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Registry No. Acetylene, 74-86-2.

Tungsten Vinvlidenes 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 complexes² 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 ¹³C α -carbon⁵ chemical shift (328.4, 2; 336.3, 3) and appropriate ${}^{1}J_{CH}$ coupling constants at the β -carbon (162 Hz, 2; 157 Hz, 3). A meridional geometry is indicated by ³¹P¹H NMR spectra for both 2 and 3. Unusually small ${}^{1}J_{WP}$ 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 $^{1}J_{WP}$ coupling constants (245 Hz, 2; 242 Hz, 3) are typical of phosphorus nuclei trans to carbonyl ligands.⁶ The ν_{CO} frequencies

(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 M(CO)₃(dppe)(solvent) preparations are reported in ref 11b.

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1982, 319–326. (3) mer-W(CO)₃(dppe)(C=CHCO₂Me): ¹H NMR (CDCl₃) δ 7.5 (m, Ph), 4.42 (t, ⁴J_{HP} = 4 Hz, C=CHR), 3.51 (s, OCH₃), 2.71 (m, PCH₂CH₂P); ³P['H] NMR (CDCl₃) δ 43.0 (s, ¹J_{PW} (14%¹⁸³W) = 245 Hz), 32.5 (s, ¹J_{PW} (14%¹⁸³W) = 146 Hz); ¹³C NMR (CDCl₃) δ 328.4 (dd, ²J_{CP} = 18, 8 Hz, vinylidene C_a), 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, CO₂Me), 127–135 (m, Ph), 108.8 (dd, ¹J_{CH} = 162, ³J_{CP} = 13 Hz, C=CHR), 50.3 (q, ¹J_{CH} = 146 Hz, OCH₃, 30.0, 28.0 (m, PCH₂CH₂P). (4) mer.W(CO)(dpre)(C=CH(C,H_3)); ¹H NMR (CDCL) δ 6 94–7 73

(d) $_{CH}^{(1)}$ (D) $_{CH}^{(2)}$ (D) $_{ID}^{(2)}$ (D) $_{ID}^$

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Table I. $\nu(C=0)$ Frequencies for $W(CO)_3(dppe)(L)$ Complexes

geo- metry	L	$\nu_{\rm CO},{\rm cm}^{-1}a$	ref
fac	THF (1)	1928 (s), 1830 (s), 1810 (s)	this work
fac	HC≡CCO₂Me	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 CO ^c	1950 (s), 1873 (s), 1844 (s) 2012 (m), 1905 (s), 1882 (s)	12b 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)	1 2 b

^a Spectra recorded in THF unless otherwise noted. ^b Data reported for CH, Cl, solution spectrum. ^c Compare with 2016, 1912, 1901, and 1876 cm⁻¹ reported for ClCH₂CH₂Cl 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 $mer-W(CO)_{31}dppe)(C=CHCO_{2}Me)$ (2)

Res August	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=CHCO₂Me) (2) showing the atomic labeling scheme.

Scheme I



listed in Table I reinforce the conclusion⁷ that vinylidene ligands are powerful π -acids.

The meridional geometry of 2 was confirmed by X-ray crystallography⁸ (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 tungstenvinylidene 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)(η^2 -olefin) isomers.¹¹ Solution infrared spectra taken after 1 and RC₂H are combined (Table I) are compatible with a simple facial alkyne π -adduct (cf. olefin data); a facial vinylidene would probably exhibit higher v_{CO} frequencies than are observed. In view of the importance of alkyne π_{\perp} donation in octahedral d⁴ 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 d⁶ complexes.

Protonation of 3 with HBF_4 ·Me₂O 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 $(\pi$ - $C_5H_5)[P(OMe)_3]_2W = C-CH_2-t-Bu$ 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.

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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.

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(8) The crystal selected was monoclinic of space group P_{21}/n with unit cell dimensions of a = 12.459 (3) Å, b = 16.227 (6) Å, c = 16.056 (6) Å, and $\beta = 110.22$ (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.

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Inorg. Chem. 1982, 21, 466-468. (13) Cl(dppe)(OC)₂W=CCH₂Ph. IR (CH₂Cl₂) ν_{CO} 2000, 1935 (s); ¹H NMR (CD₂Cl₂) δ 7.8-7.0 (m, Ph), 2.92 (m, PCHHCHHP) 2.83 (t, ⁴J_{HP} = 3.7 Hz, CH₂Ph), 2.64 (m, PCHHCHHP); ³¹P{¹H} NMR (CDCl₃) δ 39.1 (s, ¹J_{PW} (14% ¹⁸³W) = 231 Hz); ¹³C NMR (CDCl₃) 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, CH₂Ph), 27.3 (m, PCH₂CH₂P). (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.

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

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Over forty years have elapsed since Gilman and Bebb¹ 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 Rodriguez⁴ 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, SO₂NR₂, CONR₂ CONHR, CH₂NR₂, OCH₂OCH₃, NHCOR, oxazoline; moderate activators, OR, NR₂, SR, CF₃, F; weak activators, CH₂OH, CH(OR)₂, imidazolidine. From the most recent work of Martin⁸ 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.⁹⁶ Using stop-flow techniques, Beak and co-workers detected complex formation between an N,N-dimethyl-2,4,6triisopropylbenzamide 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 inferred¹⁰ 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 ¹³C NMR. When R_2NH is a highly hin-

$$R_2 NH + LiR \rightleftharpoons R_2 NLi + RH \tag{1}$$

dered amine such as diisopropylamine or tetramethylpiperidine

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