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

K. R. Birdwhistell, S. J. Nieter Burgmayer, and
J. L. Templeton*

W. R. Kenan, Jr. Laboratories
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Received July 5, 1983

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$_2$Me (**2**) and R = C$_6$H$_5$ (**3**). Stoichiometric addition of methyl propiolate (HC$_2$CO$_2$Me) 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$_2$Cl$_2$/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{^{1}H} 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$_2$Me	1985 (s), 1920 (s), 1873 (s)	this work
fac	HC≡CPh	1967 (s), 1894 (s), 1855 (s)	this work
fac	H$_2$C=CH$_2$ [b]	1950 (s), 1873 (s), 1844 (s)	12b
	CO [c]	2012 (m), 1905 (s), 1882 (s)	this work
mer	C=CHCO$_2$Me (**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$_2$Cl$_2$ solution spectrum. [c] Compare with 2016, 1912, 1901, and 1876 cm^{-1} reported for ClCH$_2$CH$_2$Cl 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$_2$Me) (**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)

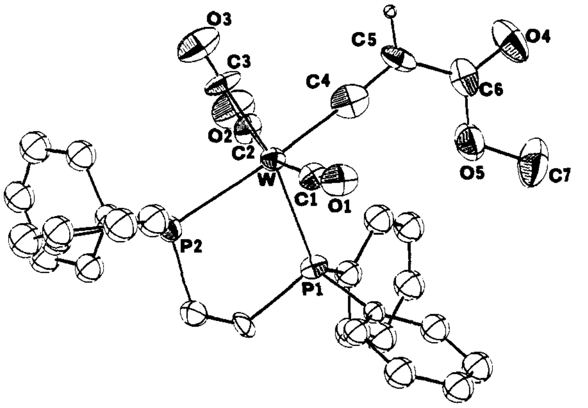
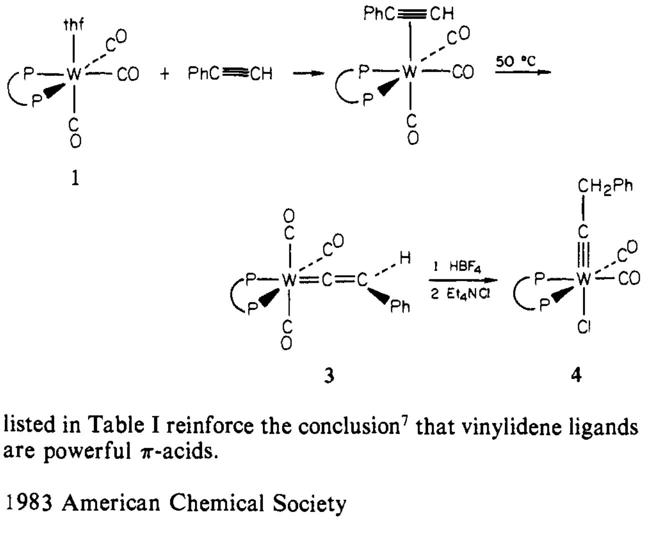


Figure 1. An ORTEP view of W(CO)$_3$(dppe)(C=CHCO$_2$Me) (**2**) showing the atomic labeling scheme.

Scheme I



---

(1) dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; 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.

(2) Terminal alkynes produce metal vinylidene complexes in other systems, particularly with cationic reagents. (a) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532–1539. (b) Nesmeyanov, A. N.; Aleksandrov, G. G.; Antonova, A. B.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1976**, *110*, C36–C38. (c) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471–1485. (d) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483–3486. (e) Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319–326.

(3) *mer*-W(CO)$_3$(dppe)(C=CHCO$_2$Me): ^{1}H 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$_2$CH$_2$P); ^{31}P{^{1}H} 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$_\alpha$), 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$_2$Me), 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$_2$P).

(4) *mer*-W(CO)$_3$(dppe)(C=CH(C$_6$H$_5$)): ^{1}H 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{^{1}H} 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$_\alpha$), 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$_2$P).

(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.

(6) (a) Grim, S. O.; Wheatland, D. A.; McFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573–5577. (b) Grim, S. O.; McAllister, P. R.; Singer, R. M. *J. Chem. Soc., Chem. Commun.* **1969**, 38–39. (c) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* Springer-**1978**, *16*, 126, 133.

0002-7863/83/1505-7789$01.50/0

The meridional geometry of **2** was confirmed by X-ray crystallography[8] (see Figure 1 and Table II). The vinylidene plane (C4-C5-C6) lies near the W-P1-P2-C3-C4 plane (9.2°) such that the vacant C_α p orbital overlaps with the most available d π electron pair as expected.[9] Comparison of the W-C4 distance of 1.98 Å with the W-C carbene distance of 2.15 Å in $(OC)_5W{=}CPh_2$[10] underscores the strength of the tungsten-vinylidene linkage. The W-P2 bond, trans to the vinylidene, is 0.05 Å longer than W-P1 in accord with the W-P coupling constant discussion above.

Initial formation of a π-bound alkyne adduct is suggested by spectral data as well as by analogy to reactions of **1** with olefins which generate *fac*-$W(CO)_3(dppe)(\eta^2\text{-olefin})$ isomers.[11] Solution infrared spectra taken after **1** and RC_2H are combined (Table I) are compatible with a simple facial alkyne π-adduct (cf. olefin data); a facial vinylidene would probably exhibit higher ν_{CO} frequencies than are observed. In view of the importance of alkyne $\pi_\perp$ donation in octahedral d^4 complexes,[12] *we suggest that the alkyne-to-vinylidene rearrangement is promoted by the unfavorable four-electron two-center $d\pi$-$\pi_\perp$ conflict in these d^6 complexes.*

Protonation of **3** with $HBF_4{\cdot}Me_2O$ in CH_2Cl_2 followed by addition of $[Et_4N]Cl$ generates the neutral Fischer type carbyne, $(dppe)(OC)_2ClW{\equiv}CCH_2Ph$ (**4**),[13] with chloride trans to the multiple metal-carbon bond (Scheme I). Electrophilic attack at a vinylidene β-carbon has been anticipated,[14] and bridging vinylidenes have been converted to cationic bridging carbynes by electrophilic reagents.[15] Reversible deprotonation of $(\pi\text{-}C_5H_5)[P(OMe)_3]_2W{\equiv}C\text{-}CH_2\text{-}t\text{-}Bu$ to an ionic vinylidene has been reported.[16] The protonation of **3** is reversible by treatment with either 1,8-bis(dimethylamino)naphthalene or alumina.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Tables of X-ray data collection parameters (III), positional and thermal parameters (IV), complete bond distances (V) and angles (VI), and observed and calculated structure factors (VII) for **2** (28 pages). Ordering information is given on any current masthead page.

---

(7) (a) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55-67. (b) Bellerby, J. M.; Mays, M. J. *Ibid.* **1976**, *117*, C21-C22.

(8) The crystal selected was monoclinic of space group $P2_1/n$ with unit cell dimensions of a = 12.459 (3) Å, b = 16.227 (6) Å, c = 16.056 (6) Å, and β = 110.22 (3)° with Z = 4. Of the 7109 reflections monitored, 2919 independent reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement, which converged to R = 6.3% and R_w = 4.7% with hydrogens in calculated positions, phenyl carbons refined isotropically, and all other heavy atoms refined anisotropically.

(9) The observed orientation places the vinylidene acceptor orbital in competition with one CO and both dppe P nuclei while rotation by 90° would result in competition with two CO ligands and the trans dppe P for d π electron density.

(10) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127-2134.

(11) (a) Birdwhistell, K. R., unpublished results. (b) Schenk, W. A.; Muller, H. *Chem. Ber.* **1982**, *115*, 3618-3630.

(12) (a) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713-7721. (b) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466-468.

(13) $Cl(dppe)(OC)_2W{\equiv}CCH_2Ph$. IR ($CH_2Cl_2$) ν_{CO} 2000, 1935 (s); ^1H NMR (CD_2Cl_2) δ 7.8-7.0 (m, Ph), 2.92 (m, PC*H*HC*H*HP) 2.83 (t, $^4J_{HP}$ = 3.7 Hz, C*H*$_2$Ph), 2.64 (m, PCH*H*CH*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 39.1 (s, $^1J_{PW}$ (14% ^{183}W) = 231 Hz); ^{13}C NMR ($CDCl_3$) δ 276.3 (t, $^2J_{PC}$ = 9 Hz), 212.1 (dd $^2J_{PC}$ = 48, 6 Hz, 2 CO), 125-136 (Ph), 55.1 (t, $^1J_{CH}$ = 126 Hz, *C*H$_2$Ph), 27.3 (m, P*C*H$_2$*C*H$_2$P).

(14) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974-982.

(15) Lewis, L. N.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 403-404.

(16) Gill, D. S.; Green, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1037-1038.

(17) **Note Added In Proof**: Conversion of terminal metal vinylidenes to carbynes has been reported in related systems. (a) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, 673-675. (b) Mayr, A.; Schaefer, K. C.; Huang, E. Y. "186th ACS National Meeting Abstracts"; The American Chemical Society: Washington, D.C., 1983; Inorganic Contribution No. 266.

Ortho Lithiation of Monosubstituted Benzenes: A Quantitative Determination of pK_a Values in Tetrahydrofuran

Robert R. Fraser,* Monique Bresse, and Tarek S. Mansour

Ottawa-Carleton Institute for Research
and Graduate Studies in Chemistry
Ottawa, Canada K1N 9B4

Received May 31, 1983

Over forty years have elapsed since Gilman and Bebb[1] first described the ortho-directing effect of the methoxy substituent during the metalation of anisole. At almost the same time this "ortho metalation" reaction was being studied independently by Wittig and Fuhrman.[2] In the intervening years metalation of many monosubstituted benzenes has been investigated, mostly with respect to their ease of ortho lithiation. In general, substituents that possessed one or more atoms having an unshared pair (basic site) activated the ortho position toward metalation.[3] In a recent review, Gschwend and Rodriguez[4] provide an excellent summary of this field. From their estimates, in combination with other more recent assessments by Beak and Snieckus,[5] Winkle and Ronald,[6] and Meyers and Avila,[7] the following approximate order of activating influence in "ortho lithiation" is obtained: Strong activators, SO_2NR_2, $CONR_2$ CONHR, CH_2NR_2, OCH_2OCH_3, NHCOR, oxazoline; moderate activators, OR, NR_2, SR, CF_3, F; weak activators, CH_2OH, $CH(OR)_2$, imidazolidine. From the most recent work of Martin[8] the cyano group appears to rank with the most potent of activating substituents. Although there is qualitative value in this ordering of substituents, Beak and Snieckus point out that any understanding of the activating strength will require fundamental kinetic and thermodynamic information. The first mechanistic evidence in two related systems has been uncovered very recently by the research groups of Beak[9a] and Meyers.[9b] Using stop-flow techniques, Beak and co-workers detected complex formation between an *N*,*N*-dimethyl-2,4,6-triisopropylbenzamide and *sec*-butyllithium prior to metalation at the *N*-methyl group. Meyers, Rieker, and Fuentes were able to isolate a complex formed between *tert*-butylformamidines and *tert*-butyllithium that, in certain solvents, leads to metalation α to nitrogen. Similar complex formation in the ortho metalation reaction has long been inferred[10] but never proven. We wish to report thermodynamic information, specifically pK_a data for monosubstituted benzenes in tetrahydrofuran (THF), thereby providing a direct measure of the acidifying effect of a substituent on the proton ortho to it.

We have recently described the measurement of the relative acidities of amines vs. weak hydrocarbon acids in tetrahydrofuran.[11] The method involved a direct measurement of the equilibrium (1) using ^{13}C NMR. When R_2NH is a highly hindered amine such as diisopropylamine or tetramethylpiperidine

$$R_2NH + LiR \rightleftharpoons R_2NLi + RH \qquad (1)$$

---

(1) Gilman, H.; Bebb, R. L. *J. Am. Chem. Soc.* **1939**, *61*, 109.

(2) Wittig, G.; Fuhrman, G. *Chem. Ber.* **1940**, *73*, 1197.

(3) Gilman, H.; Morton, J. W. *Org. React.* **1954**, *8*, 258.

(4) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1.

(5) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.

(6) Winkle, M. R.; Ronald, R. C. *J. Org. Chem.* **1982**, *47*, 2101.

(7) Meyers, A. I.; Avila, W. B. *Tetrahedon Lett.* **1980**, 3335.

(8) Krizan, T. D.; Martin, J. C. *J. Org. Chem.* **1982**, *47*, 2681; *J. Am. Chem. Soc.* **1983**, *105*, 6155.

(9) (a) Al-Aseer, M.; Beak, P.; Hay, D.; Kempf, D. J.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2080. (b) Meyers, A. I.; Rieker, W. F.; Fuentes, L. M. *Ibid.* **1983**, *105*, 2082.

(10) Roberts, J. D.; Curtin, D. Y. *J. Am. Chem. Soc.* **1946**, *68*, 1658. It is perhaps pertinent that the crystal structures of dimeric and tetrameric 1-litho-2-[(dimethylamino)methyl]benzene indicate the presence of an N-Li bond: Johann, T. B.; Jastrzebski, B. H.; van Koten, G.; Koynijin, M.; Starn, C. H. *Ibid.* **1982**, *104*, 5490. Nevertheless the pK_a of its conjugate acid is not strongly lowered.

(11) Fraser, R. R.; Bresse, M.; Mansour, T. S. *Chem. Commun.* **1983**, 620.

0002-7863/83/1505-7790$01.50/0 © 1983 American Chemical Society