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Preliminary communication

ACIDITIES OF ARENETRICARBONYLCHROMIUM(0) COMPLEXES IN TETRAHYDROFURAN

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Summary

The measurement of acidities of arenetricarbonylchromium(0) complexes in tetrahydrofuran reveals the acid-strengthening effect of complexation to be 6–7 p*K* units and the p*K* of benzene to be 41.

Since the first synthesis of η^6-benzenetricarbonylchromium(0) in 1958 [1], much has been learned about the effect of complexation on the reactivity of the aromatic ring in this and other arenetricarbonylchromium complexes. Nicholls and Whiting [2], noted the enhancement of acidity of the carboxyl group in the benzoic acid complex relative to benzoic acid. They also noted the ease of nucleophilic addition to the ring, a reaction subsequently studied extensively for synthetic purposes by Semmelhack and co-workers [3]. Another effect noted was an enhancement in acidity of the protons on the aromatic ring [4] and in the benzylic position [5]. Studies of these acid strengthening effects have, until now, been mainly qualitative [6]. In this communication we wish to report the direct determination of the p*K*'s of four arenechromium tricarbonyls in tetrahydrofuran, to provide quantitative evidence of the structure and thermodynamic stabilities of their conjugate bases.

The compounds studied are the tricarbonylchromium(0) complexes of benzene, **1**, anisole, **2**, toluene, **3**, and *N,N*-diisopropylbenzamide, **4** *. The acidities of these four compounds were determined as described previously [8] by measuring *K* for the equilibrium [1] in which RH represents either a dialkylamine or another weak carbon acid.

$$\text{H-arene Cr(CO)}_3 + \text{RLi} \leftrightarrows \text{Li-arene Cr(CO)}_3 + \text{RH} \qquad (1)$$

Table 1 present the values for *K*, and the resultant p*K*'s for **1**–**4**. An important component of these measurements was to determine the site of lithiation in the

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* The only new compound, **4**, was prepared from the amide and hexacarbonylchromium in dioxane-acetonitrile using the procedures of Tate and coworkers [7].

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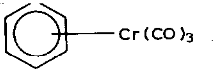
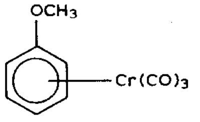
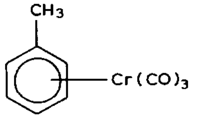
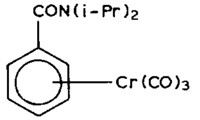
TABLE 1

ARENETRICARBONYLCHROMIUM ACIDITIES

Compound	RH (pK_a) [a]	K [b]	ΔpK	pK	pK(H)	pK(ArH)
 **1**	TMP(37.3)	> 100	> 2.0	< 35.3		
	DIPA(35.7)	52	1.7	34.0	34.8	41.2 [d]
 **2**	BTSA(25.8)	< 0.01	< −2.0	> 27.8		
	DIPA(35.7)	> 20	> 1.3	< 34.4		
	thiophene(33.0)	2	0.3	32.7	33.0	39.0 [c]
 **3**	DIPA(35.7)	> 100	> 2	< 33.7		
	thiophene(33.0)	0.2	−0.7	33.7		
 **4**	thiophene(33.0)	> 10	> 1	< 32.0		
	xanthene(31.4)	4 [e]	0.6	30.8	31.1	37.8 [c]

[a] Abbreviations are TMP for 2,2,6,6-tetramethylpiperidine, DIPA for diisopropylamine and BTSA for bis(trimethylsilyl)amine. [b] All K's, except in e, determined from peak heights of all 4 species, providing values for pK in acidity per molecule. [c] Ref. 9. [d] Estimated value, see text. [e] K determined from $([RH]/[RLi])^2$.

complex. As previously found for anisole [9], lithiation of **2** takes place in the *ortho* position. This was established by the excellent agreement (usually < 0.6 ppm) between the ^{13}C shifts in lithio-**2** and those calculated from additivity using the shifts for **2** and the observed lithiation shifts for **1** *. This conclusion was confirmed by isolation of the methylation product of **2** after decomplexation, whose identity was established by GC/MS and ^{13}C as a single product, 2-methylanisole. Lithiation of **3** was shown by ^{13}C to have occurred at the methyl group only using additivity. The ^{13}C shielding observed for Li-**3** did not agree with those calculated for *ortho*-lithiation but gave good agreement for those calculated for alpha lithiation using the lithiation shifts for the transformation toluene → benzyllithium or for diphenylmethane bis(tricarbonylchromium) to its α-lithio derivative [10]. The site of lithiation of **4** must be assumed to be *ortho* as only very broad peaks were observed for Li-**4**.

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* Lithiation caused the ^{13}C signals for the aromatic carbons of **1** (δ 95.2 ppm) to shift downfield at the *ortho* (+14.4 ppm) and the *meta* positions (+3.3 ppm) and upfield at the *para* positons (−1.5 ppm). To illustrate the use of additivity one predicts that introduction of lithium at the 2-position of the anisole complex **2** will cause C(3) (δ 98.3 ppm) to also shift downfield by 14.4 ppm to δ 112.7 ppm. The observed signal in lithiated **2** appeared at 112.2 ppm.

Compound Li-**2**, having lithium at an *ortho* carbon, is the thermodynamically stable product as indicated by the observation of all four species in equilibrium [1]. Earlier reports of the metalation of **2** by butyllithium [4], also described only *ortho* product, possibly from a "kinetic" or directed metalation as observed for many substituted benzenes [9]. For synthetic purposes, recent studies have shown that metalation of the t-butyldimethylsilyl and tri-isopropylsilyl ethers of phenol yield increasing amounts of *meta*- and *para*-lithiation with increasing bulk at silicon [11].

Exclusive removal of a methyl proton in **3** ($pK = 33.7$) is surprising since the aromatic protons in **1** exhibit the same pK. That the aromatic protons in **3** have an appreciably higher pK than in **1**, probably reflects the electron-donating effect of the methyl group. Deprotonation of **3** by butyllithium, reported to give a mixture of all possible lithio derivatives [5], is in contrast, a kinetically controlled process. It is noteworthy that deprotonation of **3** (and of **1**, **2** and **4**) by lithium diisopropylamine is rapid at 0°C (< 15 min) and thus of synthetic utility.

The acidity data for **1**, **2** and **4** provide an estimate for the pK of benzene in THF. In **2** and **4** the pK has been lowered by 6 and 6.7 units respectively as a result of complexation. The pK of benzene can therefore be estimated to be about 6.4 pK units greater than the value for **1**, i.e., about 41.2. This is in line with the earlier value of 43 reported for benzene in cyclohexylamine [12].

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