Annulation Reaction of (Triphenylmethyl)allene on a Cationic Metal Complex and the Reaction Mechanism

Iuan-Yuan Wu, Jian-Hua Tsai, Bor-Chen Huang, Shinn-Chi Chen, and Ying-Chih Lin*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

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Treatment of $CpW(CO)_3CH_2C{\equiv}CH$, **1a** ($Cp = \eta^5$-C_5H_5), with Ph_3CPF_6 ($Ph = C_6H_5$) generates a cationic η^2-(triphenylmethyl)allene (tritylallene) complex $[CpW(CO)_3(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **2a**. When reacted with excess Me_3NO, complex **2a** liberates free tritylallene $CH_2{=}C{=}CHCPh_3$, **3**. In acetonitrile, the tritylallene ligand of **2a** undergoes an annulation reaction followed by decomplexation to give a mixture of 1,1-diphenyl-1,4-dihydronaphthalene, **4a**, and 1,1-diphenyl-1,2-dihydronaphthalene, **4b**. The first step of the cyclization is the intramolecular nucleophilic attack of the phenyl groups on the metal-coordinated allene moiety generating an arenium intermediate. Deprotonation of this intermediate by PPh_3 affords a neutral metal–vinyl complex $Cp(CO)_3W[\sigma\text{-}(C_{10}H_7)(C_6H_5)_2]$, **7a**, which has been isolated. Protonation of complex **7a** with HBF_4 gives **4a** and **4b** quantitatively. In the initial stage of this protonation, a π-complex $Cp(CO)_3W[\eta^2\text{-}(C_{10}H_8)(C_6H_5)_2]BF_4$, **9b**, is observed and a fast workup enables isolation of **9b** for spectroscopic characterization. Complex **9b** gives **4b** exclusively. The mechanism for the cyclization reaction is established by a spectroscopic characterization of **7a** especially through 2D NMR techniques. The isomerization pathway that leads to **4b** is established by protonation reaction of **7a** using CF_3COOD. Reactivity of such a cyclization reaction in a number of metal systems is rationalized by the electron donor/acceptor ability of the metal fragment.

Introduction

Organic propargyl and allenyl compounds[1] as well as their transition metal derivatives[2] have attracted a great deal of attention in recent years as new types of organic and organometallic intermediates that may have unusual reactivities. In the reaction of a metal propargyl complex with a strong acid, the electrophilic addition at the terminal carbon atom generates a π-allene ligand.[3] This transformation has been inferred in nonconcerted [3 + 2] cycloadditions of the propargyl ligand with a number of electrophiles, affording both carbocyclic and heterocyclic five-membered rings.[4] In such a cycloaddition, the propargyl ligand has been shown to behave as a 1,3-dipole and electrophilic attack on the γ-carbon of the propargyl ligand creates a nucleophile capable of subsequent addition to the α-carbon, leading to the five-membered ring. This feature is not limited to these complexes but has been shown to occur as well with the related allylic, cyclopropyl, and cyclopropylmethyl complexes.[2c] In a different system where a triple bond is appended to a chromium or tungsten carbene complex, the triple bond participates in a [2 + 2] cycloaddition with an enol ether.[5] A similar [2 + 2] cycloaddition of the double bond of cyclohexanone onto a propynyl ligand assisted by $AlBr_3$ to give a four-membered ring has been reported by Rosenblum.[6] Transformation of an iron σ-but-2-ynyl complex to metalated *p*-xylene in the presence of acid is one of a few examples that form a six-membered ring from complexes with a C≡C containing ligand.[2c]

As the application of polyaromatic compounds has received growing attention,[7] we thought use of the above mentioned reactivities of the propargyl ligand might be employed to synthesize polyaromatic compounds by using the trityl cation Ph_3C^+ as an electrophile. In the literature, electrophilic addition of the trityl cation to a metal-coordinated organic substrate resulting in carbon—carbon bond formation has been reported,[8] even though the

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(1) (a) Block, E.; Putman, D. *J. Am. Chem. Soc.* **1990,** *112,* 4072. (b) Ischii, H.; Ishikawa, T.; Fakeda, S.; Veki, S.; Suziki, M.; Marayama, T. *Chem. Pharm. Bull.* **1990,** *38,* 1775. (c) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992,** *114,* 5476. (d) Curran, D. P.; Liu, H. *J. Am. Chem. Soc.* **1992,** *114,* 5863. (e) Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992,** *114,* 6580.

(2) (a) Casey, C. P.; Underiner, T. L.; Vosejpka, P. C.; Gavney, J. A., Jr.; Kiprof, P. *J. Am. Chem. Soc.* **1992,** *114,* 10826. (b) Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992,** *114,* 6597. (c) Rosenblum, M.; Watkins, J. C. *J. Am. Chem. Soc.* **1990,** *112,* 6316. (d) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990,** *105,* 35. (e) Rosenblum, M. *J. Organomet. Chem.* **1985,** *300,* 191. (f) Krivykh, V. V.; Taits, E.; Petrovskii, P. V.; Struchkov, Y. T.; Yanovskii, A. I. *Mendeleev Commun.* **1991,** 103. (g) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985,** *287,* 247. (h) Collins, M. A.; Feng, S. G.; White, P. A.; Templeton, J. L. *J. Am. Chem. Soc.* **1992,** *114,* 3771. (i) Huang, T. M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993,** *115,* 1170. (j) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993,** *115,* 2994.

(3) (a) Benaim, J.; Merour, J. Y.; Roustan, J. L. *C. R. Acad. Sci., Ser. C* **1971,** *272,* 789. (b) Lichtenberg, D. W.; Wojcicki, A. *J. Organomet. Chem.* **1975,** *94,* 311.

(4) (a) Roustan, J. L.; Charrier, C. *C. R. Acad. Sci., Ser. C* **1969,** *268,* 2113. (b) Rosenblum, M. *Acc. Chem. Res.* **1974,** *7,* 122. (c) Wojcicki, A. In *Fundamental Research in Organometallic Chemistry*; Tustsui, M., Ishii, Y., Huang, Y., Eds.; Van Nostrand-Reinhold, New York, 1982; p 569. (d) Welker, M. E. *Chem. Rev.* **1992,** *92,* 97. (e) Chan, D. M. T. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol 5, p 271.

(5) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990,** *112,* 6419 and references therein.

(6) Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Organometallics* **1982,** *1,* 1679.

(7) Franck, H. G.; Stadelhofer, J. W. *Industrial Aromatic Chemistry: Raw Materials, Processes, Products*; Springer-Verlag, Berlin, 1988.

(8) (a) Harris, P. J.; Knox, S. A. R.; Mckinney, R. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978,** 1009. (b) Schrock, R. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974,** 951. (c) Lewis, J.; Parkins, A. W. *J. Chem. Soc. A* **1967,** 1150. (d) Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961,** *83,* 497. (e) Casey, C. P.; Yi, C. S.; Gavney, J. A., Jr. *J. Organomet. Chem.* **1993,** *443,* 111.

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reagent is used mostly for the purpose of hydride abstraction.[9] Considering the nucleophilic nature of the C≡C triple bond, it is reasonable to expect carbon—carbon bond formation in the reaction of a metal propargyl complex with the trityl cation, thus leading to the formation of a π-tritylallene ligand. It is our interest to study the feasibility of carbon—carbon formation and its subsequent cyclization in the reaction of the trityl cation with a metal propargyl complex as a new strategy for the synthesis of a polyaromatic compound. Herein, we report the preparation of a cationic tungsten carbonyl complex containing a π-bonded (triphenylmethyl)allene ligand and its cyclization reaction that efficiently leads to two polyaromatic compounds each containing a new six-membered ring. Through isolation and spectroscopic characterization of two crucial intermediates in this cyclization reaction and comparison of reactivities in several metal systems, the detailed mechanism of this process is elucidated.

Results and Discussion

Synthesis of Cationic Metal Complexes with a η^2-(Triphenylmethyl)allene Ligand. Treatment of the propargyl complex $Cp(CO)_3WCH_2C{\equiv}CH$, **1a**, with Ph_3CPF_6 in THF results in an immediate precipitation of a cationic π-allene complex $[Cp(CO)_3W(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **2a**. Addition of ether to the mixture causes more precipitate to form and increases the isolated yield to greater than 80%. Complex **2a**, as a solid, is air stable[10] but undergoes a novel cyclization in CH_3CN or CH_2Cl_2 at room temperature, giving a mixture of two polyaromatic organic products, 1,1-diphenyl-1,4-dihydronaphthalene, **4a**, and 1,1-diphenyl-1,2-dihydronaphthalene, **4b**, within 20 min in essentially quantitative yield. Details on this transformation will be described below. If kept at low temperatures (<−10 °C), the solution of **2a** is stable indefinitely. The mass spectrum and microanalytical data for **2a** are consistent with its formulation. In the IR spectrum, the ν(CO) stretching of **2a**, all above 2000 cm^{-1}, indicates the cationic character of the complex.[11] In the ^1H NMR spectrum of **2a**, the resonances attributed to the CH_2 and the CH protons of the allene moiety appear at δ 2.13 and 7.61, respectively, with $^4J_{H-H}$ = 3.5 Hz. In the ^{13}C NMR spectrum of **2a**, a resonance at δ −0.2 is assigned to the terminal carbon of the allene ligand.[12] These data establish the π-coordination of the terminal double bond of the tritylallene ligand. The corresponding complex $[(C_5H_4CH_3)(CO)_3W(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **2b**, containing a methylcyclopentadienyl ligand, a better electron donor, is prepared similarly and shows higher stability toward decomposition.

The nucleophilic nature of the C≡C triple bond of the propargyl ligand is also observed in the Mo and Mn propargyl complexes. The molybdenum complex $[Cp(CO)_3Mo(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **11**, is prepared in a similar manner, but in lower yield. Complex **11** is characterized by spectroscopic methods and microanalytical data. The reaction of $(CO)_5MnCH_2C{\equiv}CH$, **13**, with Ph_3CPF_6 yields a solid mixture containing $[(CO)_5Mn(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **12**. But **12** is so reactive that attempts to purify it by dissolving it in a number of solvents result in immediate decomposition even at −30 °C. The identity of **12** is therefore determined by the solid state IR spectrum and its decomposition product **4a**.

Concerning formation of the tritylallene complexes, there are two points worth noting. (1) In the reaction of $L_nMCH_2C{\equiv}CR$ with strong acid, affording a cationic η^2-monosubstituted allene complex, trans periplanar participation of the metal concerted with addition of H^+ results in a stereospecific formation of the syn isomer. This intermediate is converted to a more stable anti isomer, i.e. M and R trans, through a transition state in which the metal is near the substituent.[13] The reaction of the trityl cation with a propargyl complex should directly generate the anti periplanar conformer without having to go through the cis conformer. (2) The carbon—carbon bond formation occurs at the γ-carbon of the propargyl unit. For comparison, several earier reports[3a,4a] on the reaction of nucleophile (Nuc) with a metal propargyl carbonyl complex revealed that the CO is susceptible to nucleophilic attack. And the subsequent carbon—carbon bond formation by coupling of the CO—Nuc group with the propargyl ligand takes place at the β-site of the C-3 unit. We have reported the transformation of the σ-propargyl to a σ-allenyl ligand on a tungsten metal[14] and found another regiospecificity of carbon—carbon bond formations in the reactions of tungsten σ-allenyl complexes with nucleophiles;[15] namely, the carbon—carbon bond formation of the σ-allenyl complex occurs at the α-carbon of the C-3 unit.

Cyclization of the η^2-(Triphenylmethyl)allene Ligand on the Tungsten Metal. In acetonitrile, the tritylallene ligand of complex **2a** undergoes a novel [3 + 3] cyclization reaction[16] and produces two polyaromatic organic compounds, **4a** and **4b**, after decomplexation; see Scheme I. This reaction also generates a known $Cp(CO)_3W(CH_3CN)^+$ cation. At room temperature, the reaction is completed within 20 min with 85% (sum of **4a** and **4b**) isolated yield. There is no effect on the rate of the reaction under a 1 atm of CO atmosphere. Compounds **4a** and **4b**, easily discriminated by their NMR spectra, are separated by column chromatography and are identified by spectroscopic methods including an HMBC[17] (heteronuclear multiple bond connectivity) NMR spectrum. In the ^1H NMR spectrum of **4b**, the CH_2 group appears as a well-resolved doublet of doublet (dd) resonance at δ 3.18 through coupling only with two vinyl protons. In comparison, the corresponding CH_2 group of **4a**, being near to the aromatic proton of the dihydronaphthalene, exhibits an unresolved broad resonance at δ 3.34, since the dd pattern from the coupling with vinyl protons is further split by coupling with an aromatic proton through $^4J_{H-H}$.

(9) (a) Casey, C. P.; Marder, S. R. Organometallics **1985**, *4*, 411. (b) Lewis, J.; Parkins, A. W. *J. Chem. Soc. A* **1969**, 953; **1967**, 1150. (c) Green, M. L. H.; Massey, A. G.; Moelwyn-Hughes, J. T.; Nagy, P. L. I. *J. Organomet. Chem.* **1967**, *8*, 511. (d) Deeming, A. J.; Ullah, S. S.; Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2093. (e) Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 145.

(10) Typical η^2-allene complexes and their bonding: (a) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1984**, 992. (b) Kashiwagi, T.; Yasuoka, N.; Kasai, N.; Kukudo, M. *J. Chem. Soc., Chem. Commun.* **1969**, 317. (c) Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* **1976**, *20*, 81. (d) Hewitt, T. J.; DeBoer, J. J. *J. Chem. Soc. A* **1971**, 817.

(11) Fischer, E. O.; Fichtel, K. *Chem. Ber.* **1961**, 1200.

(12) Similar upfield ^{13}C NMR shifts were observed for coordinated methylene carbons of the allene complexes, see: Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164. Ref 1a.

(13) Foxman, B.; Marten, A.; Rosan, S.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160.

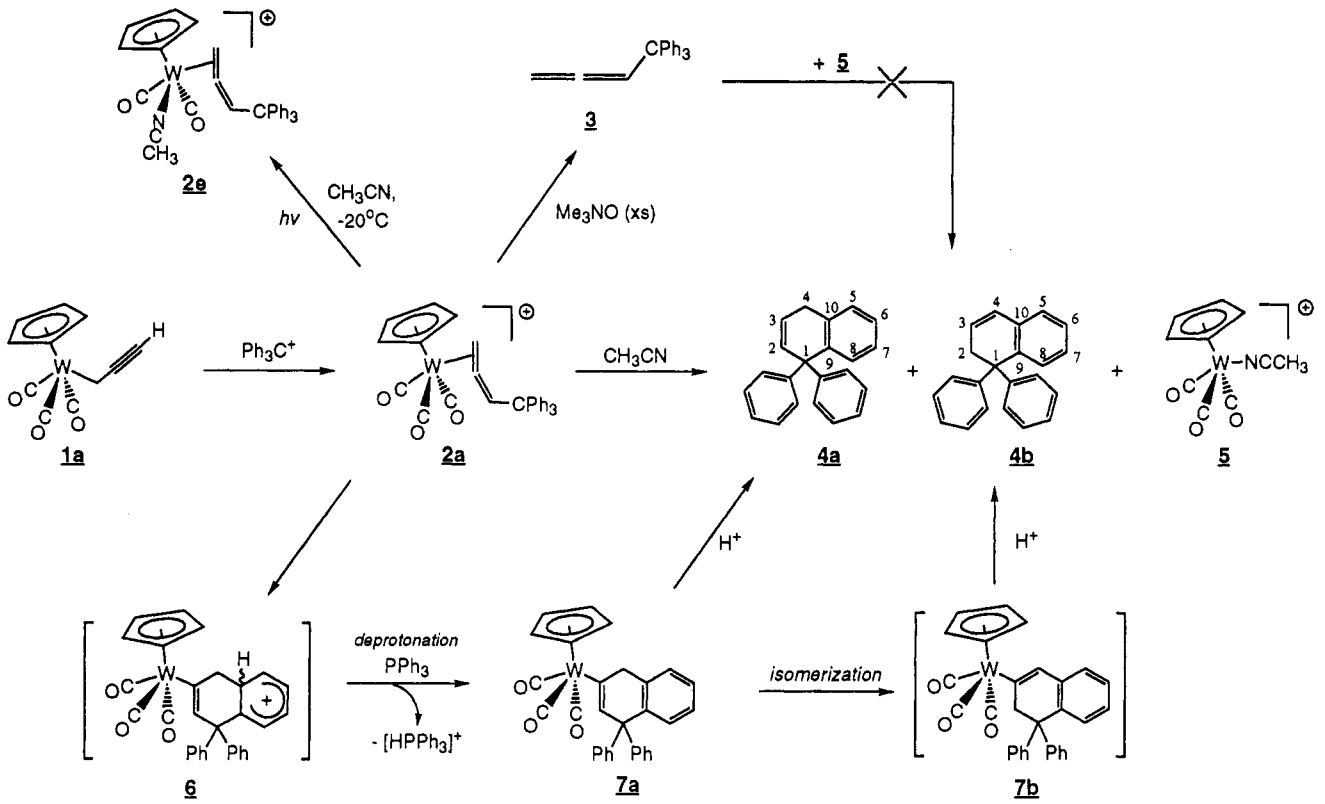
(14) Keng, R. S.; Lin, Y. C. *Organometallics* **1990**, *9*, 289.

(15) Tseng, T. W.; Wu, I. Y.; Lin, Y. C.; Chen, C. T.; Chen, M. C.; Tsai, Y. J.; Cheng, M. C.; Wang, Y. *Organometallics* **1991**, *10*, 43.

(16) A [3 + 3] cycloaddition involved heteroatoms had been reported. Leung, T. W.; Christoph, G. Y.; Wojcicki, A. *Inorg. Chim. Acta* **1983**, *76*, L281.

(17) (a) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093. (b) Bax, A.; Marion, D. *J. Magn. Reson.* **1988**, *78*, 186. (c) Titman, J. J.; Neuhaus, D.; Keeler, J. *J. Magn. Reson.* **1989**, *85*, 111.

Scheme I



Compounds **4a** and **4b** are not interconvertable when heated or when under photolytic conditions. The **4a**:**4b** ratio depends on the reaction temperature. If the reaction is carried out at room temperature and in pure acetonitrile, the **4a**:**4b** ratio is 3:1. At 100 °C, the ratio becomes 1:1. Compound **4b** becomes even less abundant (10:1) if the reaction is carried out in a 20:80 CH_3CN:THF solvent system at 0 °C. At room temperature, the methylcyclopentadienyl complex **2b** gives a mixture of **4a** and **4b** with the same 3:1 ratio, but in a slower rate. It takes about 1 h to complete the cyclization reaction of **2b**. Reaction of (1,1,3,3-tetramethylallyl)lithium with naphthalene gave also a mixture of the monosubstituted 1,2- and 1,4-dihydronaphthalene. The ratio of isomers depends on the route and substituents on the naphthalene used.[18]

We observe this same cyclization reaction in several other cationic metal complexes containing tritylallene ligand. For example, the manganese complex **12** which cannot be purified, readily decomposed upon dissolution, giving only **4a**. Compound **4a** can also be isolated in higher yield directly from the reaction of **13** with Ph_3CPF_6 without having to go through the isolation of **12**. Dissolving the molybdenum complex **11** in CH_3CN also gives **4a**. In these reactions, the weaker metal–carbon bonds in the Mn and Mo systems preclude isomerization from occurring thus no **4b** is observed.

Release of Tritylallene Ligand from 2a and Photosubstitution Reaction of 2a. Treatment of **2a** with excess Me_3NO in CH_2Cl_2 at −10 °C affords free tritylallene molecule $Ph_3CCH{=}C{=}CH_2$, **3**. This colorless compounds is separated from the reaction mixture by hexane extraction, purified by column chromatography, and identified by elemental analysis and spectroscopic methods. In the reaction, the metal fragment is decomposed, presumably via decarbonylation by Me_3NO, and no attempt is made to identify the product. In the IR spectrum of **3**, the stretching of the cumulative double bond is observed as a weak absorption at 1958 cm^{-1}. In the ^1H NMR spectrum, the allene CH_2 and CH groups of **3** appear as doublet and triplet resonances at δ 4.72 and 6.26, respectively, with a coupling constant of $^4J_{H-H} = 6.6$ Hz, close to the $^4J_{H-H} = 6.7$ Hz of $Cp(CO)_3W(\sigma\text{-}CH{=}C{=}CH_2)$. Analogous tin and germanium compounds have been known.[19]

At −20 °C, photolysis of **2a** by UV irradiation in CH_3CN produces a substitution product $[Cp(CO)_2(CH_3CN)W(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **2e**, in moderate yield. The methylene protons of **2e** are inequivalent and display two resonances at δ 2.53 and 1.50 in its ^1H NMR spectrum. This is consistent with the cis assignment of the CO groups. Other than these resonances, the NMR data for the tritylallene group of **2e** are very similar to those for **2a**. The mass spectrum and microanalytical data for **2e** are consistent with its formulation. Interestingly, unlike **2a**, complex **2e** is stable and would not undergo cyclization at room temperature. On the basis of this result and that observed in the Mo, Mn, and other W systems, it is concluded that the rate of cyclization of the metal-coordinated tritylallene decreases as the metal becomes more electron-rich by coordinating with better donor ligands. The rate of cyclization decreases in the following order:

$$Mn(CO)_5 > CpMo(CO)_3 > CpW(CO)_3 > Cp'W(CO)_3 \gg CpW(CO)_2(CH_3CN) \text{ (no reaction)}$$

Compound **3** is not transformed to **4a** or **4b** under a number

(18) (a) Cabral, J.; Fraenkel, G. *J. Am. Chem. Soc.* **1992**, *114*, 9067. (b) Marshall, J. L.; Faehl, L. G.; McDaniel, J. R., Jr.; Ledford, N. D. *J. Am. Chem. Soc.* **1977**, *99*, 321.

(19) (a) Corey, E. J.; Yu, C. M.; Lee, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 878. (b) Masson, J. C.; Le Quan, M. *Bull. Soc. Chim. Fr.* **1967**, 777. (c) Le Quan, M.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1965**, 45. (d) Seyferth, D.; Jula, T. F.; Dertouzos, H.; Pereyre, M. *J. Organomet. Chem.* **1968**, *11*, 63. (e) Russel, G.; Herold, L. L. *J. Org. Chem.* **1985**, *50*, 1037.

of reaction conditions. For example, photolysis of 3 in the presence of $Cp(CO)_3W(CH_3CN)^+$ cannot produce 4a or 4b but only induces decomposition of the tungsten cation.

Mechanism of the Cyclization Reaction. Formation of 4a and 4b has led us to consider possible mechanisms for the cyclization of tritylallene and subsequent isomerization. A plausible mechanism, based on the known reactivity of the metal propargyl complex[20] and aromatic electrophilic substitution,[21] is shown in Scheme I. In this mechanism, the first step involves intramolecular cyclization of tritylallene, generating a metal vinyl intermediate 6 containing an arenium ion. In this process, one of the phenyl groups serves as a nucleophile. The second step is a deprotonation of 6, giving a neutral complex 7a. This is followed by a protonolysis of the M–C bond to give 4a. To account for the formation of 4b, isomerization is required. The isomerization of the double bond in the nonaromatic six-membered ring generates 7b which gives 4b, again by protonolysis. No prior CO dissociation is required in the mechanism, consistent with the observation that the presence of CO does not change the rate of reaction.

Isolation of the σ-1,4-Dihydronaphthalene Complexes by Deprotonation. In this mechanism, the deprotonation step (from 6 to 7a) should be followed by a fast protonolysis, since in acetonitrile the cyclization is completed in 20 min and no intermediate is observed when the reaction is monitored by NMR. To hinder the reprotonation step, we carry out the cyclization reaction in a solvent saturated with PPh_3 as a proton sponge. Deprotonation of the intermediate 6 by PPh_3 yields a neutral σ-1,4-dihydronaphthalene complex, $Cp(CO)_3W[\sigma\text{-}(C_{10}H_7)(C_6H_5)_2]$, 7a, and a phosphonium salt $HPPh_3^+$ which are observed in the ^1H and ^{31}P NMR spectra, respectively. The phosphonium salt acts as a weak acid to convert 7a to 4a and 4b but at a much slower rate. When separated from the phosphonium salt, complex 7a is stable and protonation of 7a with HBF_4 again yields rapidly and quantitatively 4a and 4b. Complex 7a is purified by column chromatography and characterized by spectroscopic methods. The mass spectrum and microanalytical data for 7a are consistent with its formulation. The neutral complex 7a shows IR ν(CO) stretching absorptions in a lower frequency region than that of 2a. The structure of 7a is established by a combination of ^1H and ^{13}C 1D and 2D NMR spectra. The coupling constant $^4J_{H-H}$ of 1.3 Hz between the CH_2 and CH of 7a is relatively small compared with the corresponding value of 6.6 Hz for free tritylallene 3 and the value of 3.5 Hz for 2a (see Table I) and is very close to that in a tungsten σ-cyclopentene complex $Cp(CO)_3W[\eta^1\text{-}C_5H_3(CN)_4]$ obtained from the reaction of TCNE with 1a.[14] In the ^1H–^1H COSY spectrum of 7a, the resonance at δ 3.47, attributed to the CH_2 group, shows scalar spin–spin coupling correlation with that of the aromatic proton, indicating bond connectivity resulting from cyclization of the allene unit with the phenyl group. In the 1D ^{13}C NMR spectrum of 7a, the resonance at δ 114.2 shows a pair of tungsten satellites with $^1J_{C-W}$ = 52.6 Hz and, in the HMBC experiment, this resonance also shows heteronuclear long range correlation (through $^2J_{C-H}$) with the proton resonance of the CH_2 unit at 3.47. The structure of 7a, as shown in Scheme I, is thus firmly established.

Table I. Chemical Shift Data for ^1H and ^{13}C Resonances of the α-CH_2 and γ-CH Units of Various Tritylallene Compounds and Their Cyclized Products

	chemical shift in δ				
	α-CH_2		γ-CH		
compd	^{13}C	^1H	^{13}C	^1H	$^4J_{H-H}$, Hz
2a	−0.2	2.13	142.6	7.61	3.5
2b	0.1	2.06	143.4	7.59	3.5
11	10.7	2.27	137.5	7.08	2.6
2e	8.7	2.53, 1.50	136.9	7.73	3.5
3	78.2	4.72	100.4	6.26	6.6
4a	30.1	3.34	136.3	6.33	1.9
4b	37.8	3.18	128.3	6.41	1.7
7a	48.9	3.52	153.1	6.52	1.1
14	48.2	3.49	149.4	6.47	1.3
8	29.9	3.27	146.9	6.68	
9b	45.1	3.52, 3.08	46.1	5.41	1.5

For the Mo system, complex 11 is converted to $Cp(CO)_2(PPh_3)Mo[\sigma\text{-}C(O)(C_{10}H_7)(C_6H_5)_2]$, 8, under a similar reaction condition; see Scheme II. A PPh_3-promoted CO insertion after the deprotonation step accounts for this product. The FAB mass spectrum of 8 shows the parent peak as well as the fragmentations due to the loss of two CO ligands. For the Mn system, interestingly, in the absence of PPh_3, the cyclization reaction of Mn complex 12 also yields the deprotonation product $(OC)_5Mn[\sigma\text{-}(C_{10}H_7)(C_6H_5)_2]$, 14, and 4a. Complexes 8 and 14 are both thermally stable and are characterized by microanalytical data and spectroscopic methods. The fact that the same cyclization of tritylallene occurs on three different metals indicates that metal plays a simple role in increasing the electrophilicity of the π-coordinated allene ligand. This is consistent with the relative rate observed in complexes 2a, 2b, 2e, 11, and 12. Bearing all good π-acceptor CO ligands, the Mn complex 12 displays the highest rate of cyclization. The better electron-donating methylcyclopentadienyl group in 2b relative to Cp in 2a slightly retards the reaction rate, while CH_3CN, a donor ligand, in 2e completely suppresses the reaction. The cycloaddition of the tritylallene ligand displaying nucleophilic nature (i.e. the reaction is accelerated by the electron-withdrawing capability of the metal fragments) is quite different from the cycloaddition of metal propargyl complexes. In a kinetic study on the cycloaddition of a series of metal propargyl complexes with *p*-toluenesulfonyl isocyanate (TSI),[22] it was found that the reaction is first order in *each* metal complex and TSI and the bimolecular rate constants decrease as a function of M in the order

$$CpCr(NO)_2 > CpFe(CO)_2 > CpMo(CO)_3 > CpW(CO)_3 > Mn(CO)_5$$

Since the rate determining step was found to be the first step, i.e. an electrophilic attack in nature, it was not unexpected that a better σ-bonding ligand should lead to an acceleration in the rate of cycloaddition.

Protonolysis and Isomerization of the σ-1,4-Dihydronaphthalene Complex. Monitoring the protonation reaction of 7a with HBF_4 in $CDCl_3$ by ^1H NMR, we observe immediate formation of a mixture of 4a and 4b. Interestingly, along with their formation, another intermediate $Cp(CO)_3W[\eta^2\text{-}(C_{10}H_8)(C_6H_5)_2]BF_4$, 9b, is also formed at the initial stage of the reaction. A fast workup enables

(20) Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585.
(21) (a) Carey, F. A.; Sundberg, R. T. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; Chapter 10. (b) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240. (c) Ridd, J. H. *Acc. Chem. Res.* **1971**, *4*, 248. (d) Streitweiser, A., Jr.; Mowery, P. C.; Jesaitis, R. G.; Lewis, A. *J. Am. Chem. Soc.* **1970**, *92*, 6529.
(22) Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585.

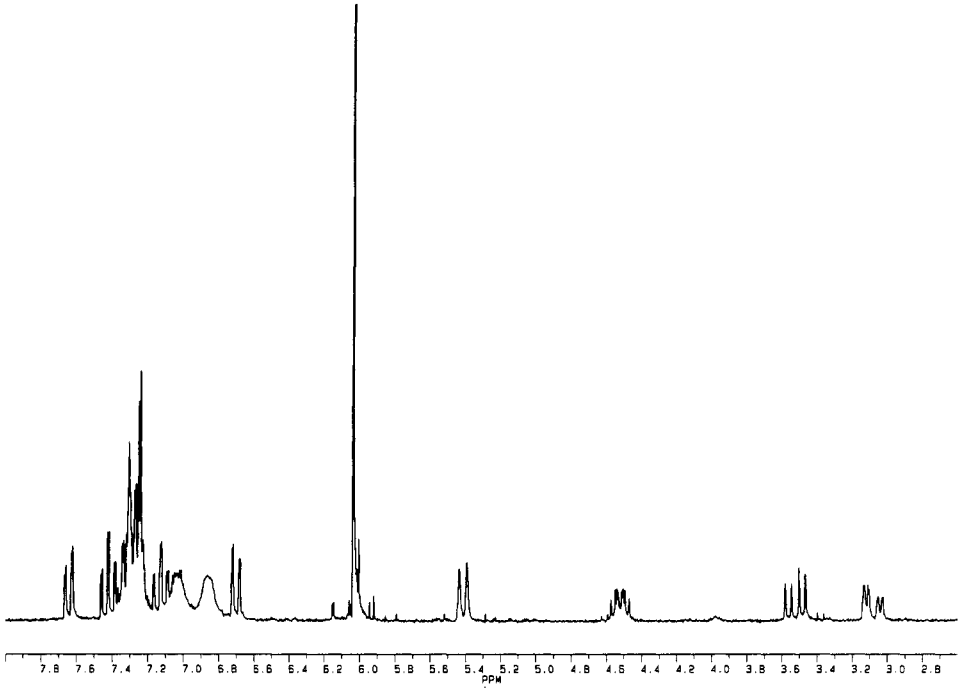
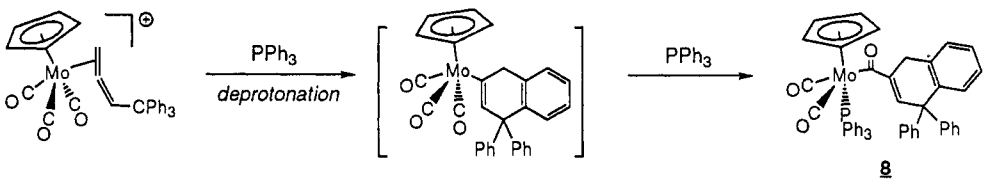
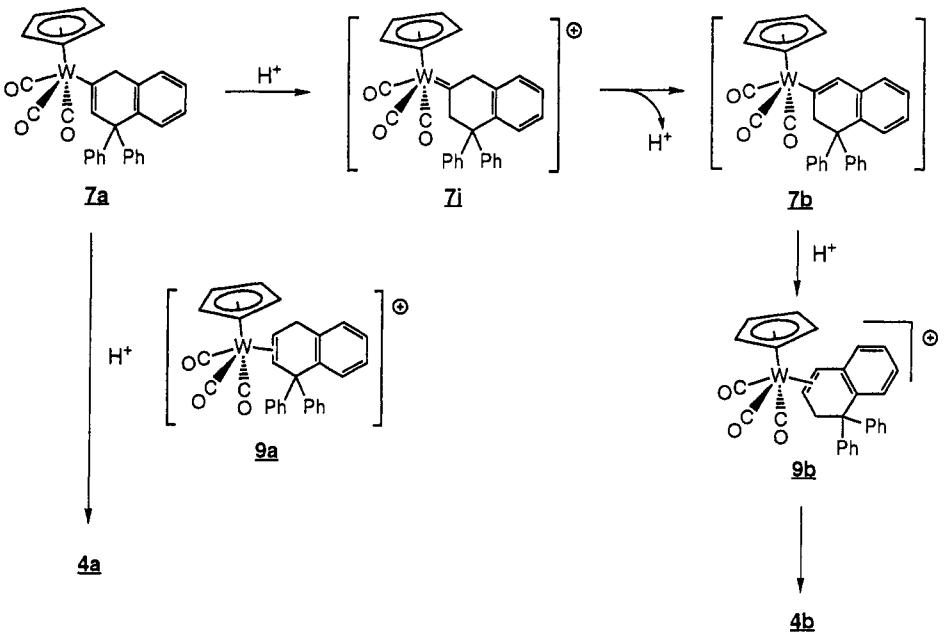


Figure 1. ^1H NMR spectrum of $Cp(CO)_3W[\eta^2\text{-}(C_{10}H_7)(C_6H_5)_2]^+$, **9b**.

Scheme II



Scheme III



isolation of this cationic intermediate in 41% yield; see the Experimental Section. The ^1H NMR spectrum of **9b**, as shown in Figure 1, displays a pair of multiplet resonances at δ 3.08 and 3.52 with a geminal coupling constant of 15.7 Hz, assignable to the two inequivalent protons of the CH_2 unit. The spectrum also displays two multiplet resonances at δ 4.52 and 5.41, assignable to the two olefin protons. The two olefin resonances appear at reasonably higher field (relative to δ 6.00 and 6.41 of the free compound) owing to metal coordination. Complex **9b** converts to **4b** in solution quantitatively. On the basis of these data, the structure of **9b** is assigned as a π-coordinated 1,2-dihydronaphthalene complex, shown in Scheme III.

Spectroscopic characterization and reactions of **9b** reveal details on the protonolysis and isomerization of **7a**. In **7a**, there are two possible sites for protonation. Protonation at the α-carbon causes direct cleavage of the M–C bond, affording **4a**. In comparison, protonation at the β-carbon affords a cationic carbene intermediate **7i**. It is known that an α-alkoxy substitution permits easier alkylation of

the β-carbon in a neutral vinyl complex.[23] In our system, the ratio for products from the protonation at the α-carbon to that at the β-carbon is about 1:1 which is probably not the equilibrium ratio of **4a** and **4b**. Deprotonation at C-4 from **7i** gives **7b**. Interestingly, reprotonation of **7b** at the α-carbon does not cause immediate cleavage of the M–C bond but, instead, results in a formation of a π-olefin complex **9b**. An alternative pathway to **9b** is a direct hydrogen migration which is excluded by the deuteration experiment described below. Compound **4b** is then formed by decomplexation.

Protonation of **7a** with CF_3COOD in $CDCl_3$ reveals how product **4b** is obtained. Analysis of the ^1H NMR spectra and the mass spectra of the products (see Experimental Section) discloses the site and numbers of deuteration. The reaction affords compound **4a**-d_1 specifically deuterated at C-3 and compound **4b**-d_2 specifically deuterated at C-3 and C-2. Complex **4b**-d_2 arises from deprotonation of **7i** to give **7b** followed by reprotonation to give **9b** and then decomplexation to afford **4b**. Transformation directly from **7i** to **9b** should give **4b**-d_1, with deuteration only at C-2, which is not observed. It is interesting to note that protonations of **7a** and **7b** behave differently. As protonation of **7b** generates a π-coordinated olefin complex **9b**, protonation of **7a** directly gives a product of M–C cleavage; **9a** is not observed. Stabilization of **9b** may be attributed to the conjugated double bond (with an aromatic ring system). Complex **7b** is not observed.

Several similar organic cyclization reactions involving heteroatoms are known. For example, the addition of thiol groups to allenic intermediates gives five- and six-membered sulfur rings[24] possibly through nucleophilic attack. The Claisen rearrangement of aryl propargyl ether gave benzopyrans or, if in the presence of excess CsF, 2-methylbenzofurans.[1b] The effect of ring size and chain length on the course of the intramolecular photocyclization of various cycloalkenones containing terminal allene groups has been investigated.[25] To our knowledge, the annulation reaction observed in the cationic tritylallene complexes **2a**, **2b**, **11**, and **12** is the first example of a cyclization reaction for an organic molecule with aryl and allene units that involves no heteroatom.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum line, drybox, and standard Schlenk techniques. NMR spectra were recorded on Bruker AM-300WB and AC-200 spectrometers and are reported in units of parts per million with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93). IR spectra were measured on a Perkin-Elmer 983 instrument, and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. Fast atom bombardment and electron impact mass spectra were determined with a JEOL SX-102A spectrometer. Diethyl ether and CH_2Cl_2 were distilled from CaH_2 and stored over molecular sieves prior to use. Benzene and THF used were distilled from sodium–benzophenone. All other solvents and reagents were reagent grade and used without further purification. $W(CO)_6$ was purchased from Strem Chemical and Ph_3CPF_6, PPh_3, and Me_3NO were purchased from Janssen Chimica. Propargyl bromide was purchased from Merck and was distilled in a small quantity before use. Complexes $[CpW(CO)_3]_2$[26] and $CpW(CO)_3CH_2C{\equiv}CH$, **1a**, $(C_5H_4CH_3)W(CO)_3CH_2C{\equiv}CH$, **1b**, $CpMo(CO)_3CH_2C{\equiv}CH$, **10**, and $(CO)_5MnCH_2C{\equiv}CH$, **13**,[27] were prepared according to the literature methods. The tungsten anion $CpW(CO)_3^-$ was prepared from the Na/Hg reduction of $[CpW(CO)_3]_2$.

NMR Spectroscopy. Two-dimensional NMR experiments were performed on a Bruker AM-300 wide-bore spectrometer operating at observation frequencies of 300.133 and 75.45 MHz for ^1H and ^{13}C, respectively. The instrument was controlled by an ASPECT-3000 pulse programmer. Proton and carbon 90° pulses were calibrated at 8.8 and 5.0 μs, respectively. The ^1H 90° pulse from the decoupler coil was calibrated as 8.9 μs.

High resolution 1D proton and carbon spectra were recorded at 32K and 32K data points, respectively, and were not zero-filled. The 2D COSY (homonuclear ^1H–^1H shift correlated) spectrum was recorded with a π/2 mixing pulse (COSY90). The data matrix was 1K × 1K after zero filling in t_1. The number of increments in t_1, scans, and phase cyclings were 256, 8, and 8 respectively. A relaxation delay of 1 s was used, and the sweep width was 3000 Hz. Proton–carbon chemical shift correlations were established using the standard Bruker pulse sequence XHDEPT.[28] The one-bond ^1H–^{13}C shift correlation spectrum resulted from a 512 × 1024 data matrix size with 96 scans per t_1 value and a delay time between scans of 1 s, including a 3.45-ms τ period and an appropriate acquisition period. Long-range proton–carbon connectivities were established by indirect detection via a modified HMBC pulse sequence.[17] The multiple-bond ^1H–^{13}C shift correlation spectra resulted from 256 × 2048 data matrix sizes with 160 scans (preceded by 2 dummy scans) per t_1 value and a delay time between scans of 1.2 s. The acquisition time was 24 ms in the t_1 dimension. In the experiment, Δ_1 and Δ_2 durations of 3.4 and 62 ms, respectively, were used. In the spectra, sine bell functions with the approprite phase shift were employed, and symmetry correlations were applied only to the data matrices of the 2D COSY spectra.

Synthesis of Cationic Metal η²-(Triphenylmethyl)allene Complexes. A sample of **1a** (1.12 g, 2.70 mmol) was dissolved in 20 mL of CH_2Cl_2 to give a yellow solution. Addition of Ph_3CPF_6 (1.15 g, 2.97 mmol in 10 mL of CH_2Cl_2) to this solution at 0 °C led to some yellow precipitate. Ether (20 mL) was added to produce more precipitate. The solution was filtered, and the solid was washed with 3 × 20 mL of a 1:2 CH_2Cl_2/ether mixture. Removal of the residual solvent in solid under vacuum gave the light yellow product $[Cp(CO)_3W(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **2a** (yield 85%, 1.75 g). Complex **2a** is air stable as a solid and should be kept below −10 °C in solution. Spectroscopic data for **2a**: IR (cm^{-1}, KBr) 2105 (m), 2054 (s), 2015 (s, CO), 843, 827 (s, PF_6); ^1H NMR (25 °C, CD_3CN) δ 7.61 (t, J_{H-H} = 3.5 Hz, 1H, =CH), 7.30–7.06 (m, 15H, aromatic CH), 5.99 (s, 5H, Cp), 2.13 (d, 2H, J_{H-H} = 3.5 Hz, CH_2); ^{13}C NMR (−10 °C, CD_3CN) δ 204.0, 194.7 (CO), 150.2 (=C=), 142.6 (=CH–), 146.5, 130.6, 128.9, 127.5 (aromatic carbon), 92.6 (Cp), 66.6 (CPh_3), −0.2 (=CH_2); MS (FAB) *m/z* 617 ($M - PF_6^+$), 589 ($M^+ - PF_6 - CO$), 561 ($M^+ - PF_6 - 2CO$), 533 ($M^+ - PF_6 - 3CO$). Anal. Calcd for $[C_{30}H_{23}O_3W]PF_6$: C, 47.39; H, 3.05. Found: C, 47.19; H, 3.35. Complex $[(C_5H_4CH_3)(CO)_3W(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **2b**, was prepared similarly with 85% isolated yield (0.66 g from 0.39 g of **1b**). Spectroscopic data for **2b**: IR (cm^{-1}, KBr) 2102 (m), 2052 (s), 2016 (s, CO), 832 (s, PF_6); ^1H NMR (25 °C, CD_3CN) δ 7.59 (t, J_{H-H} = 3.5 Hz, 1H, =CH), 7.37–7.06 (m, 15H, aromatic CH), 5.94, 5.79 (m, 4H, C_5H_4-Me), 2.28 (s, 3H, CH_3), 2.06 (d, 2H, J_{H-H} = 3.5 Hz, CH_2); ^{13}C NMR (−10 °C, CD_2Cl_2) δ 198.8, 194.0 (CO), 150.0 (=C=), 143.4 (=CH–), 148.2, 129.7, 128.2, 126.8 (aromatic carbon), 114.6, 92.2, 87.4 (C_5H_4Me), 65.9 (CPh_3), 14.2 (CH_3), 0.1 (=CH_2); MS (FAB) *m/z* 631 ($M - PF_6^+$), 603 ($M^+ - PF_6 - CO$), 575 ($M^+ - PF_6 - 2CO$), 547 ($M^+ - PF_6 - 3\,CO$). Anal. Calcd for $[C_{31}H_{25}O_3W]PF_6$: C, 48.08; H, 3.25. Found: C, 48.14; H, 3.44.

(23) (a) Smith, D. E.; Gladysz, J. A. *Organometallics* **1985**, *4*, 1480. (b) Casey, C. P.; Vosejpka, P. C.; Askham, F. A. *J. Am. Chem. Soc.* **1990**, *112*, 3713.

(24) Kwart, H.; George, T. J. *J. Chem. Soc., Chem. Commun.* **1970**, 433.

(25) Dauben, W. G.; Shapiro, G.; Luders, L. *Tetrahedron Lett.* **1985**, *26*, 1429.

(26) Manning, A. R.; Birdwhistell, R.; Hackett, P. *J. Organomet. Chem.* **1978**, *157*, 239.

(27) Thomasson, J. E.; Robinson, P. W.; Ross, D. A.; Wojcicki, A. *Inorg. Chem.* **1971**, *10*, 2130.

(28) Bendall, M. R.; Pegg, D. T. *J. Magn. Reson.* **1983**, *53*, 144.

A Mo analogue $Cp(CO)_3Mo(\eta^2\text{-}CH_2{=}C{=}CHPh_3)PF_6$, **11** (2.02 g, 2.99 mmol, 83% yield), can be similarly prepared from the reaction of $Cp(CO)_3MoCH_2C{\equiv}CH$ (1.01 g, 3.60 mmol) with Ph_3CPF_6 (1.40 g, 3.61 mmol). Spectroscopic data for **11**: IR (cm^{-1}, KBr) 2106 (m), 2059 (s), 2022 (s, CO), 845, 825 (s, PF_6). ^1H NMR (25 °C, CD_3CN) δ 7.38–7.04 (m, 15H, aromatic CH), 7.08 (t, J_{H-H} = 2.6 Hz, 1H, =CH), 5.94 (s, 5H, Cp), 2.27 (d, 2H, J_{H-H} = 2.6 Hz, CH_2); ^{13}C NMR (−20 °C, CD_3CN) δ 216.6, 209.3 (CO), 156.6 (=C=), 137.5 (=CH–), 146.2, 130.5, 128.9, 127.6 (aromatic carbon), 95.1 (Cp), 65.6 (CPh_3), 10.7 ($=CH_2$); MS (FAB) *m/z* 531 ($M - PF_6^+$), 503 ($M^+ - PF_6 - CO$), 447 ($M^+ - PF_6 - 3CO$). Anal. Calcd for $[C_{30}H_{23}O_3Mo]PF_6$: C, 53.59; H, 3.44. Found; C, 53.62; H, 3.39.

A similar procedure was used for the preparation of the Mn analogue $(CO)_5Mn(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)PF_6$, **12** (0.94 g, probably not pure) from the reaction of $(CO)_5MnCH_2C{\equiv}CH$ (0.50 g, 2.1 mmol) with Ph_3CPF_6 (1.01 g, 2.58 mmol) in 70 mL of CH_2Cl_2 at −20 °C. The solution was kept at this temperature *without* stirring for 30 min to give a light yellow precipitate which was washed with 2:1 ether/CH_2Cl_2 after filtration. Purification was not possible since it decomposed upon dissolution, even at −30 °C. Spectroscopic data for **12**: IR (cm^{-1}, KBr) 2136 (m), 2043 (s), 2006 (s) ν(CO); MS (FAB) (contaminated with other unidentified species) *m/z* 477 ($M - PF_6^+$), 421 ($M^+ - PF_6 - 2CO$), 393 ($M^+ - PF_6 - 3CO$), 365 ($M^+ - PF_6 - 4CO$), 337 ($M^+ - PF_6 - 5CO$). Anal. Calcd for $[C_{27}H_{18}O_5Mn]PF_6$: C, 52.11; H, 2.92. NMR spectroscopic data for **12** cannot be obtained since the complex decomposed as soon as it was dissolved in solution, even at −30 °C. The confirmation of this complex was obtained from the decomposition experiment described below.

Reaction of 2a with Excess Me_3NO. A sample of **2a** (0.38 g, 0.50 mmol) was suspended in 40.0 mL of a 1:1 CH_2Cl_2/CH_3OH cosolvent system. A solution of Me_3NO (0.60 g in 20 mL of methanol) was added via syringe over 5 min, and the resulting mixture was stirred for 10 min at −10 °C. The reaction mixture was allowed to warm to room temperature. After removal of solvent under reduced pressure, the red-brown residue was extracted with 2 × 30 mL of hexane. The extracts were evaported to dryness, and the crude organic product was subjected to column chromatography on silica gel eluted by pentane. The first band was colorless and, after removal of the solvent, gave (triphenylmethyl)allene powder (0.12 g, yield 85%). Mp: 98.5–99.0 °C (uncorrected). Spectroscopic data for $CH_2{=}C{=}CHC(C_6H_5)_3$, **3**: IR (cm^{-1}, KBr) 1958 (m, allene); ^1H NMR ($CDCl_3$) δ 7.27, 7.14 (m, 15H, Ph), 6.26 (t, J_{H-H} = 6.6 Hz, 1H, CH), 4.72 (d, 2H, J_{H-H} = 6.6 Hz, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ 208.3 (=C=), 146.2, 129.9, 127.6, 125.4 (Ph), 100.4 (=CH), 78.2 ($=CH_2$), 58.8 (CPh_3); MS (FAB) *m/z* 282 (M^+), 283 ($M^+ + 1$). Anal. Calcd for $C_{22}H_{18}$; C, 93.57; H, 6.42. Found: C, 93.50; H, 6.50.

Substitution Reaction of 2a by Photolysis. A sample of **2a** (0.081 g, 0.11 mmol) was dissolved in 0.8 mL of CH_3CN at −20 °C. The solution in the NMR tube was photolyzed by UV irradiation from a medium pressure Hg lamp at this temperature for 25 min. The solvent was replaced by CD_3CN. The NMR spectrum of this solution indicated formation of $[Cp(CO)_3(CH_3CN)W]PF_6$ (ca. 35% of the total product) and a new product (ca. 65%). A 3-mL aliquot of CH_2Cl_2 and 40 mL of ether were than added to the CD_3CN solution. This solution was first filtered and, in the filtrate, yellow crystals formed within 2 h at 0 °C. After filtration, the powder was washed with 2 × 10 mL of hexane then dried under vacuum. This powder was identified as $[Cp(CO)_2(CH_3CN)W(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]PF_6$, **2e** (0.030 g, isolated yield 36%), on the basis of its spectroscopic data. Spectroscopic data for **2e**: IR (cm^{-1}, CH_2Cl_2) 2041 (s), 1981 (s, CO); ^1H NMR (25 °C, CD_3CN) δ 7.73 (t, J_{H-H} = 3.5 Hz, 1H, =CH), 7.29–7.13 (m, 15H, aromatic CH), 5.81 (s, 5H, Cp), 2.53 (dd, 1H, J_{H-H} = 8.6, 3.5 Hz, one of CH_2), 2.28 (s, 3H, CH_3CN), 1.50 (dd, 1H, J_{H-H} = 8.6, 3.5 Hz, one of CH_2); ^{13}C NMR (25 °C, CD_3CN) δ 212.1 (CO), 164.4 (=C=), 136.9 (=CH–), 147.3, 131.0, 128.9, 127.4 (aromatic carbon), 93.6 (Cp), 66.1 (CPh_3), 8.7 ($=CH_2$), 4.8 (CH_3CN); MS (FAB) *m/z* 631 ($M - PF_6^+$), 590 ($M^+ - PF_6$, CH_3CN), 562 ($M^+ - PF_6$, CH_3CN, CO), 534 ($M^+ - PF_6$, CH_3CN, 2CO). Anal. Calcd for $[C_{31}H_{26}O_2NW]PF_6$: C, 48.14; H, 3.39. Found: C, 48.10; H, 3.41.

Cyclization Reaction of the (Triphenylmethyl)allene Ligand on the Tungsten Cation. (A) A sample of **2a** (0.20 g, 0.26 mmol) was dissolved in 10.0 mL of CH_3CN. The solution was stirred at room temperature for 30 min. The solvent was removed under vacuum to give a yellow oily product. This was redissolved in 5 mL of CH_2Cl_2 and, after 30 mL of hexane was added, gave a yellow precipitate. After filtration, the powder was washed with 2 × 10 mL of ether and then dried under vacuum. This powder was identified as $[Cp(CO)_3W(CH_3CN)]PF_6$, **5** (0.13g, yield 95%), from spectroscopic data. The solvent of the filtrate was removed under vacuum, and then the crude organic products were subjected to column chromatography on silica gel eluted by hexane. The first band gave 1,4-dihydro-1,1-diphenylnaphthalene (0.048 g, yield 64%), and the second band gave 1,2-dihydro-1,1-diphenylnaphthalene (0.015 g) in 21% yield. Spectroscopic data for **5**: IR (cm^{-1}, KBr) 2057 (s), 1964 (vs), 1953 (s, CO), 835 (s, PF_6); ^1H NMR (CD_3CN) δ 6.01 (s, 5H, Cp), 2.54 (s, 3H CH_3); ^{13}C NMR (CD_3CN) δ 223.3, 217.2 (CO), 95.4 (Cp), 5.9 (CH_3); MS (FAB) *m/z* 376 ($M^+ - PF_6$), 348 ($M^+ - PF_6 - CO$), 335 ($M^+ - PF_6 - NCMe$), 320 ($M^+ - PF_6 - 2CO$), 292 ($M^+ - PF_6 - 3CO$). Spectroscopic data for 1,4-dihydro-1,1-diphenylnaphthalene $C_{10}H_8(Ph)_2$, **4a**: ^1H NMR (25 °C, $CDCl_3$) δ 7.27–6.90 (m, 14H, 2Ph and dihydronaphthalene H-5–8), 6.33 (dt, J_{H-H} = 9.8, 1.9 Hz, 1H, =CH), 6.10 (dt, J_{H-H} = 9.8, 3.7 Hz, 1H, =CH), 3.34 (dd, J_{H-H} = 3.7, 1.9 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 148.2, 140.8, 134.9, 130.6, 129–126 (Ph), 136.3 (C-2), 123.5 (C-3), 54.1 (C-1), 30.1 (C-4); MS (FAB) *m/z* 282 (M^+), 283 ($M^+ + 1$); Mp 104–105 °C. Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.42. Found: C, 93.45; H, 6.35. Spectroscopic data for 1,2-dihydro-1,1-diphenylnaphthalene $C_{10}H_8(Ph)_2$, **4b**: ^1H NMR ($CDCl_3$) δ 7.27–6.79 (m, 14H, Ph and naphthalene H-5–8), 6.41 (dt, J_{H-H} = 9.5, 1.7 Hz, 1H, =CH), 6.00 (dt, J_{H-H} = 9.5, 4.4 Hz, =CH), 3.18 (dd, J_{H-H} = 4.4, 1.7 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 146.2, 141.6, 134.5, 129.2, 129–126, 126.6 (Ph), 128.3 (C-4), 127.2 (C-3), 52.8 (C-1), 37.8 (C-2). Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.42. Found: C, 93.49; H, 6.45.

(B) The same reaction was carried out in 20:80 acetonitrile/THF solvent system. Complex **2a** (0.20 g, 0.26 mmol) was suspended in 4 mL of THF at room temperature, and 1 mL of CH_3CN was added. The procedures for reaction and purification were the same as that in (A). The relative yields of 1,4-dihydro-1,1-diphenylnaphthalene (90%) and 1,2-dihydro-1,1-diphenylnaphthalene (10%) were determined by the integration of CH_2 resonances in the NMR spectrum before separation from each other by column chromatography.

(C) Under CO atmosphere, complex **2a** (0.08 g, 0.11 mmol) was dissolved in 1.0 mL of CD_3CN at −10 °C. At this temperature, the solution was divided into two 0.5-mL portions. One was subjected to CO atmosphere by bubbling CO through the solution, and then this was transferred to a NMR tube which had been flushed by CO gas. The other was transferred into another NMR tube under nitrogen. Both tubes were brought to room temperature, and the reaction was monitored by NMR spectra. Formation of organic products was monitored by the CH_2 resonances at 3.47 ppm. Within experimental error, both reactions were complete in 20 min.

(D) The cyclization reaction of **2b** was carried out using the same procedure as that for (A). The reaction produced $[(C_5H_4CH_3)(CO)_3W(CH_3CN)]PF_6$ (isolated yield 85%), **4a** (62%), and **4b** (20% based on **2b**). Spectroscopic data for $[(C_5H_4CH_3)(CO)_3W(CH_3CN)]PF_6$: IR ($cm^{-1}$, KBr) 2055 (s), 1964 (vs), 1950 (s, CO), 830 (s, PF_6); ^1H NMR (CD_3CN) δ 6.01, 5.67 (m, 4H, C_5H_4Me), 2.54 (s, 3H, CH_3CN), 2.11 (s, 3H, CH_3); ^{13}C NMR (CD_3CN) δ 223.0, 216.5 (CO), 95.1, 89.6 (Cp), 14.2 (CH_3), 6.0 (CH_3CN); MS (FAB) *m/z* 390 ($M^+ - PF_6$), 362 ($M^+ - PF_6 - CO$), 351 ($M^+ - PF_6 - NCMe$), 334 ($M^+ - PF_6 - 2CO$), 306 ($M^+ - PF_6 - 3CO$).

Cyclization Reaction of the Metal-Coordinated (Triphenylmethyl)allene in the Presence of PPh_3. (A) Tungsten Complex. An acetonitrile solution (20 mL) of **2a** (0.57 g, 0.75 mmol) at−10 °C was added to a triphenylphosphine saturated

dichloromethane (20-mL) solution. The solution was stirred at room temperature for 30 min. The solvent was removed under vacuum followed by extraction with 2 × 50 mL of hexane. Evaporation of solvent, followed by recrystallization from hexane at −20 °C, yields yellow crystals of $Cp(CO)_3W[\sigma\text{-}C_{10}H_7(C_6H_5)_2]$, **7a** (0.36 g, yield 78%). Spectroscopic data for **7a**: IR (cm^{-1}, THF) 2010 (s), 1921 (vs), 1910 (vs); ^1H NMR ($CDCl_3$) δ 7.30–6.70 (m, 14H, Ph, H-5–8), 6.52 (t, J_{H-H} = 1.3 Hz, 1H, =CH), 5.31 (s, 5H, Cp), 3.52 (d, J_{H-H} = 1.3 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 218.0 (CO), 153.1 (=CH), 148.2, 141.0, 138.5, 129.7, 129.0, 127.8, 126.7, 125.7, 125.6 (aromatic C), 114.2 (W—C, J_{W-C} = 52.6 Hz), 92.0 (Cp), 57.6 (CPh_3), 48.9 (CH_2); MS (FAB) *m/z* 616 (M^+), 588 (M^+ − CO), 560 (M^+ − 2CO), 532 (M^+ − 3CO). Anal. Calcd for $C_{30}H_{22}O_3W$: C, 58.65; H, 3.61. Found: C, 58.49; H, 3.55.

(B) Molybdenum Complex. A triphenylphosphine saturated acetonitrile solution (2 mL) was added to a flask containing a solid sample of **11** (0.10 g, 0.15 mmol) at −20 °C. The solution was warmed slowly and stirred at room temperature for 30 min. The precipitate thus formed was filtered and then washed with 2 × 10 mL of acetonitrile to give light green crystals of $Cp(CO)_2(PPh_3)Mo[\sigma\text{-}C(O)C_{10}H_7(C_6H_5)_2]$, **8** (0.070 g, yield 60%). Spectroscopic data for **8**: IR (cm^{-1}, KBr) 1933 (m), 1851 (vs), 1577 (m); ^1H NMR ($CDCl_3$) δ 7.39–6.62 (m, 14H, Ph, H-5–8), 6.68 (m, 1H, =CH), 5.00 (d, J_{P-H} = 1.3 Hz, 5H, Cp), 3.27 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 238.4 (J_{P-C} = 22.7 Hz, CO), 146.9 (=CH), 141.0–125.6 (aromatic C), 97.6 (Cp), 56.1 (CPh_3), 29.9 (CH_2); MS (FAB) *m/z* 793 (M^+ + 1), 764 (M^+ − CO), 736 (M^+ − 2CO). Anal. Calcd for $C_{48}H_{37}O_3PMo$: C, 73.09; H, 4.73. Found: C, 73.00; H, 4.59.

Cyclization Reaction of the (Triphenylmethyl)allene Ligand on the Manganese Cation. A sample of **12** (0.20 g) was dissolved in 10.0 mL of CH_3CN. The solution was stirred at room temperature for 1 h. The solvent was removed under vacuum to give a yellow oily product. This was extracted with 2 × 20 mL of hexane, and analysis by TLC indicated that there are two products. After solvent removal in vacuo, these crude products were subjected to column chromatography on silica gel and eluted by hexane. The first band gave 1,4-dihydro-1,1-diphenylnaphthalene (0.018 g, yield 20%; assumed **12** is a pure compound). The second bond give a light yellow product identified as $(CO)_5Mn[\sigma\text{-}C_{10}H_7(C_6H_5)_2]$, **14** (0.041 g, yield 27%; assumed **12** is a pure compound). Spectroscopic data for **14**: IR (cm^{-1}, hexane) 2109 (w), 2016 (vs), 1990 (m); ^1H NMR ($CDCl_3$) δ 7.28–7.02 (m, 13H, Ph), 6.66 (m, 1H, H-6 of naphthalene), 6.47 (br, 1H, =CH), 3.49 (d, 2H, $=CH_2$); ^{13}C NMR ($CDCl_3$) 209.3 (CO), 149.4 (=CH), 148.0–125.7 (Ph), 113.5 (Mn—C), 57.6 (CPh_3), 48.2 ($=CH_2$); MS (FAB) *m/z* 476 (M^+), 420 (M^+ − 2CO), 392 (M^+ − 3CO), 364 (M^+ − 4CO), 336 (M^+ − 5CO, base peak). Anal. Calcd for $C_{27}H_{17}O_5Mn$: C, 68.08; H, 3.60. Found: C, 67.96; H, 3.53.

Protonation of 7a Using HBF_4. This experiment was carried out in an NMR tube and the reaction monitored by NMR spectra. An aliquot of HBF_4 was added to a $CHCl_3$ solution (0.5 mL) of **7a** (0.05 g, 0.08 mmol) in an NMR tube at room temperature. The color changed from yellow to light orange. The solvent was quickly removed in vacuo, and the residue was redissolved in 0.5 mL of CD_3CN. The NMR spectra of the reaction mixture was monitored for 1 h. Other than **4a** and **4b**, an intermediate **9b** was observed and slowly transformed to **4b**. Isolation of **9b** was achieved by the following procedures. Protonation of **7a** (0.30 g, 0.49 mmol) was again carried out in 5 mL of $CHCl_3$ at room temperature with HBF_4 (0.1 mL, 54% in diethyl ether). The solution was reduced in volume until a precipitate just formed (but not to dryness). Diethyl ether was then added to cause more precipitate formation. The yellow-brown precipitate was collected by filtration followed by washing with ether to give $Cp(CO)_3W[\eta^2\text{-}C_{10}H_8(C_6H_5)_2]$, **9b** (0.14 g, 0.2 mmol, yield 41%). Spectroscopic data for **9b**: ^1H NMR (CD_3CN) δ 7.66–6.68 (m, 14H, Ph), 6.04 (s, 5H, Cp), 5.41 (br, d, J_{H-H} = 8.8 Hz, 1H, =CH), 4.52 (ddd, J_{H-H} = 8.8, 6.9, 5.1 Hz, 1H, =CH), 3.52 (dd, AB, J_{H-H} = 15.7, 6.9 Hz, 1H, C*H*H), 3.08 (ddd, ABX, J_{H-H} = 15.7, 5.1, 1.5 Hz, 1H, CH*H*); ^{13}C NMR (CD_3CN) δ 211.2, 205.5 (CO), 147.1–127.1 (Ph), 92.2 (Cp), 73.3 (=CH), 56.4 (CPh_3), 46.1 (=CH), 45.1 (CH_2); MS (FAB) *m/z* 617 ($M^+ - BF_4$), 589 ($M^+ - BF_4$ − CO), 561 ($M^+ - BF_4$ − 2CO), 533 ($M^+ - BF_4$ − 3CO). Anal. Calcd for $[C_{30}H_{23}O_3W]BF_4$: C, 51.32; H, 3.30. Found: C, 51.21; H, 3.35.

Protonation of 7a Using CF_3COOD. Protonation of **7a** with CF_3COOD was carried out using a procedure similar to that mentioned above. No attempt was made to isolate **9b**. The reaction afforded compound **4a**-d_1 specifically deuterated at C-3 and compound **4b**-d_2 specifically deuterated at C-3 and C-2. The ratio of **4a** to **4b** was 2:1. The site of deuteration was determined by ^1H NMR. For **4a**-d_1, the resonance attributed to the methylene protons on C-4 with integration of two protons (relative to a well resolved resonance of H-6 in the dihydronaphthalene ring system) shows a narrower doublet pattern (compared to that of **4a**-d_0) due to lack of $^3J_{H-H}$ coupling (D on C-3). The relatively weak resonance of the olefin proton on C-3 (from residual proton in CF_3COOD) at δ 6.10 shows a clear coupling pattern, indicating no deuteration at C-2. The proton resonance of C-2 at δ 6.10 shows a complicated coupling pattern, i.e. overlapped resonances of **4a**-d_1 and **4a**-d_0. This evidence indicates exclusive deuteration at the C-3 position. There is approximately 14% protonation product **4a**-d_0, estimated from integration of these resonances. For **4b**-d_2, the corresponding CH_2 (H-2) resonance with the relative integration of only *one* proton shows a broad pattern due to the $^2J_{H-D}$ coupling, good evidence for the existence of a CHD group. The H-3 resonance is very weak, indicating high deuteration at this site. There is approximately 20% protonation product. These deuterated products were also separated by chromatography and analyzed by mass spectra. Parent peaks M + 1^+ and M + 2^+ were observed for **4a**-d_1 and **4b**-d_2, respectively. Their intensity relative to the corresponding nondeuterated ones are consistent with those observed in NMR.

Protonation of 14 Using CF_3COOH. This experiment was carried out in a NMR tube, and the reaction was monitored by NMR spectra. An aliquot of CF_3COOH (0.1 mL) was added to a $CDCl_3$ solution (0.5 mL) of **14** (0.05 g, 0.11 mmol) in an NMR tube at room temperature. The color changed from light yellow to orange. The NMR spectra of the reaction mixture indicated the formation of **4a**; no **4b** was observed. **4a** was purified by hexane extraction followed by column chromatography. The isolated yield was 95%.

Conclusion

Electrophilic attack of a trityl cation to the σ-coordinated propargyl ligand affords a π,η^2-coordinated tritylallene complex. Intramolecular cyclization of the tritylallene assisted by coordination to W metal gives a mixture of 1,1-diphenyl-1,2-dihydronaphthalene and 1,1-diphenyl-1,4-dihydronaphthalene. Such a cyclization reaction proceeds via a nucleophilic attack of an aryl group followed by deprotonation of the arenium proton and reprotonation at the α-carbon. This mechanism is established by the isolation of a metal vinyl complex. Protonation of this metal vinyl complex takes place at both the α-carbon and β-carbon. In the case of β-carbon protonation, a π-olefin intermediate was isolated and thus led to disclosure of the cyclization mechanism. Study on the reactivity of such a cyclization reaction in a number of metal systems indicates that a metal with a good π-acceptor ligand promotes the cyclization reaction.

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