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, $PCHHCHHP$) 2.83 (t, $^4J_{HP}$ = 3.7 Hz, CH_2Ph), 2.64 (m, $PCHHCHHP$); $^{31}P\{^1H\}$ 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, CH_2Ph), 27.3 (m, PCH_2CH_2P).

(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.

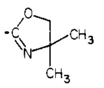
(9) (a) Al-Aseer, M.; Beak, P.; Hay, D.; Kempf, D. J.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2080. (b) Meyers, A. I.; Rieker, W. F.; Fuentes, L. M. *Ibid.* **1983**, *105*, 2082.

(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

Table I. Acidities of Monosubstituted Benzenes, C_6H_5R, in THF

substituent (R)	% metalation[a] (°C)[b]	pK_a[c]
$-N(CH_3)_2$	0	⩾40.3
$-CH_2N(CH_3)_2$	0	⩾40.3
$-C{\equiv}CC_6H_5$	0	⩾40.3
$-NHCOC(CH_3)_3$	0	⩾40.5
-OLi	0	⩾40.5
-OTHP	6	40.0
$-OCH_3$	16	39.0
$-OC_6H_5$	33	38.5
$-SO_2N(C_2H_5)_2$	32 (−40)	38.2
	36 (−40)	38.1
-CN	36 (−78)	38.1
$-CON[CH(CH_3)_2]_2$	45 (−40)	37.8
$-OCON(C_2H_5)_2$	60 (−70)	37.2

[a] A qualitative indication of the substituent effect. [b] If other than 27 °C, the temperature at which metalation and spectral acquisition were performed. [c] pK_a is calculated from log K in eq 1, using the pK_a value of 37.3 for tetramethylpiperidine,[11] and includes the statistical correction factor for the number of acidic protons. [d] THP = 2-tetrahydropyranyl, for which THF–hexane was used as solvent.

(TMP), the lithium–hydrogen exchange reaction is slow on the NMR time scale permitting observation and integration of the signals for all four species. The integral data provide a value for K that represents the difference in acid strengths of R_2NH vs. RH, i.e., $\log K = \log K_{R_2NH} - \log K_{RH}$, providing a value for ΔpK_a.[12] For most of the measurements of K, we have used tetramethylpiperidine as the reference acid ($pK_a = 37.3$)[11] as its acidity was very close to that of many of the monosubstituted benzenes, thereby providing the most accurate measurement of K. For the determination of concentrations by integral measurements, methine signals were chosen for the hydrocarbon acid and its anion on the basis of their being well resolved. The β methylene signals in TMP and lithium tetramethylpiperidide (LTMP) were used to determine the ratio of these two species.[13]

The results of the acidity measurements are presented in Table I. The pK_a values are reported relative to 2-methyl-1,3-dithiane,[11] previously chosen as an arbitrary standard assigned a $pK_a = 37.8$, the value reported for its acidity in cyclohexylamine.[14] Since TMP has been found to be 0.5 pK units more acidic, its pK_a of 37.3 serves as reference for equilibrium (1). The most potent acidifying influence is exhibited by the *N,N*-diethylcarbamate derivative of phenol, whose pK_a is found to be 37.2 since it is 60% metalated by LTMP.[15] This result is consistent with the disclosure this year by Snieckus and Sibi[16] that the metalation and subsequent reaction of this compound with electrophiles proceed in high yields (73–86%). Seven other substituents showed appreciable acidifying effects causing metalation in the 6–50% range. In the case of benzonitrile, its pK_a could only be measured by trapping experiments as the *o*-lithio derivative has only limited stability, even at −78 °C. This instability was reported very recently by Krizan and Martin who described the "in situ" trapping of the anion with trimethylsilyl chloride in high yield. As a result of their experience,[17] we chose to measure the extent of lithiation of benzonitrile at −78 °C by adding methanol-*d* after 3- and 12-min intervals from the mixing of LTMP with benzonitrile. The recovered benzonitrile was found to contain 27% and 36% deuterium, respectively, by mass spectral analysis. Longer intervals before quenching led to appreciable decomposition. From the small increase in deuterium content in the 12- vs. 3-min sample, we can estimate the deuterium content at equilibrium to be close to 36%. The determination of K for the other substituted benzenes was done by ^{13}C NMR and then corroborated by a quenching experiment using methanol-*d*.[18] For each compound the observed deuterium incorporation agreed with the percent metalation by ^{13}C to within the experimental error.

Another significant feature of the data in Table I is the lack of correspondence between the order of activating of substituents (toward an alkyllithium in ether) and the pK_a values in THF. The sulfonamide and carboxamide substituents, generally considered to be the strongest activators,[19] exhibit pK_a values in the same range as four other substituents, the oxazoline and three ethers. Each of the nitrogen substituents, dimethylamino, (dimethylamino)methyl, and carbamate, was too weakly acidic ($pK_a \geq 40.3$) to be measurable in spite of their recognized activating strengths. Clearly, our results reaffirm the importance of kinetic factors in the ortho lithiation reaction with alkyllithiums, as indicated by the aforementioned findings of Beak and Meyers.[9] In this connection it is important to note that the lithiations with LTMP were all very fast ($t_{1/2} \leq 5$ min at 0 °C). For comparison, the metalation of anisole with butyllithium in ether has a reported half-life of several hours.[4]

In summary, these acidity measurements provide a thermodynamic order for the acid-strengthening effect of substituents at the position ortho to it. The fact that the observed effects differ significantly from those obtained during lithiations with alkyllithiums provides corroborative evidence for the importance of an intermediate complex. The observation of an extremely strong acidifying effect for phenyl *N,N*-diethylcarbamate augures well for its utility in synthesis, particularly in competitive metalations, since the anion can also undergo *ortho* migration under properly controlled conditions.[16] The fact that the majority of substituents give rise to very similar pK_a values would indicate a continuing need for the synthetic chemists to survey a variety of conditions when regioselective deprotonation of a di- or trisubstituted benzene is required.

Acknowledgment. We thank NSERC Canada for financial support.

Registry No. $C_6H_5N(CH_3)_2$, 91-66-7; $C_6H_5CH_2N(CH_3)_2$, 103-83-3; $C_6H_5C{\equiv}CC_6H_5$, 501-65-5; $C_6H_5NHCOC(CH_3)_3$, 6625-74-7; C_6H_5OLi, 555-24-8; C_6H_5OTHP, 4203-50-3; $C_6H_5OCH_3$, 100-66-3; $C_6H_5OC_6H_5$, 101-84-8; $C_6H_5SO_2N(C_2H_5)_2$, 1709-50-8; C_6H_5CN, 100-47-0; $C_6H_5CON[CH(CH_3)_2]_2$, 20383-28-2; $C_6H_5OCON(C_2H_5)_2$, 65009-00-9; LTMP, 38227-87-1; 4,5-dihydro-4,4-dimethyl-2-phenyloxazole, 19312-06-2.

---

(12) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley-Interscience: New York, 1975; p 183.

(13) Each sample was prepared in a 10-mm septum-capped NMR tube (Wilmad Glass, Buena, NJ) fitted with an argon inlet and outlet. To a solution of 1.5 mequiv of amine in 2 mL of freshly distilled THF at 0 °C was added 1.5 mequiv of methyllithium in ether. After 15 min a solution of 1.5 mequiv of hydrocarbon in 1 mL of THF was added at 0 °C. The cap was wrapped in parafilm and the tube then warmed and transferred to the probe of a Varian FT-80 NMR spectrometer operating at 27 °C. In a few instances metalation and spectral acquisition were done at low temperature to avoid side reactions. Spectra were accumulated using a small pulse angle (30°) and a 2-s repetition rate. That differential relaxation times were unimportant was shown by extending repetition rate to 3 s without affecting integral ratios. Other factors of quantiative influence, such as differential NOE's were eliminated by using an empirically derived correction factor. This factor, applied to the methylene signals of TMP and LTMP, was arrived at by measuring the integral for TMP prior to then after the addition of 0.5 equiv of methyllithium as well as that of the LTMP produced, both relative to naphthalene present as an internal standard. We estimate the accuracy of K to be ±30%, leading to an uncertainty in ΔpK of ± 0.2 pK units.

(14) Streitwieser, A., Jr.; Guibé, F. *J. Am. Chem. Soc.* **1978**, *100*, 4532.

(15) This base has been shown to be 1.6 pK units stronger than LDA, which provides a value of 35.7 for the pK_a of diisopropylamine in THF: Fraser, R. R.; Baignée, A.; Bresse, M; Hata, K. *Tetrahedron Lett.* **1982**, 4195.

(16) Snieckus, V.; Sibi, M. P. *J. Org. Chem.* **1983**, *48*, 1935.

(17) We are grateful to Professor Martin for his helpful comments on our initial studies of benzonitrile by ^{13}C NMR which proved to be unreliable due to the competing side reactions. We also wish to acknowledge fruitful discussions with Professor P. Beak.

(18) The ortho-lithiation product is recognized by the appearance of six new signals in the aromatic region. Furthermore, the additivity of substituent effects gives predicted shifts generally in agreement with those observed to within 2 ppm, the effect of Li as a substituent vs. H being +43, +12.9, −2.4, and −3.1 at the ipso, ortho, meta, and para positions, respectively: Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. *J. Phys. Chem.* **1969**, *73*, 1624. The percent metalation as reflected in the deuterium content of each quenched sample was determined by using a VG 7070-E mass spectrometer.

(19) While both are considered to be potent, there is conflicting evidence as to the order of activating strength; see: Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34. Meyers, A. I.; Lutowski, K. *J. Org. Chem.* **1979**, *44*, 4464.