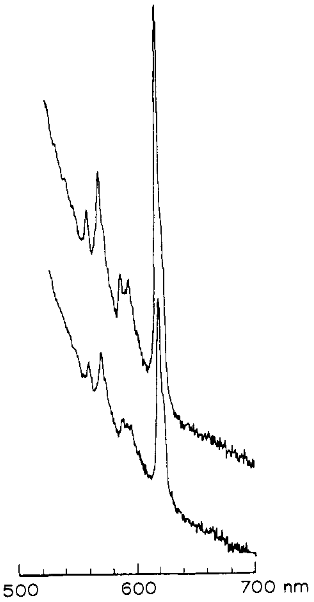
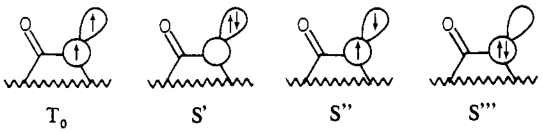


Figure 2. Top: Ultraviolet spectrum (520–700 nm) of α-ketocarbene **7** prepared by irradiation (365 ± 8 nm, 45 min) of **1** in an argon matrix. Bottom: The same sample after irradiation (625 ± 8 nm) for 62 min showing the decrease in α-ketocarbene.

by photosensitized decomposition of α-diazoketones also do not give Wolff rearrangement.[4-6]

We sought a system in which the chemistry and spectroscopy of an α-ketocarbene could be studied. Increasing strain in the transition state for ring contraction should suppress Wolff rearrangement. Diazoketones **1**, **2**, and **3** seemed ideal precursors that impose increasingly severe strain limitations. Irradiations (>338 nm)[17] of each of these diazoketones matrix isolated in argon at 10–15 K gave clean Wolff rearrangement to the ketene (Scheme I) (**4**, 2127 cm^{-1}; **5**, 2127 cm^{-1}; **6**, 2128 cm^{-1}). Diazo ketone **1** gives no Wolff rearrangement product in solution either thermally or photochemically.[12,13] Irradiation of **1**, **2**, and **3** does not give the ketenes unless they are isolated in an inert matrix. Irradiation of **1** (365 ± 8 nm)[17] matrix isolated in argon at 10 K gives the α-ketocarbene **7** as the sole primary product (see trapping evidence below). The α-ketocarbene is characterized by its infrared spectrum (1665, 1015, and 767 cm^{-1}, (Figure 1), its ultraviolet spectrum (λ_{max} 621.3, 597.1, 590.3, 573.4, and 563.2 nm, Figure 2), and its electron spin resonance spectrum ($D/hc = 0.407$ cm^{-1}, $E/hc = 0.0270$ cm^{-1}, Z_1 990, X_2 4491, Y_2 5538, and Z_2 7632 G). The ground state of **7** is established as a triplet by a linear Curie law plot in the temperature range 18–30 K. The chemical identity of **7** is confirmed by trapping with oxygen in argon giving 1,8-naphthalic anhydride (**8**, identified by IR comparison with an authentic sample in argon) and with carbon monoxide in argon giving ketoketene **9**. The structure of **9** was established by independent synthesis from **10**. In the oxygen-trapping experiment, only a trace of ketene **4** was observed. The α-ketocarbene **7** is thus the primary photoproduct from diazoketone **1**. Experiments with infrared monitoring show initial formation (365 ± 8 nm) of the α-ketocarbene with subsequent photochemical conversion of this intermediate to ketene **4**. When **7** was irradiated at longer wavelength (625 ± 8 nm), the bands at 1665, 1015, and 767 cm^{-1} disappeared, and the bands characteristic of ketene **4** increased (Figure 1). The ultraviolet absorption (Figure 2) and the ESR signal due to **7** also disappear on irradiation at 625 ± 8 nm. Diazo ketone **1** is completely stable to irradiation under these conditions.

The yield of ketene **4** (measured by the intensity of the band at 2127 cm^{-1}) is inversely proportional to the concentration of oxygen or carbon monoxide in the matrix. Two conclusions come from this observation. First, ground-state (T_0) **7** is the only product



from S_1 diazo ketone, and second, under these conditions all of the observed Wolff rearrangement proceeds via **7** (T_0). Conversion of **7** to **4** is initiated by $T_0 \rightarrow T_1$ excitation of **7**. The energy of this transition is 46 kcal/mol. Calculations predict high barriers for 1,2-shifts in T_0 methylcarbene[14] but no barrier for Wolff rearrangement in the S_1 state of formylcarbene.[15] This system is conformationally mobile and rearrangement via S_1 involves rotation about the C–C bond. α-Ketocarbene **7** is not conformationally mobile, and bond migration is rigorously confined to the plane of the molecule. The lowest closed-shell singlet state (S')[16] of **7** which corresponds to S_1 in $\mathrm{H\ddot{C}CHO}$) is inappropriate for in-plane rearrangement because the in-plane hybrid orbital is filled. In fact, S''' is the ideal configuration for in-plane bond migration because it has a vacant in-plane orbital, and we suggest that intersystem crossing $T_1 \rightarrow S'''$ occurs with rapid rearrangement of **7** (S''') to **4**. The S''' state in α-ketocarbenes is stabilized by delocalization of the electron pair into the carbonyl π-system.

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Registry No. 1, 2008-77-7; **2**, 87985-99-7; **3**, 87986-00-3; **4**, 82515-17-1; **5**, 86998-10-9; **6**, 87016-12-4; **7**, 2235-15-6.

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(16) The carbene singlet states are designated S', S'', and S''' because their position in the singlet manifold relative to singlet states of the naphthalene chromophore is not known. The energies increase in the order $S' < S'' < S'''$

(17) Irradiations were carried out with an ILC Technology LX300UV 300W high-pressure xenon arc lamp. Wavelength control was provided by either cut-off filters (0% transmittance of wavelengths shorter than the specified value) or a Kratos GM252-20 high-intensity quarter meter grating monochromator (16-nm band-pass centered at the specified value).

Mechanism of Ziegler-Natta Polymerization of Acetylene: A Nutation NMR Study

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Received August 11, 1983

In spite of the widespread commercial application of Ziegler-Natta catalysis in olefin polymerization, the mechanism of the fundamental carbon-carbon bond-forming reaction in this process is not well understood.[1] Currently available data do not distinguish between the more traditional four-center olefin insertion mechanism of Cossee and Arlman[2] and the recent metallacycle proposal of Green and co-workers.[3]

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(1) For a recent discussion and leading references, see: Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479–4480.

(2) Cossee, J. *J. Catal.* **1964**, *3*, 80–88. Arlman, E. J. *Ibid.* **1964**, *3*, 89–98. Arlman, E. J.; Cossee, P. *Ibid.* **1964**, *3*, 99–104.

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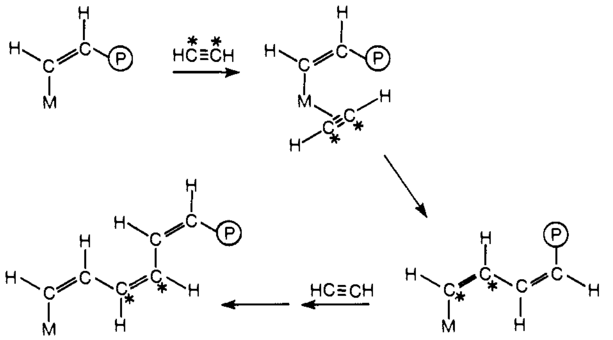
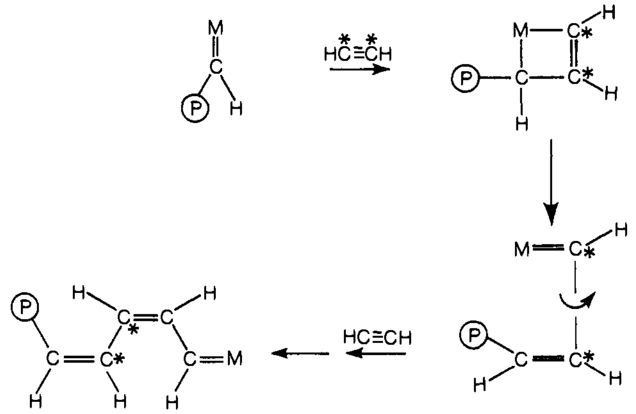
Scheme I



Scheme II



A similar dichotomy exists in the related question of acetylene polymerization, where comparable mechanisms have been proposed. The direct four-center acetylene insertion mechanism is illustrated in Scheme I,[4] while the metallacycle mechanism suggested by Katz is shown in Scheme II.[5] In contrast to the olefin case, however, a clear-cut distinction can be drawn between these two mechanisms. Scheme I predicts that the two carbons of a given monomer unit will end up doubly bonded to one another in the resulting polymer; according to Scheme II these carbons will be connected by a single bond. We present here the results of an experiment designed to test this difference and demonstrate that, at least in the case of acetylene polymerization by the particular Ziegler–Natta catalyst system employed, the predictions of Scheme I are observed.

The keys to this experiment are the use of doubly ^{13}C-labeled acetylene monomer and the use of nutation NMR spectroscopy to measure the bond distance between these labeled carbons in the resulting polymer. We have previously shown that the nutation technqiue can be used to determine bond lengths in amorphous or polycrystalline solids to an accuracy of $\sim 1\%$.[6] Essentially, this procedure relies on the fact that the dipole–dipole splitting of two bonded magnetic nuclei (in this case ^{13}C) varies inversely as the third power of the internuclear separation. The nutation technique is used to eliminate the effects of chemical shift anisotropy, which mask this information in the conventional ^{13}C spectrum of a nonordered solid material. To avoid interference from longer range dipole–dipole splittings, the bonded nuclei must be relatively isolated from other ^{13}C nuclei. We have achieved this situation in polyacetylene by polymerizing a mixture of 4% doubly ^{13}C-enriched acetylene (MSD Isotopes—≥99 atom % ^{13}C) in doubly depleted acetylene (MSD Isotopes—99.9 atom % ^{12}C). This dilution also assures that each of the bonded ^{13}C pairs in the resulting polymer arises from a doubly labeled acetylene monomer, allowing us to test the above two mechanisms by determining the bond length between these atoms.

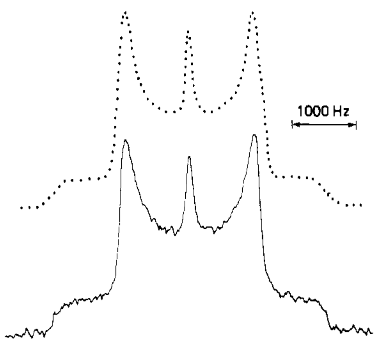


Figure 1. Proton-decoupled ^{13}C nutation NMR spectrum at 77 K of doubly labeled *cis*-$(CH)_x$ (solid line). Simulation of nutation spectrum of *cis*-$(CH)_x$ using a 1.37 Å C–C bond length (dotted line). The peak in the middle is due to isolated ^{13}C nuclei.

The acetylene mixture was polymerized by the method of Ito *et al.* using a titanium tetra-*n*-butoxide/triethylaluminum catalyst mixture in toluene.[7] The polymerization was carried out at 196 K to provide the cis–transoid isomer of polyacetylene. The polymer films were washed free of catalyst residue and packed into sample tubes under drybox conditions before being sealed under vacuum. The samples were stored at 77 K before use to avoid isomerization to the trans–transoid isomer.[8–10] A detailed description of the nutation technique has been published previously.[6]

The proton-decoupled ^{13}C nutation spectrum of a *cis*-polyacetylene sample prepared in this manner is shown in Figure 1. The relatively sharp peak in the center arises from isolated ^{13}C nuclei in the sample. The symmetrically disposed satellites and shoulders are the expected features of the doublet pattern arising from the dipole–dipole splitting of the adjacent ^{13}C nuclei in a powder sample.[6] This spectrum can be fit using a comprehensive simulation program, with the desired carbon–carbon bond distance as the only adjustable parameter. The best fit to the observed spectrum (shown as the dotted curve in Figure 1) corresponds to a bond length of 1.37 Å, a value clearly indicative of a carbon–carbon double bond and not a single bond.[11] These results require that in the polymerization process the carbons of a given monomer unit end up doubly bonded, in agreement with the predictions of Scheme I.

Thus, these data indicate that, at least for this particular Ziegler–Natta catalyst system, the metallacycle mechanism is not operative. The extent to which these results can be generalized to other types of catalysts and to olefin polymerization mechanisms is currently under investigation.[12]

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(9) We find that the cis–trans isomerization process leads to a scrambling of the bonding sequence such that an almost equal distribution of singly and doubly bonded labeled-carbon pairs is generated. For a discussion of this process and its implications for the proposed soliton theories of defect formation and electronic transport in polyaceylene,[10] see: Yannoni, C. S.; Clarke, T. C. *Phys. Rev. Lett.* **1983**, *51*, 1191.

(10) For leading references pro and con, see: Etemad S.; Heeger A. J.; MacDiarmid, A. G. *Annu. Rev. Phys. Chem.* **1982**, *33*, 443–469. Tomkiewiez Y.; Schultz T. D.; Brom H. B.; Taranko, A. R.; Clarke, T. C.; Street, G. B. *Phys. Rev. B* **1981**, *24*, 4348–4363.

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(12) Katz, T. J.; Yannoni, C. S., unpublished results.

Acknowledgment. We thank the Office of Naval Research and the National Science Foundation (CHE-81-08998) for partial support of this work and R. D. Kendrick for his assistance in both instrumentation and implementation of the simulation program.

Registry No. Acetylene, 74-86-2.

Tungsten Vinylidenes and Carbynes from Terminal Alkyne Reagents

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Terminal alkynes react with *fac*-$W(CO)_3$(dppe)(THF) (**1**)[1] to form neutral vinylidene complexes[2] of the type *mer*-$W(CO)_3$(dppe)(C=CRH) with R = CO_2Me (**2**) and R = C_6H_5 (**3**). Stoichiometric addition of methyl propiolate (HC_2CO_2Me) to a yellow THF solution of **1** followed by heating at 50 °C generates a deep red solution, which yields an organge solid upon solvent removal and trituration. Florisil chromatography and recrystallization from CH_2Cl_2/cyclohexane produce **2** as red-orange crystals in 70% yield (based on $W(CO)_4$(dppe)). Phenylacetylene addition to **1** leads to an analogous product, **3**, with alumina chromatography used to purify the green material (65% yield). Both **2**[3] and **3**[4] have been characterized by NMR. The vinylidene ligands were identified by their characteristic ^{13}C α-carbon[5] chemical shift (328.4, **2**; 336.3, **3**) and appropriate $^1J_{CH}$ coupling constants at the β-carbon (162 Hz, **2**; 157 Hz, **3**). A meridional geometry is indicated by $^{31}P\{^1H\}$ NMR spectra for both **2** and **3**. Unusually small $^1J_{WP}$ values characterize the high-field ^{31}P signal in each complex (145 Hz, **2**; 155 Hz, **3**). We attribute this to the strong trans influence of the vinylidene ligands since the larger $^1J_{WP}$ coupling constants (245 Hz, **2**; 242 Hz, **3**) are typical of phosphorus nuclei trans to carbonyl ligands.[6] The ν_{CO} frequencies listed in Table I reinforce the conclusion[7] that vinylidene ligands are powerful π-acids.

Table I. ν(C≡O) Frequencies for $W(CO)_3$(dppe)(L) Complexes

geometry	L	ν_{CO}, cm^{-1} [a]	ref
fac	THF (**1**)	1928 (s), 1830 (s), 1810 (s)	this work
fac	HC≡CCO_2Me	1985 (s), 1920 (s), 1873 (s)	this work
fac	HC≡CPh	1967 (s), 1894 (s), 1855 (s)	this work
fac	$H_2C=CH_2$ [b]	1950 (s), 1873 (s), 1844 (s)	12b
	CO [c]	2012 (m), 1905 (s), 1882 (s)	this work
mer	C=$CHCO_2Me$ (**2**)	2018 (m), 1948 (m), 1911 (s)	this work
mer	C=CHPh (**3**)	2002 (m), 1940 (s), 1900 (vs)	this work
mer	dimethyl fumarate [b]	2006 (s), 1934 (s), 1887 (s)	12b

[a] Spectra recorded in THF unless otherwise noted. [b] Data reported for CH_2Cl_2 solution spectrum. [c] Compare with 2016, 1912, 1901, and 1876 cm^{-1} reported for $ClCH_2CH_2Cl$ solution data in: Grim, S. O.; Briggs, W. L.; Barth, R. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* 1974, *13*, 1095–1099.

Table II. Selected Bond Distances and Angles for *mer*-$W(CO)_3$(dppe)(C=$CHCO_2Me$) (**2**)

atoms	distance, A	atoms	angle, deg
W-P1	2.526 (3)	W-C4-C5	173 (1)
W-P2	2.575 (3)	P2-W-C4	176.5 (3)
W-C1	2.04 (1)	P1-W-C3	167.0 (4)
W-C2	2.10 (1)	C1-W-C2	168.9 (4)
W-C3	2.05 (1)	C1-W-C3	87.3 (4)
W-C4	1.98 (1)	C1-W-C4	85.0 (4)
C4-C5	1.30 (1)	C1-W-P1	90.7 (3)

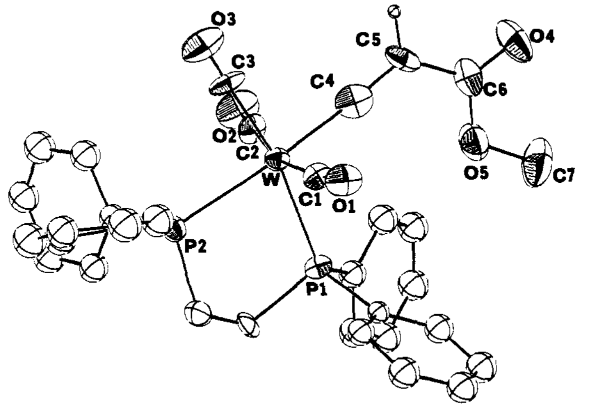
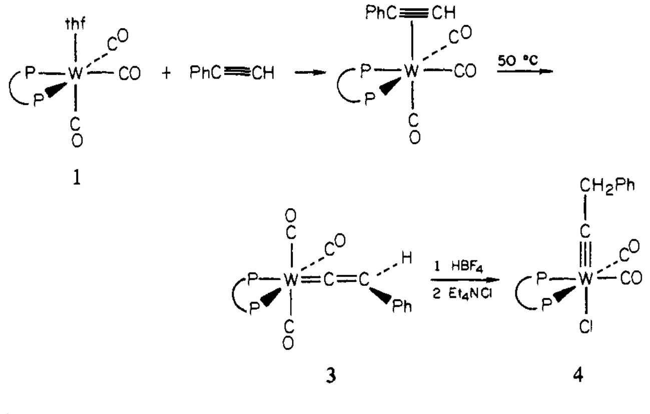


Figure 1. An ORTEP view of $W(CO)_3$(dppe)(C=$CHCO_2Me$) (**2**) showing the atomic labeling scheme.

Scheme I



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[1] dppe = $Ph_2PCH_2CH_2PPh_2$; THF = tetrahydrofuran. **1** was prepared by photolysis of $W(CO)_4$(dppe) in THF (see Table I for IR data). A series of $M(CO)_3$(dppe)(solvent) preparations are reported in ref 11b.

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[3] *mer*-$W(CO)_3$(dppe)(C=$CHCO_2Me$): ^1H NMR ($CDCl_3$) δ7.5 (m, Ph), 4.42 (t, $^4J_{HP}$ = 4 Hz, C=CHR), 3.51 (s, OCH_3), 2.71 (m, PCH_2CH_2P); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 43.0 (s, $^1J_{PW}$ (14% ^{183}W) = 245 Hz), 32.5 (s, $^1J_{PW}$ (14% ^{183}W) = 146 Hz); ^{13}C NMR ($CDCl_3$) δ 328.4 (dd, $^2J_{CP}$ = 18, 8 Hz, vinylidene C_α), 208.5 (dd, $^2J_{CP}$ = 22, 9 Hz, CO trans to P), 201.9 (t, $^2J_{CP}$ = 6 Hz, 2 CO trans to each other), 168.8 (s, *C*O_2Me), 127–135 (m, Ph), 108.8 (dd, $^1J_{CH}$ = 162, $^3J_{CP}$ = 13 Hz, C=*C*HR), 50.3 (q, $^1J_{CH}$ = 146 Hz, OCH_3, 30.0, 28.0 (m, P*C*H_2*C*H_2P).

[4] *mer*-$W(CO)_3$(dppe)(C=$CH(C_6H_5)$): ^1H NMR ($CDCl_3$) δ 6.94–7.73 (m, Ph), 4.99 (dd, $^4J_{PH}$ = 6.7, 3.6 Hz, C*H*Ph), 2.55 (m, PC*H_2*C*H_2*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 45.4 (s, $^1J_{PW}$ (14% ^{183}W) = 242 Hz), 35.6 (s, $^1J_{PW}$ (14% ^{183}W) = 155 Hz); ^{13}C NMR ($CDCl_3$) δ 336.3 (dd, $^2J_{PC}$ = 17, 8 Hz, vinylidene C_α), 211.5 (dd, $^2J_{PC}$ = 21, 9 Hz, CO trans to P), 202.3 (t, $^2J_{PC}$ = 6 Hz, 2 CO trans to each other), 123–136 (Ph), 117.7 (dd, $^1J_{CH}$ = 157, $^3J_{CP}$ = 12 Hz, C=*C*HPh), 30.4, 28.7 (m, P*C*H_2*C*H_2P).

[5] (a) Baker, P. K.; Barker, G. K.; Green, M.; Welch, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 7811–7812. (b) Wong, A.; Gladysz, J. A. *Ibid.* **1982**, *104*, 4948–4950. (c) Davidson, A.; Selegue, J. P. *Ibid.* **1978**, *100*, 7763–7765. (d) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628–634. (e) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471–1483.

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