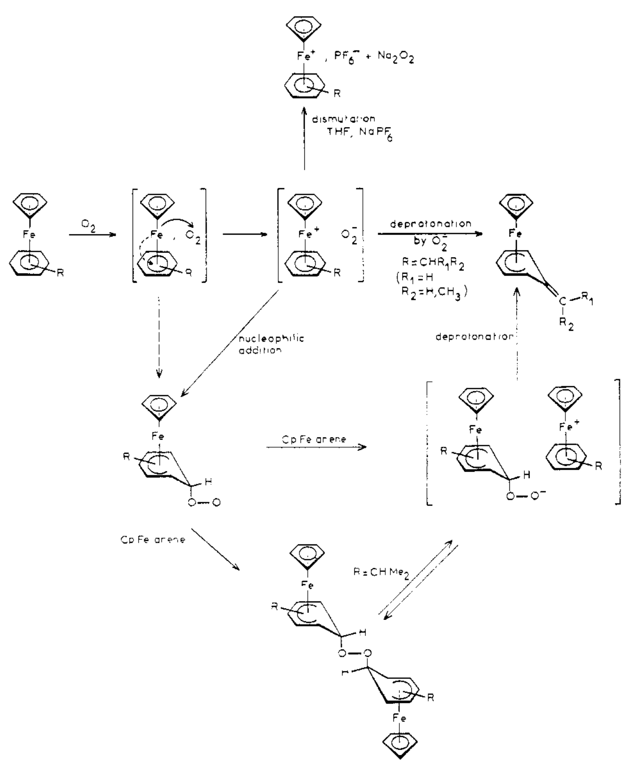
Scheme IX



Fe^{II} peroxides. The balance between these two reactions is reached in the case of a tertiary hydrogen (the isopropylbenzene complex): the kinetic product (peroxide) is characterized at low temperature and transformed to the thermodynamic product (resulting from a formal H abstraction) at −17 °C.

The salt effect is best explained in terms of the versatile reactivity of $O_2^{\bullet-}$ in the ion pair [$CpFe^+$(arene),$O_2^{\bullet-}$] always formed in the first reaction step subsequent to interaction via a charge-transfer complex. In this ion pair, $O_2^{\bullet-}$ can act as a base (deprotonation of an alkyl substituent of the arene activated by $CpFe^+$) and as a nucleophile (in the absence of benzylic H, nucleophilic addition to the benzene ring of the cation) or it can disproportionate to O_2 and O_2^{2-}. The latter process may itself be induced by the salt effect (Na^+). Scheme IX accounts for these various possibilities of reaction of $O_2^{\bullet-}$ following the initial outer-sphere electron transfer.

The present study not only emphasizes the versatile reactivity of $O_2^{\bullet-}$ but also illustrates our concept aimed at obtaining reactive radical anions (such as $O_2^{\bullet-}$) by electron transfer from an organometallic electron reservoir in common solvents of low dielectric constants such as ethers or hydrocarbons. In the present case, this concept led to a remarkable C–H activation, extremely sensitive to the presence of salts and generalized to primary, secondary, and tertiary hydrogens of the entire series of arenes which can be complexed to $CpFe^+$. Application of this activation to more sophisticated aromatic structures can now be envisaged.

Acknowledgment. We thank Drs. D. Catheline, P. Guênot, A. M. Madonik, and S. Sinbandhit (Rennes) for helpful assistance and the CNRS for partial financial support. We are also grateful to Dr. B. Tchoubar for stimulating discussions.

Registry No. **7**, 69022-30-6; $\mathbf{7}^+BF_4^-$, 32758-59-1; $\mathbf{7}^+OH^-$, 112596-51-7; **7**+PF_6^-, 33435-42-6; $\mathbf{7}^+I^-$, 112596-52-8; **8**, 72576-18-2; **10**, 51812-05-6; $\mathbf{10}^+BF_4^-$, 1277-51-6; **11**, 83617-47-4; **13**, 70414-97-0; **14**, 112596-57-3; $\mathbf{15}^+BF_4^-$, 112621-10-0; **16**, 112596-58-4; $\mathbf{17}^+PF_6^-$, 83528-74-9; **18**, 86584-13-6; **20**, 98162-09-5; $\mathbf{20}^+PF_6^-$, 32760-80-8; **21** (isomer 1), 112596-59-5; **21** (isomer 2), 112596-60-8; **22**, 72585-91-2; **25**, 78230-46-3; **27**, 112596-53-9; $\mathbf{28}^+PF_6^-$, 112596-54-0; THF, 109-99-9; 18-crown-6, 17455-13-9; [CpFe($C_6H_5CH_2COC_6H_5$]PF_6, 86584-12-5; [CpFe($C_6HMe_4CH_2COC_6H_5$)]PF_6 (isomer 1), 112621-12-2; CpFe(η^5-$C_6HMe_4CH_2$) (isomer 2), 112596-56-2; n-$Bu_4N^+PF_6^-$, 3109-63-5; K_+PF_{6-}, 17084-13-8; $Na^+PF_6^-$, 21324-39-0; $Na^+BF_4^-$, 13755-29-8; Na^+F^-, 7681-49-4; O_2, 7782-44-7; $O_2^{\bullet-}$, 11062-77-4; toluene, 108-88-3; pentane, 109-66-0; $CpFe^I(C_6H_3Me_3)$, 51812-08-9.

Formation of a Tungsten Vinylvinylidene Complex from Addition of Alkyne to $(dppe)(OC)_3W{=}C{=}CHPh$

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Reaction of *mer*-$(dppe)(OC)_3W{=}C{=}CHPh$ with dimethyl acetylenedicarboxylate (DMAC) results in formation of *Z* and *E* isomers of a vinylvinylidene product, $(dppe)(OC)_3W{=}C{=}C(COOCH_3)C(COOCH_3){=}CHPh$. The reaction presumably proceeds through an η^1-cyclobutenyl complex prior to forming the final product which reflects net insertion of the added alkyne into the C_α–C_β bond of the vinylidene reagent. The kinetically formed *Z* isomer is rapidly converted to the *E* isomer by light, with a photostationary state ratio of 1:8 *Z*/*E*. Infrared and ^1H and ^{13}C NMR data are reported for both isomers. The X-ray crystal structure of the *Z* isomer shows an octahedral tungsten environment and an approximate cisoid geometry for the vinylvinylidene fragment. The compound crystallizes in space group $P2_1/c$ with four molecules per unit cell (a = 11.140 (4) Å, b = 18.047 (6) Å, c = 19.850 (7) Å; β = 94.87 (3)°; V = 3976.3 Å^3; ρ(calcd) = 1.521 g/cm^3). Full-matrix least-squares refinement of 358 variables using 4146 data with $I \geq 3\sigma(I)$ converged with unweighted and weighted residuals of 4.1% and 3.1%, respectively.

Introduction

The chemistry of metal vinylidene complexes has blossomed during the past decade. An excellent review by Bruce and Swincer[1] provides a comprehensive overview of this area. Rearrangement of terminal alkyne ligands to vinylidene ligands is common for octahedral d^6 deriv-

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(1) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* 1983, *22*, 59.

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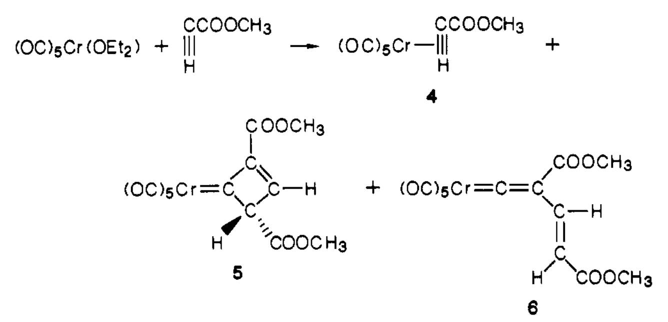
Scheme I



atives[2-4] and offers a convenient entry to this class of organometallic compounds. Other routes to metal vinylidene complexes involve electrophilic addition to metal acetylide precursors[5] or, less commonly, proton abstraction from metal carbyne complexes.[6] Much of the chemistry of vinylidene ligands fits nicely into the theoretical framework set forth by Kostic and Fenske[7] which outlined guidelines for β-addition of electrophiles and α-addition of nucleophiles to metal vinylidenes.

More recently vinylidenes have been invoked as intermediates in the polymerization of alkynes. In a study of alkyne polymerizations with d^6 tungsten monomers, Geoffroy and co-workers[8] established that tungsten vinylidene monomers are capable of polymerizing alkynes; presumably metallocyclobutene-type complexes are key intermediates. Werner and co-workers[9] have also observed reactions at the M=C portion of $M{=}C{=}CR_2$ moieties.

In contrast to reaction at the metal–C_α multiple bond, activation of the C_α–C_β double bond of vinylidene has been proposed by Berke et al.[10] Addition of MAC (methyl acetylenecarboxylate) to $(OC)_5Cr(OEt_2)$ gives three products (Scheme I). The rearrangement of 4 is proposed to form a vinylidene complex, which then incorporates a second molecule of MAC to form an η^1-cyclobutenyl complex (**5**) and a vinylvinylidene complex (**6**).

In a related reaction, we have taken advantage of the nucleophilicity of the β-carbon of $(dppe)(OC)_3W{=}C{=}C(H)Ph$ (dppe = bis(diphenylphosphino)ethane) to add an electron-withdrawing alkyne (DMAC = dimethyl acetylenedicarboxylate). The net result is insertion of the alkyne into the vinylidene C_α–C_β bond to form a vinylvinylidene complex. We report here the synthesis and properties of both the *Z* and *E* isomers of $(dppe)(OC)_3W{=}C{=}C(COOCH_3)C(COOCH_3){=}CHPh$. The structure of the *Z* isomer has been crystallographically determined.

Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl; methylene chloride was distilled from CaH_2; all other solvents were purged with nitrogen and used without further purification. Dimethyl acetylenedicarboxylate (DMAC) was distilled and stored over dry alumina. $W(CO)_3(dppe)({=}C{=}C(H)Ph)$ was prepared according to literature methods.[4]

Infrared spectra were recorded on a Beckman IR 4250 spectrometer and calibrated with a polystyrene standard. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Varian XL 400 (400 MHz) spectrometer. Photolysis was performed by using a sun lamp.

***mer*-$(dppe)(OC)_3W{=}C{=}C(COOCH_3)C(COOCH_3){=}C(H)Ph$ (Isomer Mix).** A solution of DMAC (4.4 mmol, 0.63 g) and *mer*-$(dppe)(OC)_3W{=}C{=}C(H)Ph$ (1.96 mmol, 1.51 g) in 50 mL of THF was heated to gentle reflux for 6 h, resulting in a color change from emerald green to deep red. The reaction was monitored by IR. Solvent removal left a red tar. Chromatography on alumina with diethyl ether (Et_2O) and THF first eluted unreacted starting material with 1:1 Et_2O/THF followed by a red product band with 1:3 Et_2O/THF (this step removed the side product $(dppe)(OC)_2W(DMAC)_2$, which remained on the column). Further chromatography on Florisil resulted in collection of one red band with 1:3 Et_2O/THF as eluent. The *Z* isomer of the vinylvinylidene product selectively crystallized from a 1:1 Et_2O/THF solution of this band. The crystals were filtered and washed with Et_2O. The filtrate was stripped to an oil and triturated with 2-methylbutane to produce a red powder containing both *Z* and *E* isomers. Total yield of crystals and powder was 1.01 g (57%). Pure *E* isomer proved difficult to isolate, and the data below for the *E* isomer were obtained on 1:8 mixtures of *Z*/*E*.

Z isomer: IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2012 m, 1952 s, 1915 vs, $\nu_{C=O}$ (cm^{-1}) 1715 m, 1670 m; ^1H NMR (CD_2Cl_2) δ 7.71–7.04 (m, 25 H, Ph), 6.84 (s, 1 H, C=CH), 3.66, 3.39 (s, 3 H each, $COOCH_3$), 2.90–2.60 (m, 4 H, PCH_2CH_2P); ^{13}C NMR ($CDCl_3$) δ 326.6 (dd, $^2J_{CP}$ = 20, 8 Hz, W=C), 208.0 (dd, $^2J_{CP}$ = 22, 10 Hz, CO trans to P), 201.0 (t, $^2J_{CP}$ = 8 Hz, trans CO's), 170.3 (d, $^3J_{CH}$ = 12 Hz, vinyl $COOCH_3$), 167.7 (s, vinylidene $COOCH_3$), 137.0–126.5 (m, Ph), 122.3 (dd, $^3J_{CP}$ = 11 Hz, $^3J_{CH}$ = 6 Hz, W=C=*C*), 51.5, 50.0 (q, $^1J_{CH}$ = 146 Hz, $COOCH_3$), 30.2–28.0 (m, PCH_2CH_2P). Anal. Calcd: C, 56.72; H, 3.99; W, 20.17. Found: C, 56.41; H, 4.31; W, 20.41.

E isomer: IR (CH_2Cl_2) ν_{CO} (cm^{-1}) 2012 m, 1952 s, 1913 vs, $\nu_{C=O}$ (cm^{-1}) 1710 m, 1675 m; ^1H NMR (CD_2Cl_2) δ 7.66–7.05 (m, 26 H, Ph, C=CH), 3.74, 3.51 (s, 3 H each, $COOCH_3$), 2.90–2.60 (m, 4 H, PCH_2CH_2P); ^{13}C NMR ($CDCl_3$) δ 325.5 (dd, $^2J_{CP}$ = 18, 8 Hz, W=C), 208.3 (dd, $^2J_{CP}$ = 22, 8 Hz, CO trans to P), 201.6 (t, $^2J_{CP}$ = 5 Hz, trans CO's), 169.8 (d, $^3J_{CH}$ = 5 Hz, vinyl $COOCH_3$), 167.8 (s, vinylidene $COOCH_3$), 138.9–122.4 (m, Ph), 117.2 (t, $^3J_{CP}$ = 12 Hz, $^3J_{CH}$ = 12 Hz, W=C=*C*), 52.1, 50.5 (q, $^1J_{CH}$ = 146 Hz, $COOCH_3$), 30.2–27.6 (m, PCH_2CH_2P). Anal. Calcd: C, 56.72; H, 3.99; W, 20.17. Found: C, 57.01; H, 4.74; W, 20.13.

Light-Catalyzed Isomerization. A sealed NMR tube containing a saturated solution of 10:1 *Z*/*E* isomers in $CDCl_3$ was cooled to 0 °C and exposed to a sunlamp for 50 min, resulting in conversion to a *Z*/*E* isomer ratio of 1:8 as determined by ^1H NMR integration of $COOCH_3$ methyl signals.

Collection of Diffraction Data. Red crystals of the *Z* isomer were grown by layering diethyl ether over a methylene chloride solution of the material. A ruby plate of dimensions 0.15 × 0.30 × 0.60 mm was selected, mounted on a glass wand, and coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[11] Twenty-five centered reflections found in the region $10.0° < \theta < 13.0°$ and refined by least-squares calculations indicated a monoclinic cell. The cell parameters are listed in Table I.

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[10] Berke, H.; Harter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 929.

[11] Programs used during solution and refinement were from the Enraf-Nonius structure determination package.

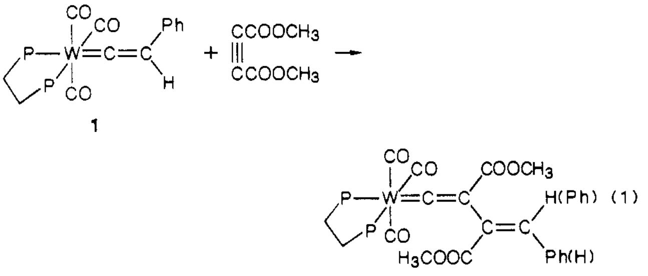
Diffraction data were collected in the quadrant $\pm h,+k,+l$ under the conditions specified in Table I. Three reflections chosen as intensity standards were monitored every 3 h and showed no significant (<1.5%) decay. The crystal was checked for orientation every 300 reflections and was recentered if necessary. Psi scans with nine reflections having $80° < \chi < 90°$ were collected, and an empirical absorption correction was applied (the corrections ranged from 0.8916 to 1.0000). Only data with $I > 3\sigma(I)$[12] were used in structure solution and refinement. The data were corrected for Lorentz–polarization effects during the final stages of data reduction.

Solution and Refinement of the Structure. Solution of the structure was straightforward from application of the heavy-atom method. Space group $P2_1/c$ was confirmed and the position of the tungsten atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations.

Least-squares refinement[13] of the 53 non-hydrogen atoms, varying all but the dppe phenyl carbons anisotropically, produced unweighted and weighted residuals of 4.7% and 3.9%,[14] respectively. Hydrogen atom positions were calculated by using C–H distance of 0.95 Å and an isotropic thermal parameter of 6.0 Å^2. Further refinement resulted in residuals of R = 4.1% and R_W = 3.1%.[15] The final difference Fourier map had no peak greater than 0.33 e/Å^3.

Results

Synthesis. DMAC adds to (dppe)(OC)$_3$W=C=C(H)Ph to ultimately produce a vinylvinylidene product (eq 1).



1

2 (3)

(1)

Two equivalents of DMAC were heated with 1 to 60 °C in THF solution. The extent of reaction was monitored by a decrease in intensity of the IR absorption of the ester C=O stretch in free DMAC, by a slight shift of the metal carbonyl infrared bands to higher wavenumber, and by a color change of the solution from green to red. Excess DMAC causes (dppe)(OC)$_2$W(DMAC)$_2$ to form (IR (ν_{CO}, THF) 2030 s, 1980 s cm^{-1}).[16] This byproduct was separated from the vinylvinylidene product by chromatography on alumina.

Formation of two isomers was evident from ^{1}H NMR. Two sets of methyl peaks corresponding to (i) an initial kinetic isomer (**2**, δ 3.66, 3.39) which is converted by light to (ii) a second isomer (**3**, δ 3.74, 3.51) were evident. The ^{13}C NMR chemical shifts differ only slightly for the two isomers, suggesting similar connectivity. The proton signal arising from the vinylidene C_β proton of the reagent appears at 6.84 ppm in the kinetic isomer but was not directly observed in the second isomer. A 2D NMR experiment (^{1}H vs ^{13}C) was performed on **2** to locate the carbon carrying the original C_β proton. A carbon signal at 129.0 ppm was correlated with the 6.84 ppm proton, consistent with the proton being attached to an uncomplexed vinyl carbon. In the ^{13}C NMR, vinylidene C_α (δ 326.6) and C_β (δ 122.3) signals were observed. A subsequent X-ray structure confirmed the vinylvinylidene structure.

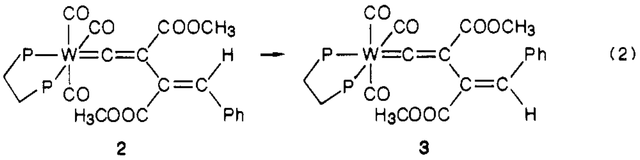
Table I. Crystallographic Data Collection Parameters for 2

Crystal Data	
mol formula	$WP_2O_7C_{43}H_{36}$
fw, g/mol	910.56
cryst dimens, mm	0.15 × 0.30 × 0.60
space group	$P2_1/c$
cell parameters	
a, Å	11.140 (4)
b, Å	18.047 (6)
c, Å	19.850 (7)
β, deg	94.87 (3)
V, Å^3	3976.3
Z	4
d(calcd), g/cm^3	1.521
Collection and Refinement Parameters	
radiatn (wavelength, Å)	Mo Kα (0.71073)
monochromator	Zr filter
linear abs coeff, cm^{-1}	32.11
scan type	$\omega/1.33\theta$
bkgd	25% of full scan width on both sides
θ limits, deg	$2 < \theta < 25$
quadrant collected	$\pm h,+k,+l$
total no. of reflctns	6977
data with $I \geq 3\sigma(I)$	4146
R	4.1%
R_w	3.1%
GOF	1.60
no. of parameters	358
largest parameter shift	0.19

Table II. Selected Bond Distances (Å) for 2

W-P(1)	2.595 (2)	C(4)-C(5)	1.376 (7)
W-P(2)	2.532 (2)	C(5)-C(6)	1.482 (8)
W-C(1)	1.97 (1)	C(5)-C(8)	1.443 (8)
W-C(2)	2.029 (8)	C(6)-C(7)	1.345 (9)
W-C(3)	1.991 (7)	C(6)-C(10)	1.501 (8)
W-C(4)	1.899 (6)		

The stereochemistry of the two isomers was probed on the basis of comparison of $^3J_{CH}$ coupling constants between the vinyl proton and the carbon substituents cis and trans to that proton[17] (eq 2). For the kinetic isomer **2**,$^3J_{CH}$



(2)

2 3

values were 6 Hz for the vinylidene β-carbon and 12 Hz for the ester carbon attached to the vinyl fragment, indicating that the proton is trans to the ester carbon (*Z* isomer). For the second isomer, **3**, the $^3J_{CH}$ value to the vinylidene β-carbon is 12 Hz, with $^3J_{CH}$ only 5 Hz to the ester carbon, indicating the proton is trans to the β-carbon (*E* isomer).

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(12) $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count, and ρ = 0.01 is a correction factor.

(13) The function minimized was $\sum w(|F_o| - |F_c|)^2$.

(14) $R_{\text{unweighted}} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{\text{weighted}} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(15) Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, J. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.

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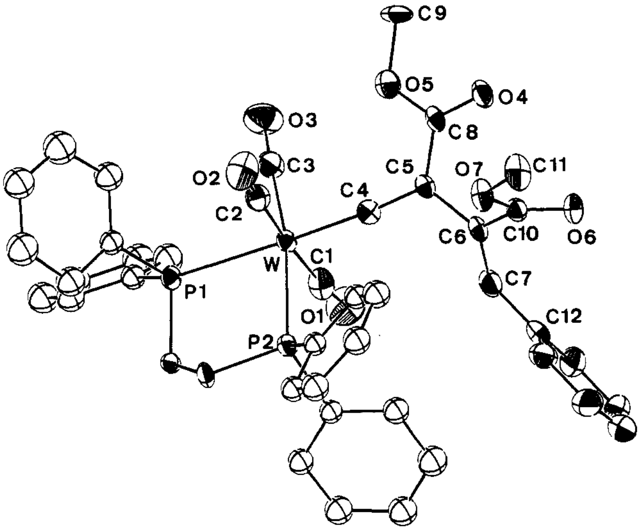


Figure 1. ORTEP drawing showing atomic numbering scheme for **2**.

Table III. Selected Angles (deg) for 2

P(1)–W–P(2)	79.12 (5)	C(1)–W–C(4)	88.1 (3)
P(1)–W–C(1)	97.1 (2)	C(2)–W–C(3)	92.5 (3)
P(1)–W–C(2)	87.1 (2)	C(2)–W–C(4)	87.7 (3)
P(1)–W–C(3)	91.9 (2)	C(3)–W–C(4)	89.1 (2)
P(1)–W–C(4)	174.7 (2)	W–C(1)–O(1)	175.5 (7)
P(2)–W–C(1)	90.9 (2)	W–C(2)–O(2)	176.5 (7)
P(2)–W–C(2)	88.2 (2)	W–C(3)–O(3)	178.6 (6)
P(2)–W–C(3)	170.9 (2)	W–C(4)–C(5)	174.4 (5)
P(2)–W–C(4)	100.0 (2)	C(4)–C(5)–C(6)	120.1 (6)
C(1)–W–C(2)	175.5 (3)	C(4)–C(5)–C(8)	122.5 (6)
C(1)–W–C(3)	89.1 (3)	C(5)–C(6)–C(7)	121.9 (6)

Exposure of a solution of **2** to light (sunlamp) promoted isomerization, converting from 10:1 *Z*/*E* to 1:8 *Z*/*E* in less than 1 h. When exposed to ambient light for 4 months, the same isomer ratio was observed, suggesting that a 1:8 ratio of *Z*/*E* is a photostationary state for this system.

Molecular Structure of the *Z* Isomer. The tungsten in (*Z*)-(dppe)(OC)$_3$W=C=C(COOCH$_3$)C(COOCH$_3$)=C(H)(Ph) adopts a simple octahedral geometry, with meridional CO's and the vinylidene fragment trans to a dppe phosphorus (see Figure 1). Selected bond distances and angles and atomic positions are listed in Tables II–IV. The bulkier substituent on the vinylidene, the substituted vinyl group, is pointed toward the dppe fragment and away from the cis CO. In (dppe)(OC$_3$)W=C=C(H)(COOCH$_3$) the ester group is directed toward the cis phosphorus.[3] The vinylvinylidene four-carbon backbone has a C(4)–C(5)–C(6)–C(7) dihedral angle of 43.5°, far away from a planar cisoid geometry. The vinylidene is twisted relative to the cis WL$_4$ bonds as the W–C(5)–C6 vinylidene plane makes a dihedral angle of 24.3° with the W–P(2)–C(5) plane and 66.7° with the W–C(1)–C(5) plane.

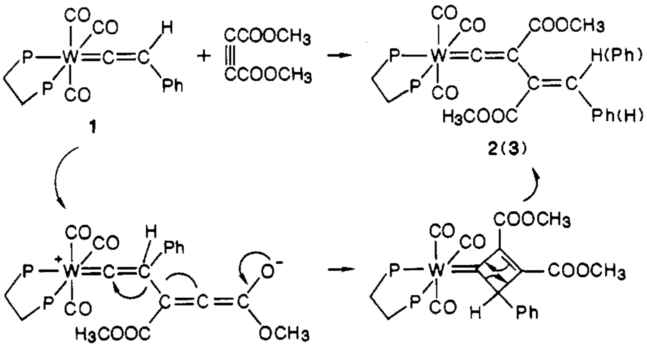
Discussion

Synthesis and Spectral Properties. Cycloaddition of alkynes across C–C double bonds has precedent in both organic[18] and organometallic[10] chemistry. In this system, the electron-poor DMAC alkyne contains two ester functionalities that draw electron density from the C–C triple bond, activating it toward nucleophilic attack by the electron-rich vinylidene C$_\beta$ carbon. The proposed reactivity pattern is presented in Scheme II. This mode of reactivity is compatible with both experimental[4,19] and

Table IV. Atomic Positions for 2

atom	*x*	*y*	*z*
W	0.29570 (3)	0.29663 (2)	0.36077 (2)
P(1)	0.3764 (2)	0.2871 (1)	0.24223 (9)
P(2)	0.1059 (2)	0.2599 (1)	0.2893 (1)
O(1)	0.3398 (6)	0.1318 (4)	0.4085 (4)
O(2)	0.2367 (5)	0.4652 (3)	0.3284 (3)
O(3)	0.5581 (5)	0.3382 (4)	0.4301 (4)
O(4)	0.2060 (5)	0.4073 (3)	0.6025 (2)
O(5)	0.3551 (5)	0.4058 (3)	0.5337 (3)
O(6)	−0.0652 (4)	0.3316 (3)	0.6058 (2)
O(7)	−0.0394 (4)	0.4076 (3)	0.5192 (2)
C(1)	0.3248 (7)	0.1929 (6)	0.3880 (4)
C(2)	0.2559 (6)	0.4040 (5)	0.3381 (4)
C(3)	0.4582 (7)	0.3227 (5)	0.4038 (4)
C(4)	0.2312 (6)	0.3124 (4)	0.4451 (3)
C(5)	0.1868 (6)	0.3309 (4)	0.5054 (3)
C(6)	0.0730 (6)	0.2975 (5)	0.5245 (3)
C(7)	0.0489 (7)	0.2249 (5)	0.5158 (4)
C(8)	0.2461 (6)	0.3837 (4)	0.5517 (3)
C(9)	0.4195 (8)	0.4563 (6)	0.5778 (5)
C(10)	−0.0180 (6)	0.3460 (4)	0.5544 (3)
C(11)	−0.1185 (8)	0.4592 (5)	0.5482 (4)
C(12)	−0.0657 (7)	0.1852 (4)	0.5246 (4)
C(13)	−0.1789 (7)	0.2133 (5)	0.5022 (4)
C(14)	−0.2819 (8)	0.1749 (5)	0.5107 (5)
C(15)	−0.2746 (8)	0.1070 (6)	0.5396 (5)
C(16)	−0.1706 (9)	0.0768 (5)	0.5612 (5)
C(17)	−0.0628 (8)	0.1138 (5)	0.5515 (4)
C(18)	0.2616 (6)	0.2354 (4)	0.1905 (4)
C(19)	0.1349 (6)	0.2634 (4)	0.1998 (4)
C(20)	0.5145 (6)	0.2365 (4)	0.2291 (4)
C(21)	0.5555 (7)	0.2326 (5)	0.1643 (4)
C(22)	0.6587 (7)	0.1908 (6)	0.1549 (4)
C(23)	0.7153 (8)	0.1545 (5)	0.2058 (4)
C(24)	0.6804 (8)	0.1573 (6)	0.2694 (5)
C(25)	0.5747 (7)	0.1998 (6)	0.2806 (4)
C(26)	0.3923 (6)	0.3726 (4)	0.1947 (4)
C(27)	0.4608 (7)	0.4296 (5)	0.2261 (4)
C(28)	0.4819 (9)	0.4938 (6)	0.1899 (5)
C(29)	0.4335 (8)	0.5028 (6)	0.1266 (5)
C(30)	0.3637 (8)	0.4503 (6)	0.0946 (5)
C(31)	0.3416 (8)	0.3835 (5)	0.1290 (4)
C(32)	0.0471 (6)	0.1669 (4)	0.3001 (4)
C(33)	−0.0164 (7)	0.1536 (5)	0.3564 (4)
C(34)	−0.0670 (8)	0.0834 (5)	0.3674 (4)
C(35)	−0.0530 (8)	0.0281 (5)	0.3217 (4)
C(36)	0.0094 (8)	0.0402 (5)	0.2683 (4)
C(37)	0.0613 (7)	0.1088 (5)	0.2553 (4)
C(38)	−0.0257 (6)	0.3179 (4)	0.2934 (3)
C(39)	−0.1132 (6)	0.3233 (4)	0.2395 (4)
C(40)	−0.2135 (7)	0.3680 (5)	0.2431 (4)
C(41)	−0.2265 (7)	0.4087 (5)	0.2992 (4)
C(42)	−0.1407 (7)	0.4068 (5)	0.3536 (4)
C(43)	−0.0400 (6)	0.3605 (4)	0.3503 (4)

Scheme II



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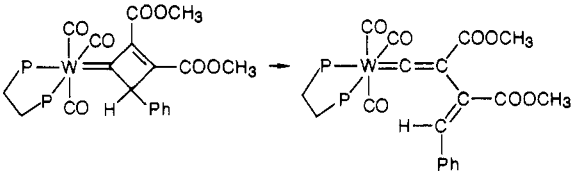
theoretical[7] vinylidene studies.

The net result of addition of DMAC to (dppe)(OC)$_3$W=C=C(H)Ph is insertion of DMAC into the C–C double bond. We believe the reaction proceeds via stepwise cycloaddition to form an η^1-cyclobutenyl complex which rapidly ring opens to form the vinylvinylidene product. No cyclized material has been detected. Initial formation of the *Z* isomer is compatible with ring opening such that the bulky phenyl group rotates away from the metal center (eq 3). Due to rotation about the W=C bond of the vinylidene, the reacting species could be one of two conformers or both. However, ring opening via phenyl group rotation away from tungsten will produce only one isomer. This geometry was confirmed for the kinetic isomer **2** by a crystal structure.



2

(3)

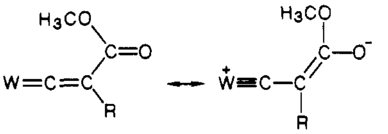
The IR intensity pattern for the three metal carbonyl modes remains constant throughout the reaction, the only change being a shift of ~10 cm^{-1} to higher frequency relative to the starting vinylidene. The intensity pattern for the three bands is consistent with a meridional CO geometry as is typical for vinylidene complexes in this system.[3] The shift to higher wavenumber probably reflects addition of the electron-withdrawing DMAC as the ester groups increase the π-acceptor ability of the vinylidene fragment.

The structure of both isomers was probed through ^{1}H and ^{13}C NMR. The C_α signals appear at very low field as is characteristic of vinylidene complexes[3,20] [*Z*, 326.6 ppm (dd, $^2J_{CP}$ = 20, 8 Hz); *E*, 325.5 ppm (dd, $^2J_{CP}$ = 18, 8 Hz)]. The C_β signals display $^3J_{CP}$ splitting [*Z*, 122.3 ppm (dd, $^3J_{CP}$ = 11 Hz, $^3J_{CH}$ = 6 Hz); *E*, 117.2 ppm (t, $^3J_{CP}$ = 12 Hz, $^3J_{CH}$ = 12 Hz)]. For the *Z* isomer, the vinyl proton was located at 6.84 ppm in the ^{1}H NMR and was used to locate the vinyl carbon (129.0 ppm) via 2D NMR. The vinyl proton of the *E* isomer was not observed and is presumed to resonate in the phenyl region.

Photochemical isomerization of the vinylvinylidene is analogous to that of α–β-unsaturated ketones. Such ketones are known to undergo isomerization about the C–C double bond when exposed to light.[21] The *Z* isomer **2** is similarly converted by light to the *E* isomer and achieves an apparent photostationary state of 1:8 *Z*/*E*.

Molecular Structure. The W–C bond length of the vinylidene fragment is 1.899 (6) Å, noticeably shorter than the W–C length of 1.98 (1) Å in (dppe)(OC)$_3$W=C=C(H)(COOCH$_3$). The C(4)–C(5) bond length is longer than that for the ester vinylidene, 1.376 (7) and 1.30 (1) Å, respectively.[3] It is important to note that the sum of the W–C_α and C_α–C_β distances are nearly equal for the two complexes, so caution must be exercised in drawing conclusions as to their relative π-back-bonding abilities. It is known that the central atom location in linear M–C–X systems is not well-defined crystallographically.[22]

A comparison of C–COOCH$_3$ distances in **2** shows a shorter bond length (1.443 (8) Å) for the vinylidene–ester linkage than for the vinyl–ester linkage (1.501 (8) Å). Furthermore the dihedral angle between the vinylidene and attached ester (planes C(4)–C(5)–C(8) and C(5)–C(8)–O(4)) is 7.1°. This suggests that delocalization of π-electron density between the vinylidene and ester fragments makes a significant resonance contribution (eq 4).



(4)

This "carbyne" resonance form is also compatible with the short W–C(4) and long C(4)–C(5) distances observed in **2**. In contrast, the C(4)–C(5)–C(6)–C(7) torsion angle between the vinylidene and vinyl groups is 43.5°, indicating that π-overlap is unimportant here. The trans influence of the vinylidene ligand is evident in the W–P bond lengths where W–P(1), trans to vinylidene, has a bond length of 2.595 (2) Å, whereas W–P(2) trans to CO, has a 2.532 (2) Å bond distance.

Conclusion

Two isomers of the vinylvinylidene complex, (dppe)(OC)$_3$W=C=C(COOCH$_3$)C(COOCH$_3$)=CHPh, have been prepared via addition of dimethyl acetylenedicarboxylate to (dppe)(OC)$_3$W=C=C(H)Ph. The kinetic *Z* isomer is converted by light to the *E* isomer. An X-ray crystal structure of the *Z* isomer reveals an octahedral geometry with the vinyl substituent on the vinylidene directed toward the cis phosphorus. Although repetition of this insertion step would lead to polymer formation, the vinylidene ester substituent of the product evidently deactivates the tungsten vinylidene toward further reaction with DMAC.

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Registry No. 1, 88035-90-9; 2, 113109-53-8; 3, 113214-82-7; DMAC, 762-42-5.

Supplementary Material Available: Tables of anisotropic and isotropic temperature factors, complete bond distances and angles, calculated hydrogen positions, and defined planes and calculated dihedral angles and an ORTEP drawing showing complete atom numbering scheme (8 pages); a listing of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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