 7 Hz*, 1 H), 6.76 (d with fine structure, J = 16 Hz, 1 H), 7.59 (m, 4 H), 8.10 (m, 2 H), 8.70 (m, 2 H). The splittings marked by a * and # were removed by irradiation at δ 2.05 and 5.75, respectively. The vinylic methyl resonance at δ 2.07, the aromatic resonances at δ 7.59, 8.10, and 8.70, and the vinylic proton couplings (J = 16 Hz) are essentially the same as those in (*E*)-9-(1-propenyl)phenanthrene (**12**):[7] δ 2.04 (dd, J = 6.6, 1.7 Hz, J_{vinylic} = 15 Hz). MS (EI) (relative intensity, %): 230 M$^+$ (100), 215 (40); m/e calcd for $C_{18}H_{14}$ 230.1096, measured 230.1098.

During the course of 2 days a sample of **8** in $CDCl_3$ deposited a blue solid precipitate, and the solution became colorless. Chromatography on silica gel gave **11** as the only isolable product. Its ^{1}H NMR spectrum was identical with that of the sample prepared above.

Phenanthro[9,10-*b*]-2-methylcyclopentadiene (10). ^{1}H NMR ($CDCl_3$): δ 2.32 (d, J = 1.5 Hz, 3 H), 3.73 (s, 2 H), 7.09 (d, presumably the center pair of a sextet, removed by irradiation at δ 2.32 (J = 1.4 Hz, 1 H), 7.50–7.66 (m, 4 H), 7.92–7.97 (m, 1 H), 8.09–8.14 (m, 1 H), 8.67–8.75 (m, 2 H). The positions of the

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(29) A number of examples average to 1.47 Å. They include linkages from metal allyls to C═C's [(a) Churchill, M. R. *J. Chem. Soc., Chem. Commun.* **1965**, 625. (b) Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1968**, *90*, 2031. (c) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578. (d) Bleeke, J. R.; Hays, M. K.; Wittenbrink, R. J. *Organometallics* **1988**, *7*, 1417. (e) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1988**, *7*, 1588] and metal-complexed di- and trienes to C═C's [(f) McKechnie, J. S.; Paul, I. C. *J. Am. Chem. Soc.* **1966**, *88*, 5927. (g) Bennett, M. J.; Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1968**, *90*, 903. (h) Dickens, B.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1961**, *83*, 4862].

(30) Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

resonances in the aromatic region are similar to those of other phenanthrenes (like **11**). The vinyl and methylene resonances are ca. 0.5–0.6 ppm downfield and the methyl resonance ca. 0.14 ppm downfield of the corresponding resonances in 2-methyl-1*H*-indene (δ 6.44 and 3.22, and 2.18).[8] MS (EI) (% relative intensity) 232 M$^+$ (100), 217 (79), 202 (41); *m/e* calcd for $C_{18}H_{16}$ 232.1253, measured 232.1252.

Reaction of 14 with 6a. Enyne 1 (100 mg, 0.43 mmol), metal carbene **6a** (173 mg, 0.43 mmol), and toluene (2.15 mL) were combined, degassed at ca. 10^{-5} Torr, and sealed in glass. After 2 days at room temperature, the now dark solution was stripped of solvent, and the pentane-soluble portion was chromatographed on silica gel. Pentane eluted 85 mg of a pale yellow oil, whose ^{1}H NMR spectrum was that of a mixture of 57% **15**[3a,7] and 43% **16**.[12]

Reaction of 14 with $C_6H_5C{\equiv}W(CO)_4Br$.[12] The reaction, carried out as above, but with 100 mg of **14** and 200 mg (0.43 mmol) of the metal carbyne, gave after chromatography 94 mg of the mixture, 52% of which was **15** and 48% **16**.

Phenanthro[9,10-*b*]-2-methylfuran (28). A solution of 1,1′-biphenyl-2-ethynyl-2′-carboxaldehyde (**26**) (206 mg, 1.00 mmol) and **27a** or **27b** (1.00 mmol) in 6.0 mL toluene was evacuated to 10^{-5} mm and sealed. After 5 h at 75 °C the solvent was evaporated and the residue chromatographed on silica gel, eluting with pentane–methylene chloride (10:1), giving **28**, a colorless crystalline solid [72% yield (W) and 85% yield (Cr)]: mp 127–128 °C (lit.[31] 127.5–128 °C); IR (KBr) 1590 (s), 1350 (s), 1160 (m), 1105 (m), 1040 (m), 950 (m), 805 (m), 760 (s), 725 (s); ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 3 H), 6.86 (s, 1 H), 7.48–7.65 (m, 4 H), 8.05–8.10 (m, 1 H), 8.28–8.32 (m, 1 H), 8.68–8.72 (m, 2 H); MS (EI) (relative intensity, %) 232 M$^+$ (100), 202 (25), 149 (45).

X-ray Diffraction Analysis of 8. The crystal, purple in color and 0.15 × 0.30 × 0.45 mm in size, was analyzed at ambient temperature. The diffractometer was a Nicolet R3M [Mo Kα radiation ($\bar{\lambda}$ = 0.71073 Å), $\theta/2\theta$ scan, 3.9–29.3 deg min^{-1}, 3° width]. The number of reflections measured in the range $+h,\pm k,\pm l$ ((sin $\theta)/\lambda$ limit = 0.65 Å^{-1}, $2\theta_{max}$ = 55°) was 4404 (4250 unique). Automatic indexing of 25 well-centered reflections showed the unit cell to be triclinic, space group $P\bar{1}$, with two molecules per unit cell. The cell parameters were a = 9.536 (2) Å, b = 10.270 (3) Å, c = 10.378 (2) Å, α = 71.20 (2)°, β = 86.4 (2)°, γ = 72.39 (1)°, V = 916.3 (3) Å^3, and d(calcd) = 2.10 g cm^{-3}.

Structure amplitudes were corrected empirically for absorption (the calculated absorption coefficient was 90.01 cm^{-1}) and for Lorentz and polarization factors, and the computer program used was SHELXTL, running on a Data General NOVA 4 computer.[32] The position of the tungsten atom was determined by Patterson's method, and all other atoms were located from succesive difference Fourier maps. Anisotropic refinements were applied to all non-hydrogen atoms. All hydrogens were located and their positional parameters refined with temperature factors (U) fixed for them at 0.05 Å^2. The scattering factors used were those for neutral atoms. Anomalous scattering corrections were included in the calculations of all structure factors.[33] The final residuals for 280 variables refined against the 3635 pieces of data for which $I > 3\sigma(I)$ were R = 0.027 and R_w = 0.028. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where the weight assigned each measurement was $w = [\sigma^2(F_o) + 0.001(F_o)^2]^{-1}$. The goodness-of-fit indicator $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ = 0.911. In the final refinement, no residual was greater than 0.09 esd, and the last difference Fourier map was essentially flat, the largest remaining peak being 0.89 e/Å^3.

The coordinates and thermal parameters of hydrogen and non-hydrogen atoms are listed in Tables II and III; bond lengths and angles are listed in Tables IV and V. Anisotropic temperature factors and observed and calculated structure factors are in the supplementary material.

Acknowledgment. We are grateful for the support of the National Science Foundation (CHE-85-13274) and the U.S. Navy, Office of Naval Research. Some mass spectra were analyzed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE-82-11164).

Supplementary Material Available: ^{1}H NMR spectrum, electron-impact mass spectrum, and the following data from the X-ray crystallographic analysis of **8**: (1) carbon–hydrogen bond lengths and (2) anisotropic temperature factors (4 pages); a listing of observed and calculated structure factors for **8** (22 pages). Ordering information is given on any current masthead page.

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