(10) (a) J. Fishman and M. Tomasz, *J. Org. Chem.*, **27**, 365 (1962); J. Fishman and J. S. Liang, *Tetrahedron*, **24**, 2199 (1968); W. Nagata, T. Terasawa, and K. Tori, *J. Am. Chem. Soc.*, **86**, 3746 (1964); (b) T. Nambara, S. Honma, and S. Akiyama, *Chem. Pharm. Bull.*, **18**, 474 (1970); T. Nambara, M. Numazawa, and S. Akiyama, *ibid.*, **19**, 153 (1971).

(11) This appears to be a general phenomenon for A-ring aromatic steroids; cf. ref 10b.

(12) R. E. Partch, *J. Am. Chem. Soc.*, **89**, 3662 (1967); J. R. Kalman, J. T. Pinhey, and S. Sternhell, *Tetrahedron Lett.*, 5369 (1972); H. C. Bell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, *ibid.*, 853 (1974); D. Westphal and E. Zbiral, *Justus Liebigs Ann. Chem.*, 2038 (1975). This reagent reacts with ortho bistrimethylsilylated arenes in a destructive manner.

(13) This may be compared with the synthesis of *dl*-estrone methyl ether by Torgov,[14] six steps (18%) from 6-methoxy-1-tetralone and improvements thereof,[15] eight steps (27%) from 2-methoxynaphthalene (corresponding to ~45% from 6-methoxytetraline); the synthesis of *dl*-estrone by Johnson and Bartlett,[16] fourteen steps (6.9%) from *m*-hydroxycinnamic acid; and the synthesis of *d*-estrone by Danishefsky and Cain,[17] fourteen steps (7.4%) from 2,6-lutidine, or eleven steps (13%) from 2-methylcyclopentane-1,3-dione.

(14) S. N. Ananchenko and I. V. Torgov, *Tetrahedron Lett.*, 1553 (1963).

(15) See K. Nakanishi, T. Goto, S. Itô, S. Natori, and S. Nozoe, Ed., "Natural Products Chemistry", Vol. 1, Academic Press, New York, 1974, p 487; see also N. Anand, J. Bindra, and S. Ranganathan, "Art in Organic Synthesis", Holden-Day, San Francisco, Calif., 1970.

(16) P. A. Bartlett and W. S. Johnson, *J. Am. Chem. Soc.*, **95**, 7501 (1973).

(17) S. Danishefsky and P. Cain, *J. Am. Chem. Soc.*, **98**, 4975 (1976).

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Substituent Effects in Addition of Carbanions to Arenechromium Tricarbonyl Complexes: Correlation with Arene LUMO

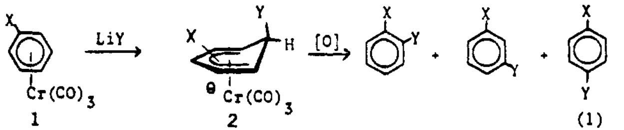
Sir:

The $Cr(CO)_3$ unit activates π-complexed arene ligands (in **1**) toward addition of nucleophiles, leading to analogues (**2**) of Meisenheimer complexes. Oxidation of **2** then gives substituted arenes, from formal replacement of hydride (eq 1).[2] In contrast to classical nuelcophilic aromatic substitution methods, this addition/oxidation pathway does not require a specific leaving group. In this sense, it is parallel with electrophilic aromatic substitution and raises anew the question of selectivity in additions to substituted arenes. The regioselectivity is particularly interesting here since the activating substituent, $Cr(CO)_3$, is symmetrically disposed with respect to the arene ring atoms and presumably activates each of them equally. Then even feeble perturbations from ring substituents could control the site of addition.

We reported the meta-directing effect (90–100% selective) of a methoxy group,[3] an apparently simple reversal of the usual directing influence in electrophilic substitution, and the less easily explained effect of a methyl group (5–50% ortho, 95–50% meta, 0% para[3]). Here we report reactions of substituted π-arene complexes (i.e., **1**) chosen to probe for factors which influence regioselectivity. Table I presents the results.[4] While we have not proven that the product mixtures are the result of kinetic control, shorter or longer reaction times (0.5 min at −78 °C to 24 h at 25 °C) do not alter the product ratios. With chlorobenzene, longer reaction times can lead to substituion for chloride,[5] but little is seen under the conditions employed here.

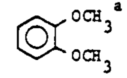
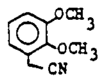
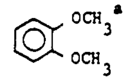
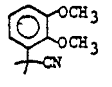
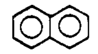
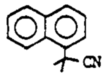
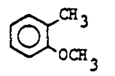
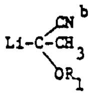
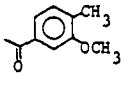
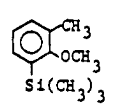
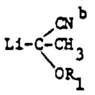
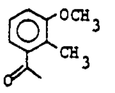
Table I. Addition/Oxidation of Carbanions with Substituted π-Arenechromium Tricarbonyl Complexes

A. Monosubstituted Arene Ligands



Entry	Substituent (X)	Carbanion (LiY)	Product Ratios o:m:p (combined yield)
1	CH_3[a]	$LiCH_2CO_2R$	28:72:0 (89%)
2	OCH_3[a]	$LiCH_2CO_2R$	4:96:0 (93%)
3	Cl	$LiCH_2CO_2R$	54:45:1 (98%)
4	Cl	$LiCH(CH_3)CO_2R$	53:46:1 (88%)
5	Cl	$LiC(CH_3)_2CO_2R$	5:95:1 (84%)
6	Cl	$LiCH_2COC(CH_3)_3$	70:24:0 (87%)
7	Cl	$LiC(CH_3)_2CN$	10:89:1 (84%)
8	Cl	Li-(1,3-dithianyl)	46:53:1 (56%)
9	$Si(CH_3)_3$	$LiC(CH_3)_2CN$	0:2:98 (65%)
10	CF_3	$LiC(CN)(OR_1)CH_3$[b]	0:30:70 (33%)
11	$N(CH_3)_2$	$LiC(CH_3)_2CN$	1:99:0 (92%)
12	$C(CH_3)_3$	$LiC(CN)(OR_1)CH_3$[b]	0:35:65 (85%)
13	CH_2CH_3	$LiC(CN)(OR_1)CH_3$[b]	0:94:6 (89%)

B. Polysubstituted Arene Ligands

	Arene Ligand	Carbanion	Major Product (yield)	
14	[a]	$LiCH_2CN$		(41%)[c]
15	[a]	$LiC(CH_3)_2CN$		(85%)[d]
16		$LiC(CH_3)_2CN$		(83%)[e]
17		[b] $Li{-}C(CN)(CH_3)(OR_1)$		(76%)[c]
18		[b] $Li{-}C(CN)(CH_3)(OR_1)$		(82%)[c]

[a] These data are reproduced from ref 3 for comparison. [b] This anion (R_1 = 1-ethoxyethyl) was developed by G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, **93**, 5286 (1971); the products are acetophenone derivatives (Y = $COCH_3$) resulting from hydrolysis of the cyanohydrin acetal unit. [c] No other isomers were detected. [d] The 1,2,4-substitution product was obtained in 12% yield. [e] The β-substituted isomer was detected, in 1% yield.

Chloride shows a directing effect similar to methyl: little para and similar amounts of ortho and meta (Table I, entries 3, 4, 6, 8) except for bulky anions, where meta is preferred (entries 5, 7). Trimethylsilyl and trifluoromethyl favor para, and naphthalene gives 99% α substitution. The more hindered position is favored with 1,2-dimethoxybenzene, even with a tertiary carbanion (entries 14, 15).[3] The para-directing effect of silicon and the meta-directing effect of methoxy can reinforce to produce a 1,2,3-substitution pattern (entry 18).[6] Steric effects seem to be comparable in magnitude with other directing effects.

A picture for the reaction pathway (**1** → **2**) which emphasizes polar effects is helpful in rationalizing many of the results. This view would take into account the expected electron polarization in **1** or the distribution of negative charge in the cyclohexadienyl unit in **2**. By the usual resonance arguments, the ortho and para positions are electronically similar, opposite from meta. However, the results with certain substrates (toluene, chlorobenzene, *o*-dimethoxybenzene) do not show similar reactivity at ortho and para positions and are not easily fit into this picture.

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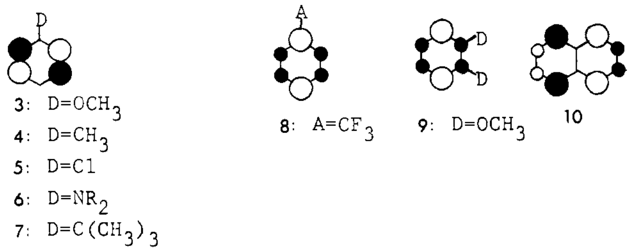

Figure 1. Estimated LUMO coefficients for substituted arenes.

Another view of the pathway would focus on HOMO-LUMO interactions, presumably HOMO (carbanion) and LUMO (arene complex).[7] The site of attack would correlate with the magnitude of the orbital coefficients at the arene atoms in LUMO (complex). Unfortunately, neither ESR data nor detailed calculations are available to specify the coefficient distribution for the arene complexes studied here. Nevertheless, we find a *useful* correlation of regioselectivity with LUMO coefficients estimated for the *free arene ligand*, ignoring any perturbation in coefficient distribution due to the $Cr(CO)_3$ unit. Structures **3–11** (Figure 1) display the estimated relative magnitude of LUMO coefficients;[10,11] the correlation with position of anion attack is quite good. Obviously, it is based on a superficial analysis of orbital interactions (ignoring the metal!) and does not necessarily reveal information about the actual mechanism. But it is simple to apply and may have some predictive value.

Discrepancies are also obvious: anisole and aniline (where ortho is not favored), and *tert*-butylbenzene (where para is favored). We are seeking a better understanding of polar effects and conformational effects in **1**, which may allow these to fit into a more refined rule for regioselectivity.[13]

References and Notes

(1) (a) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959); (b) M. F. Semmelhack, *N.Y. Acad. Sci.*, **295**, 36 (1977), and references therein.

(2) (a) For solution spectral data, see M. F. Semmelhack and M. Yoshifuji, *J. Am. Chem. Soc.*, **98**, 6387 (1976). (b) An X-ray diffraction study of **2** (R = 2-(1,3-dithianyl)) has been completed: M. F. Semmelhack, R. Farina, J. Clardy, and K. Hirotsu, submitted for publication. (c) M. F. Semmelhack, H. T. Hall, Jr., and M. Yoshifuji, *ibid.*, **96**, 6347 (1976).

(3) M. F. Semmelhack and G. Clark, *J. Am. Chem. Soc.*, **99**, 1675 (1977).

(4) In each example in Table I, the carbanion was generated at −78 °C in tetrahydrofuran (or THF–HMPA mixtures) and the arene complex was added. After the mixture had been stirred at 0 °C under argon for 0.2–1.0 h, excess iodine was added and the resulting substituted arenes were isolated. The product ratios were determined by quantitative GLC, the products were identified by comparison of spectral and GLC data with samples synthesized by standard methods, and the yields were determined by weighing the distillation fraction containing the product isomers (and nothing else). The chromium complexes were prepared by the standard method of heating the arene with chromium hexacarbonyl in dioxane for several days.

(5) M. F. Semmelhack and H. T. Hall, Jr., *J. Am. Chem. Soc.*, **96**, 7092 (1974).

(6) The trimethylsilyl substituent is attached efficiently by ortho metalation of π-anisolechromium tricarbonyl and quenching with chlorotrimethylsilane: M. F. Semmelhack, J. Bisaha, and M. Czarny, submitted for publication.

(7) The frontier orbital approximation has been applied to selectivity in electrophilic aromatic substitution[8] and to the limited information on partial rate factors for positions of nucleophilic aromatic substitution.[9]

(8) (a) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); (b) K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jpn.*, **27**, 423 (1954); (c) E. B. Pedersen, T. E. Petersen, K. Torssell, and S.-O. Lawesson, *Tetrahedron*, **29**, 579 (1973).

(9) (a) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3188 (1973); (b) N. D. Epiotis and W. Cherry, *ibid.*, **98**, 5432 (1976).

(10) (a) E. Heilbronner and P. A. Straub, "HMO", Springer-Verlag, New York, 1966; (b) K. W. Bowers in "Radical Ions", E. T. Kaiser and L. Kevan, Ed., Interscience, New York, 1968, p 211; (c) K. W. Bowers, *Adv. Magn. Reson.*, **1**, 317 (1965).

(11) These diagrams are based on simple Hückel molecular orbitals (HMO) with substituent perturbation.[10c] The patterns of LUMO coefficients from ESR spectra of radical anions are generally in line with these pictures. We assume that the LUMO for chlorobenzene will be similar to that for arenes with resonance donor substituents, and that LUMO for *o*-dimethoxybenzene is similar to LUMO for *o*-xylene (large coefficients adjacent to the substituents).[12]

(12) J. A. Bolton, *J. Chem. Phys.*, **41**, 2455 (1964).

(13) We are pleased to acknowledge financial support from the National Science Foundation and discussions with Roald Hoffmann, Tom Albright, and Barry Carpenter.

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(15) National Science Foundation Graduate Fellowship Holder, 1978–1981.

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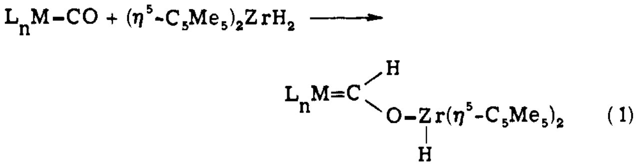
Reduction of Coordinated Carbon Monoxide to "Zirconoxy" Carbenes with Permethylzirconocene Dihydride

Sir:

We have reported the stoichiometric reduction of carbon monoxide by alkyl and hydride derivatives of bis(pentamethylcyclopentadienyl)zirconium(IV).[1,2] Most of our observations may be interpreted in terms of a sequence involving coordination of CO to the 16-electron species $(\eta^5\text{-}C_5Me_5)_2ZrR_2$ (R = H, alkyl), followed by rapid intramolecular migratory insertion of CO into either a Zr–H or Zr–C bond to generate η^2-formyl or acyl species.[2,3] The final product types observed were rationalized on the basis of an oxy carbenoid reactivity imparted to the carbonyl carbon as a result of its η^2 coordination mode.

A possible exception to this general scheme is the reaction of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ with $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (**1**) which leads over several hours under H_2 (1 atm) at 25 °C to a nearly quantitative yield of $[(\eta^5\text{-}C_5Me_5)_2ZrH]_2(\mu\text{-}OCH{=}CHO)$ (**2c**).[2,4] Since **2c** is not among the products formed in reactions of **1** with free carbon monoxide,[4] we wondered whether **1** could serve to transfer hydride directly to CO which is coordinated to another zirconium, or, more generally, to carbonyl ligands of other transition metal complexes (eq 1). Consideration of



$$L_nM{-}CO + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \longrightarrow L_nM{=}C(H){-}O{-}Zr(H)(\eta^5\text{-}C_5Me_5)_2 \qquad (1)$$

this possibility appears warranted in any case, since the hydrogen ligands of **1** are distinctly hydridic, comparable with trialkylborohydride in reactivity. The latter has recently been shown to convert a number of metal carbonyls to the corresponding formyl anions.[5-7]

In view of the large number of stable carbene complexes of molybdenum and tungsten reported, we have carried out a study of the reactions of **1** with $(\eta^5\text{-}C_5H_5)_2M(CO)$ (M = Mo, W) in hopes of observing directly the product of the proposed reaction type (eq 1). $(\eta^5\text{-}C_5H_5)_2W(CO)$[8] (**3**) does indeed react smoothly with 1 equiv of **1** in toluene solution at −80 °C to yield $(\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$ (**4**)[9] which may be isolated as red-brown crystals in 95% yield (eq 2). When this

$$(\eta^5\text{-}C_5H_5)_2W(CO) + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \longrightarrow (\eta^5\text{-}C_5H_5)_2W{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 \qquad (2)$$

reaction was carried out in a sealed NMR tube (benzene-d_6) with a molar ratio of **1**:**3** of 0.77:1.00, the spectrum shown in Figure 1 was obtained. The inequivalence of the two $(\eta^5\text{-}C_5H_5)$ rings for **4** may be attributed to a π interaction of the carbon p orbital with the filled b_2 orbital in the equatorial plane of the $(\eta^5\text{-}C_5H_5)_2W$ moiety thus firmly locking the "zirconoxy" carbene ligand with its hydrogen directed toward one cyclopentadienyl ligand and oxygen toward the other. A similar