set limit is thus ~21 kcal/mol. The contribution from f-functions seems to converge when three f-functions are used, giving an energy reduction of 9.8 kcal/mol (entries 6, 10, 11, 13). Finally, the contribution from a single g-function is 1.0 kcal/mol (entries 12, 14). We thus estimate that the MP2 basis set limiting energy difference is close to 10 kcal/mol. This is 10 kcal/mol lower than the result with the 6-311+G(2df) basis.

Metal Arene Complexes in Organic Synthesis. Hydroxylation, Trimethylsilylation, and Carbethoxylation of Some Polycyclic Aromatic Hydrocarbons Utilizing η^6-Arene–Chromium Tricarbonyl Complexes

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The deprotonation of polycyclic aromatic hydrocarbon (PAH) chromium tricarbonyl complexes (PAH = naphthalene, anthracene, phenanthrene, pyrene, fluoranthene) using an in situ technique where the PAH complex, the base (LiTMP or LDA), and the electrophile (trialkyl borate, trimethylsilyl chloride, or ethyl chloroformate) were placed in solution simultaneously resulted in hydroxylation, trimethylsilylation, or carbethoxylation of the PAH after oxidative workup where the regiochemistry was controlled by steric factors. As a result, substitution at positions of the PAHs not readily available by electrophilic substitution were obtained in some cases. Conditions minimizing isomer mixtures and factors affecting the regiochemistry and the scope of the reaction sequence were examined.

Introduction

Direct regiospecific substitution of polycyclic aromatic hydrocarbons (PAHs) larger than naphthalene has generally been fraught with difficulty. Regiochemical control of electrophilic substitution of large PAHs can generally be attained for only a few of the possible isomers in many cases.[1] Monoelectrophilic substitution in these cases can frequently be controlled to give one predominant isomer.[1] Some isomers, however, are not available by electrophilic substitution. A number of ways around this latter problem have been explored. For example, 2- or 4-substituted pyrenes have been prepared by reduction of pyrene to 4,5,9,10-tetrahydropyrene[2-4] or 1,2,3,6,7,8-hexahydropyrene,[5-7] respectively, followed by electrophilic substitution of the resulting hydroaromatic, then rearomatization to pyrene. In general, methods of this type require more steps and more involved protocols[8,9] than a direct substitution method would with consequent decreases in overall yield.

Some of the above problems could be alleviated if the recent developments in the substitution chemistry of monocyclic benzenoids, naphthalene, phenanthrene, and acenaphthalene which utilize chromium tricarbonyl (CTC) complexes[10] were applied to other PAHs. Complexation of the CTC group to benzenes increases the acidity of the ring protons by 5–8 pK_a units.[11] In addition the strong CTC electron withdrawal (roughly comparable to a NO_2 group) facilitates nucleophilic attack on the ring and nucleophilic displacement of halogen.[10]

Deprotonation reactions have not been extensively examined with PAH complexes other than the naphthalene complex.[12,13] The position of attachment of the CTC group in these complexes is known for a number of common PAHs[14] (see Scheme I). [It can readily be predicted for those which have not been prepared. Normally the terminal ring or the most aromatic ring by valence bond criteria is the ring complexed. The aromatic sextet rational[1] summarizes a good deal of this information conveniently and provides either a rationale or a prediction of where complexation has or will take place.[14]] In PAH mono-CTC complexes the ring where deprotonation will take place can, thus, be predicted. Since the CTC group can be attached and removed under relatively mild conditions and is stable to a number of chemical conditions,[15,16]

(1) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964; Vol. 1.
(2) Fu, P. P.; Lee, H. M.; Harvey, R. G. *J. Org. Chem.* **1980**, *45*, 2797–2803.
(3) Lee, H.; Harvey, R. G. *J. Org. Chem.* **1986**, *51*, 2847–2848.
(4) Harvey, R. G.; Schmolka, S.; Cortez, C.; Lee, H. *Synth. Commun.* **1988**, *18*, 2207–2209.
(5) Kirss, R. U.; Treichel, P. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 853–855.
(6) Lee, H.; Shyamasundar, N.; Harvey, R. G. *J. Org. Chem.* **1981**, *46*, 2889–2895.
(7) Sangaiah, R.; Gold, A. *J. Org. Chem.* **1991**, *56*, 6717–6720.
(8) Lee, H.; Harvey, R. G. *J. Org. Chem.* **1990**, *55*, 3787–3791.
(9) Harvey, R. G.; Hahn, J. T.; Bukowska, M.; Jackson, H. *J. Org. Chem.* **1990**, *55*, 6161–6166.
(10) Kündig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855–1864. Kalinin, V. N. *Russ. Chem. Rev.* **1987**, *56*, 682–700. Widdowson, D. A. *Phil. Trans. R. Soc. Lond. A* **1988**, *326*, 595–610.
(11) Fraser, R. R.; Mansour, T. S. *J. Organomet. Chem.* **1986**, *310*, C60–C62.
(12) Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173–1180.
(13) Kündig, E. P.; Grivet, C.; Spichiger, S. *J. Organomet. Chem.* **1987**, *332*, C13–C16.
(14) Deubzer, B.; Fischer, E. O.; Fritz, H. P.; Kreiter, C. G.; Kriebitzsch, N.; Simmons, H. D., Jr.; Willeford, B. R., Jr. *Chem. Ber.* **1967**, *100*, 3084–3096.
(15) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press; NY, **1982**, *8*, 1013–1071.
(16) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 3, pp 953–1077.

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Table I. In Situ Ring Hydroxylation of (Tetralin)$Cr(CO)_3$ (1), (Diphenylmethane)$Cr(CO)_3$ (2) and (Diphenylmethane)$[(Cr(CO)_3]_2$ (3) with $B(OBu)_3$

complex	base[a]	temp, °C	time, h	product(s)	% yield[b]
1[c]	*n*-BuLi[d]	−23	0.5[e]	90% 5,6,7,8-tetrahydro-2-naphthol 10% 5,6,7,8-tetrahydro-1-naphthol[f]	>90
1	LDA[g]		3.5	97% 5,6,7,8-tetrahydro-2-naphthol 3% 5,6,7,8-tetrahydro-1-naphthol	83
2	LDA	0	2.5	2:1 3-:4-benzylphenol	81
2	LDA	−78	0.5	3.5:1 3-:4-benzylphenol	90
3	LDA	0	5	41% 3,3′-dihydroxydiphenylmethane 36% 3,4′-dihydroxydiphenylmethane 23% 4,4′-dihydroxydiphenylmethane	95[h]

[a] The ratio of base to $B(OBu)_3$ was 5 to 3 unless otherwise noted. [b] Isolated total yield of all isomers. [c] Not an in situ procedure. [d] Two equivalents were used. [e] Time at which excess $B(OBu)_3$ was added to the reaction mixture. [f] Isomeric ratio determined by ^1H and ^{13}C NMR and GLC analyses. [g] Lithium diisopropylamide. [h] Traces of monohydroxylated materials were also found (GLC).

it should be a useful activating group for PAHs. Based on data for the naphthalene and phenanthrene–CTC complexes,[12,13,17,18] the position of deprotonation can be determined by the steric requirements of the base and the PAH. Thus, BuLi deprotonated both the 1- and 2-positions of the naphthalene complex, but LiTMP deprotonated only the 2-position. Both these deprotonation reactions were shown to be kinetically controlled.[13] Equilibrium between regioisomers only occurred in the presence of a stronger conjugate acid (e.g., diisopropylamine) than HTMP.[13] The anions were found, however, to decompose or protonate slowly even at −78 °C.

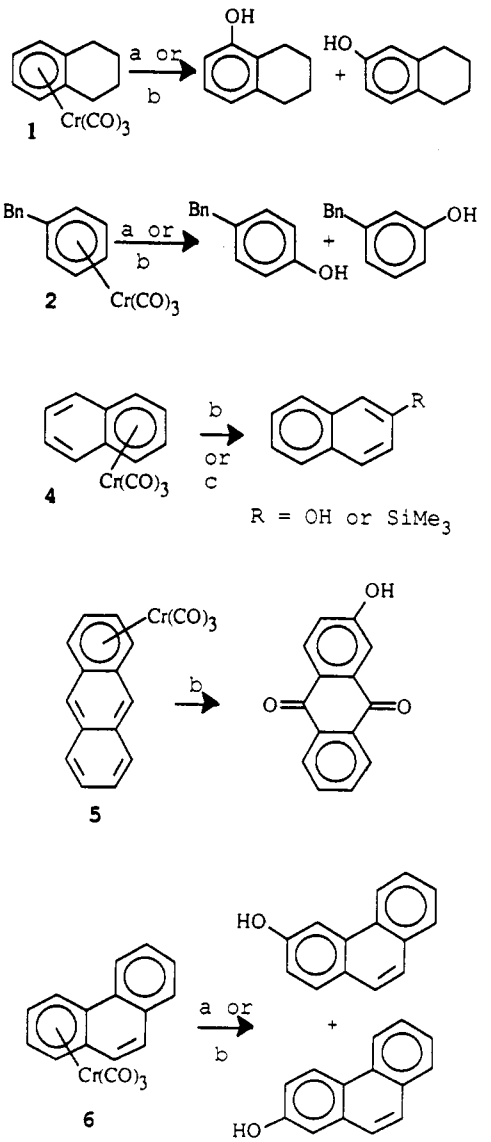
With the above results as background we set about to extend the scope of regiocontrolled deprotonation to other PAHs. Using trialkoxyboron derivatives to capture the anion followed by hydrogen peroxide oxidation, the phenolic PAH was generated and the CTC group removed in one step for all the PAHs.[19] Trimethylsilyl chloride and ethyl chloroformate were also examined as electrophiles for some of the PAHs. This procedure allows substitution on PAHs based on steric rather than electronic factors with the result that direct formation of some PAH derivatives is possible with regiochemistry different from that obtained via electrophilic substitution.

Results

Many procedures have been developed to prepare arene–CTC complexes.[16] Early work[14] indicates that thermal procedures with $Cr(CO)_6$ gave low yields for some PAHs. Several techniques utilizing $L_3Cr(CO)_3$ (L = RCN, R_3N or L_3 = naphthalene) as CTC carrier have been used. A room temperature procedure with $(pyridine)_3Cr(CO)_3$ and a Lewis acid has proven to be effective for naphthalenes.[17] Through a combination of these techniques, we have found use of $(NH_3)_3Cr(CO)_3$ and $BF_3{\cdot}Et_2O$ to be an effective, higher yielding procedure for PAH CTC complex formation than thermal procedures. The lower temperature of reaction allows more thermally labile complexes to be formed, and the use of ammonia as precursor ligand facilitates isolation and purification of the complex (see the Experimental Section).

In order to limit the number of isomers formed during deprotonation and reaction with an electrophile, the base was introduced into a mixture of the substrate and the electrophile. This allowed kinetically formed anions to be attacked by the electrophile immediately rather than allowing the anions to equilibrate before addition of the electrophile. While this procedure limited the range of electrophiles which might be used, this in situ technique allowed clean ring deprotonation in the presence of benzylic hydrogens. Preliminary work showed both LDA and LiTMP to be compatible with trialkyl borates and tri-

Scheme I[a]



[a] Conditions: (a) LDA, $B(OBu)_3$; (b) LiTMP, $B(OBu)_3$; (c) LiTMP, TMSCl; (d) KTMP, $B(OBu)_3$; each followed by H_2O_2/HOAc during workup.

(17) Oprunenko, Y. F.; Malugina, S. G.; Ustynyuk, Y. A.; Ustynyuk, N. A.; Kravtsov, D. N. *J. Organomet. Chem.* **1988**, *338*, 357–368.
(18) Treichel, P. M., Jr.; Kirss, R. U. *Organometallics* **1987**, *6*, 249–254.
(19) For stepwise procedures of lithiation, hydroxylation and decomplexation of monocyclic benzenoid systems, see: Cambie, R. C.; Higgs, P. I.; Rutledge, P. S.; Woodgate, P. D. *J. Organomet. Chem.* **1990**, *384*, C6–C8. Gill, J. C.; Marples, B. A.; Traynor, J. R. *Tetrahedron Lett.* **1987**, *28*, 2643–2644.

Table II. Time and Temperature Study on the in Situ Hydroxylation of (Diphenylmethane)$Cr(CO)_3$ (2)

base[a]	borate	temp, °C	temp, h	meta/para[b]	% yield[c]
LDA	$B(OBu)_3$	0	2.5	1.9	57
LDA	$B(OBu)_3$	0	0.5	2.1	80
LDA	$B(OBu)_3$	-78	0.5	3.5	90
LiTMP[d]	$B(OBu)_3$	-78	0.5	2.6	91
LiTMP[e]	$B(OBu)_3$	ambient	4 d	2.6	26
LDA	$B[O(i\text{-}Pr)]_3$	0	7.5	2.1	70
LDA	$PhB[O(i\text{-}Pr)]_2$	0	7.5	2.3	84[f]

[a] The ratio of base to borate was 5 to 3 unless otherwise noted. [b] Ratio determined by ^1H NMR integration and ^{13}C NMR peak heights and chemical shifts. [c] Isolated yields unless indicated. [d] Lithium 2,2,6,6-tetramethylpiperidide. [e] The stoichiometric amounts of base and $B(OBu)_3$ were used in this run. [f] GLC yield.

methylsilyl chloride, but only LiTMP to be unreactive with ethyl chloroformate.

Hydroxylation and Silylation. Hydroxylation was initially attempted using a 3:3:1 ratio of amide base:trialkoxyboron electrophile:substrate followed by an oxidative workup. This procedure gave only starting arene. When the base concentration was increased to 5:3:1, phenolic products were produced. The results from a series of reactions are summarized in Tables I–III. Apparently the equimolar amount of base and trialkoxyboron complexed strongly enough to decrease the basicity of LDA or LiTMP but not so strongly that the boron electrophile could not react with the carbanion formed on deprotonation when excess base was used. This latter reaction must also be relatively rapid because neither the tetralin or diphenylmethane complexes gave more than traces of benzylic reaction.[12] The reaction of the phenanthrene–CTC complex anion also gave only the 2- and 3-substituted derivatives with no 1- or 4-substitution detected. Literature conditions utilizing sequential addition of base (both BuLi and LDA) gave greater mixtures, particularly when the base was allowed to stand with the complex before addition of the electrophile.[13,18] Our in situ conditions allowed trapping of the initially formed anion(s) irreversibly as the boronic acid ester before isomeric equilibration of the anions could take place. This resulted in complete regiospecificity in several cases even when benzylic protons were available or when LDA was used.

The regioselectivity observed with tetralin is consistent with steric control of the reaction[12,13] and with similar results seen with the indan–CTC complex.[20] The lack of regioselectivity with the diphenylmethane–CTC complex is similar to the results obtained for a number of alkyl-substituted benzene–CTC complexes.[21] Varying conditions did not significantly change the mixtures obtained.

Reaction of the naphthalene–CTC complex was repeated[13] using the in situ conditions with TMSCl to give 2-(trimethylsilyl)naphthalene (67%) with only 9% of the 1,3-bis(trimethylsilyl)naphthalene formed despite the excess of both base and TMSCl used. Kündig et al.[13] were able to form exclusively either the 2-mono- or 1,3-bis-(trimethylsilyl) derivative using sequential LiTMP and TMSCl addition with stoichiometric amounts of reagents. These results are important because they show the peri steric interaction can be overcome. Steric hindrance ortho to the trimethylsilyl group prevented further reactions there.

Duplication of the in situ silylation procedure with the pyreneCTC complex, however, gave only 2-(trimethylsilyl)pyrene (98%). Again, no product was produced from reaction ortho to the trimethylsilyl group.

Hydroxylation of the naphthalene–, fluoranthene–, and pyrene–CTC complexes also proceeded satisfactorily using the in situ technique to form 2-naphthol (94%), 8-hydroxyfluoranthene (78%), and 2-pyrenol (59%), respectively. These reductions were very clean; the only byproduct after oxidation of the product CTC complex was the unreacted arene. The latter two preparations represent an increase in overall yield to 25% for 8-hydroxyfluoranthene from fluoranthene (the literature yield[22,23] is 10% from acenaphthylene in four steps) and to 36% for 1-pyrenol from pyrene (the literature yield[2,4] is 21% from pyrene in four steps).

Application of the hydroxylation procedure to the anthracene–CTC complex gave 2-hydroxy-9,10-anthraquinone (71%) instead of the expected 2-hydroxyanthracene. It was shown independently that the conditions of oxidation of the product anthracene borate ester complex also oxidized the 9,10-positions of anthracene. Treatment of either anthracene or the crude anthracene–CTC complex with acidic hydrogen peroxide gave a significant amount of 9,10-anthraquinone. The use of trimethylamine *N*-oxide,[24] which can convert boronic esters to alcohols, may circumvent this problem, but since the position of hydroxylation had been established, that was not attempted here.

The phenanthrene–CTC complex had been studied previously in deprotonation–alkylation reactions and found to give mainly 2- and 3-substitution in addition to some 1- and 4-derivatives.[18] Use of the in situ conditions for hydroxyl substitution generated a 1:1 mixture of 2- and 3-phenanthrols in 82% yield. The phenanthrols could not be separated by GLC or conventional chromatographic methods and were identified and quantitated by comparing the ^{13}C NMR spectrum of the reaction mixture to that of the independently synthesized materials.[25]

When the in situ hydroxylation procedure was run at -78 °C for 0.5 h with **6**, the ratio of 2- to 3-phenanthrol increased to 2.6:1. At -96 °C the ratio was further increased to 3.5:1. No 1- or 4-phenanthrol was detected by ^{13}C NMR in any run. These results are consistent with those found when complex **6** was treated sequentially with LDA at -96 °C for 15 min followed by methylation to give methylated phenanthrene in a 1:2:3:4 ratio of 3:83:14:0 in 42% yield[18] (note the 2- to 3-methylphenanthrene ratio here, 5.9:1, is higher for methylation than for hydroxylation at this temperature). Increasing the temperature and/or the reaction time resulted in a decrease in the amount of 2-isomer and an increase in the amount of 1-, 3-, and 4-isomers with the amount of 4-isomer never exceeding 5%.[18] Thus, while some selectivity was observed, it was not great enough to be synthetically useful, particularly since the products were so difficult to separate.

Attempts to extend the in situ protocol to perylene, however, were unsuccessful. The preparation and isolation of significant amounts of the perylene complex failed. The complexation was attempted thermally with $Cr(CO)_6$ and by ligand exchange with $L_3Cr(CO)_3$ (L = NH_3, CH_3CN, L_3 = naphthalene). TLC analysis of the reaction mixtures

(20) Kündig, E. P.; Perret, C.; Rudolph, B. *Helv. Chim. Acta* **1990**, *73*, 1970–1979.
(21) Card, R. J.; Trayhanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2560–2566.
(22) Kloetzel, M. C.; Mertel, H. E. *J. Am. Chem. Soc.* **1950**, *72*, 4786–4791.
(23) Rice, J. E.; LaVoie, E. J.; Hoffmann, D. *J. Org. Chem.* **1983**, *48*, 2360–2363.
(24) Davies, A. G.; Roberts, B. P. *J. Chem. Soc. C* **1968**, 1474–1478.
(25) Fieser, L. F. *Organic Syntheses*; Wiley-Interscience: New York, 1943; Collect. Vol. II, pp 482–485.

Table III. In Situ Reactions of PAHs

complex	electrophile	base[a]	time, h	product(s)	% yield[b]
4	$B(OBu)_3$	LiTMP[c]	0.5	2-naphthol	94
5[d]	$B(OBu)_3$	LiTMP	0.5	2-hydroxy-9,10-anthraquinone	71
5[e]	$B(OBu)_3$	LiTMP	5.5	2-hydroxy-9,10-anthraquinone	6
6	$B(OBu)_3$	LDA[g,h]	5.0	2-phenanthrol/3-phenanthrol (1.1:1)	82
6	$B(OBu)_3$	LiTMP	0.5	2-phenanthrol/3-phenanthrol (2.6:1)	93
6	$B(OBu)_3$	LiTMP[i]	0.5	2-phenanthrol/3-phenanthrol (3.5:1)	82
7	$B(OBu)_3$	LiTMP	0.5	2-pyrenol	59
7[e]	$B(OBu)_3$	LDA	0.75	2-pyrenol	20
7[e,j]	$B(OBu)_3$	LiTMP[f]	17	2-pyrenol	9
8	$B(OiPr)_3$	LiTMP	0.5	8-hydroxyfluoranthrene	78
8	$B(OiPr)_3$	KTMP[k]	0.5	8-hydroxyfluoranthene	37
				7,9-dihydroxy-fluoranthrene	21
4	Me_3SiCl	LiTMP	0.5	2-(trimethylsilyl)naphthalene	67
				1,3-bis(trimethylsilyl)naphthalene	9
7	Me_3SiCl	LiTMP	1.0	2-(trimethylsilyl)pyrene	98
4[l]	$ClCO_2Et$	LiTMP[m]	0.5	2-carbethoxynaphthalene	48
7	$ClCO_2Et$	LiTMP	1.25	2-carbethoxypyrene	70[n]
				1,2-dicarbethoxypyrene	6[n]
7[j]	$ClCO_2Et$	LiTMP	1.5	2-carbethoxypyrene	28[n]
				1,2-dicarbethoxypyrene	27
7[o]	$ClCO_2Et$	KTMP	1.0	2-carbethoxypyrene	62
				1,2,3-tricarbethoxypyrene	27[n]
7[p]	$ClCO_2Et$	KTMP	2.75	2-carbethoxypyrene	10[n]
				1,2,3-tricarbethoxypyrene	71

[a] All reactions were run in THF with a base to electrophile ratio of 5 to 3 at −78 °C unless otherwise noted. [b] Overall isolated yields. [c] Lithium 2,2,6,6-tetramethylpiperidide. [d] Crude 5 (about 40% complexed) was used in this run. [e] The complex was formed in situ and not isolated prior to hydroxylation under the indicated conditions. [f] Temperature was raised to ambient temperature after base addition. [g] Lithium diisopropylamide. [h] 0 °C. [i] −96 °C. [j] Run in 2 to 1 diethyl ether to THF. [k] Potassium 2,2,6,6-tetramethylpiperidide. [l] Not an in situ reaction. [m] Base to electrophile to complex ratio was 1.0 to 1.5 to 1.0. [n] GLC yield. [o] $ClCO_2Et$ and 7 were added dropwise to KTMP in THF. [p] Base to electrophile to complex ratio was 10 to 6 to 1.

indicated the formation of a small amount of the purple complex, but isolation attempts resulted in decomposition. The solubilities of perylene and the complex were very poor in conventional organic solvents and, thus, prevented rapid isolation of the CTC complex.

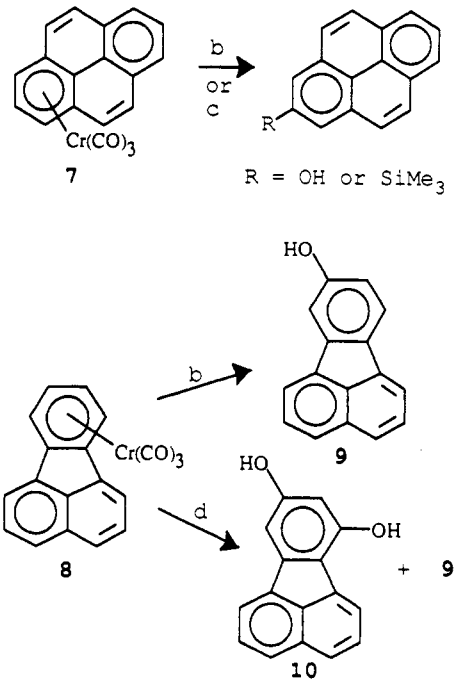
In order to develop a more convenient procedure which did not require isolation of the CTC complex, a series of reactions without isolation of intermediates was examined with anthracene, pyrene, and perylene.

Anthracene, $(NH_3)_3Cr(CO)_3$, and $BF_3{\cdot}Et_2O$ were stirred for 4 days in diethyl ether at ambient temperature. The ether was removed and the in situ hydroxylation procedure performed as before, resulting in a 6% overall yield of 2-hydroxy-9,10-anthraquinone. Although the yield was very poor, this reaction sequence indicates that PAH can be hydroxylated without isolation of the intermediate CTC complex.

2-Pyrenol was prepared in 20% overall yield starting with pyrene by using this same procedure. When an attempt was made to form the complex thermally in refluxing ether/THF from the trisamine complex, rather than with BF_3, the overall yield fell to 9%. The low yield was probably a result of low conversion to complex 7 in the absence of a suitable driving force (i.e. higher temperature or Lewis acid assistance).

Application of the sequential procedure to perylene hydroxylation so that the perylene complex would not have to be isolated was attempted. The purple reaction mixture that resulted from attempted complexation with $(NH_3)_3Cr(CO)_3$ was treated directly with LiTMP and $B(OBu)_3$, but hydroxylation was not successful. The absence of any literature reports on the preparation of perylene–CTC probably explains this result; the formation of the perylene–CTC complex warrants further investigation.[26]

Scheme II[a]



[a] Conditions: see Scheme I conditions.

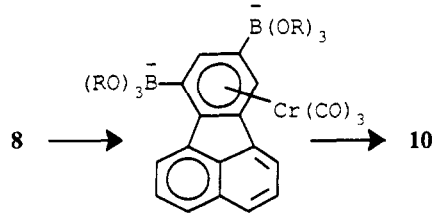
Polysubstitution. Only in the case of trimethylsilylation of naphthalene and fluoranthrene were any indications of polysubstitution detected. Only monosubstitution resulted when the in situ boronation/hydroxylation procedure was used. This situation was changed by the use of potassium 2,2,6,6-tetramethylpiperidine (KTMP) rather than LiTMP. When the fluoranthrene–CTC complex was treated with KTMP and $B(OiPr)_3$

(26) Zeiger, H. E.; Rosenkranz, J. E. *J. Org. Chem.* **1964**, *29*, 2469–2471.

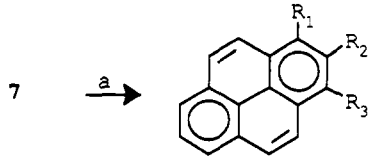
(27) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379–1389.

(28) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–168.

Scheme III



Scheme IV[a]



11 R_2= COOEt; R_1= R_3= H
12 R_1= R_2= COOEt, R_3= H
13 R_1= R_2= R_3= COOEt

[a] (a) See Table III for conditions.

followed by the acidic hydrogen peroxide workup, both 8-hydroxy- (37%) and 7,9-dihydroxyfluoranthrene (21%) were isolated.

This result is interesting for two reasons. First, the preparation of 7,9-dihydroxyfluoranthrene requires that a bis"ate" salt be formed by two metallation/boronation sequences prior to the protic workup with acetic acid and H_2O_2 (see Scheme III). This result was not observed in any of the hydroxylations done with the lithium counterion. Secondly, since LiTMP reacts at the 8-position exclusively, in the case of KTMP this suggests that the first metalation/boronation occurred at the 8-position and the second metalation/boronation, therefore, must have occurred meta to this. Thus, the meta orientation of the hydroxyl groups suggests a distinct directing influence by the $[B(OR)_3]^-$ group (either steric or electronic) that overrides any unfavorable steric interaction with the proton in the 6-position, just as was found for trimethylsilylation in the naphthalene series.

Carbethoxylation. Polysubstitution was also observed with carbethoxylation of the naphthalene–CTC complex using the standard in situ conditions with a 5:3:1 ratio of LiTMP:ethyl chloroformate:CTC complex where a mixture of products was isolated but not separated. Using a sequential addition of LiTMP followed by ethyl chloroformate, 2-carbethoxynaphthalene (48%) was isolated. The naphthalene–CTC complex apparently is more susceptible to polysubstitution than other PAH complexes.

The pyreneCTC complex under standard in situ conditions gave mainly monosubstitution with 2-carbethoxypyrene (11) (70%) formation (Scheme IV). In addition, some 1,2-dicarbethoxypyrene (12) was formed (9%). An attempt was made to optimize the conditions for formation of 1,2-dicarbethoxypyrene, but the added activation toward deprotonation made this difficult. Use of KTMP rather than LiTMP resulted in monoester 11 (58%) and 1,2,3-tricarbethoxypyrene (13) (42%) with no detectable bis-adduct 12. When the reaction was run in 2:1 diethyl ether–THF using LiTMP at standard reagent ratios, the maximum yield of the bis-ester 12 of 27% (36% by GC) was isolated along with the monoester 11 in 28% yield. The tricarbethoxy derivative 13 could be produced in 71% yield by using 10:6:1 ratio of KTMP:ethyl chloroformate:CTC complex accompanied by only 10% of the monoderivative.

Discussion

Hydroxylation of PAHs gave excellent regioselectivity in all but one case. Many regioselective 2-substitution reactions have been reported for (naphthalene)CTC (4).[12,13] The observed regioselectivity was ascribed to deprotonation at the more accessible site with sterically demanding bases such as LDA and LiTMP.[12] This same rationale predicts the observed results with (anthracene)CTC (5), (pyrene)CTC (7), and (fluoranthrene)CTC (8).

The dihydroxylation of (fluoranthene)CTC (8) was a special case. No dihydroxylation was observed using Li^+ bases. This situation is different than the bis(trimethylsilylation) of the naphthalene–CTC complex, with 2 mol of LiTMP and an excess of TMSCl. Even though a 5:3:1 ratio of base to borate to CTC complex was used, no polysubstitution was observed using the lithium counterion of the base. The change in the counterion of the base from lithium to potassium offset any unfavorable interaction with a 6-proton (see Scheme III). The use of potassium 2,2,6,6-tetramethylpiperidine in the hydroxylation of other PAH complexes was not investigated.

The phenanthrene complex 6 did not show the same regioselectivity as the other PAH complexes. The lower symmetry of phenanthrene compared to naphthalene and anthracene doubles the number of possible monosubstituted regioisomers. In keeping with the pattern found for the other complexes, deprotonation took place regioselectively at positions β to the ring junction. Consistent with literature precedent,[18] formation of the 2-lithio intermediate was favored at low temperature, although not sufficiently to make the procedure useful synthetically.

Carbethoxylation of the pyrene–CTC complex 7 using the in situ technique clearly is somewhat different than boronation or silylation. The latter two processes result in a tertiary group attached to the ring, which effectively sterically hinders the ortho positions. The carbethoxy group is electron withdrawing, smaller in size, and provides a Lewis base center to complex the amine base counterion. All these factors aid in ortho deprotonation followed by reaction with another molecule of ethyl chloroformate. When two carbethoxy groups have been attached (see 12), the remaining proton is more acidic. This allows formation of the tricarbethoxy derivative 13 under appropriate conditions.

Experimental Section

General. Metal arenes were handled under inert gases or vacuum using standard Schlenk techniques. Solvents, DPM, and tetralin were dried, distilled, degassed, and stored over molecular sieves (4 Å) under N_2 or Ar. Hexane, borates ($B(OR)_3$, R = alkyl), 2,2,6,6-tetramethylpiperidine, and boron trifluoride etherate were refluxed over CaH_2 then distilled onto 4-Å molecular sieves under N_2 or Ar. *n*-Butyllithium was titrated before use. Anthracene and pyrene were recrystallized from ethanol prior to use. (Phenanthrene)CTC was graciously supplied by a co-worker. All other commercial chemicals were used as received.

Melting points were taken on a Laboratory Devices Mel-Temp apparatus and are uncorrected. Sealed tube(st) melting points were taken in evacuated, flame-sealed capillary tubes. Thin-layer chromatography (TLC) was performed 0.2-mm-thick silica gel 60 F254 plates (EM Science). Chromatography was carried out on dry packed columns of silica gel. Solutions were dried over Na_2SO_4. NMR spectra were recorded in $CDCl_3$ solution (unless otherwise noted) on a Varian VXR-300 spectrometer. Chemical shifts are reported in ppm relative to internal Me_4Si (^1H) or internal deuterated solvent (^{13}C). IR spectra were recorded as diffuse reflectance spectra of a KBr mixture (unless otherwise noted) on a Digilab FTS-40 IR at a resolution of 4 cm^{-1}. Analytical gas–liquid chromatography (GLC) was performed with a Varian Aerograph Series 2100 instrument on $^1/_8$-in. by 6-ft glass columns packed with 3% OV-17 on 120-mesh Supelcoport. Area ratios

were determined using a HP 3390A integrator and conventional internal standard techniques with triphenylmethane as standard. Mass spectra were obtained from a Hewlett-Packard 5790A series GC interfaced (capillary direct) to a Hewlett-Packard 5970A series mass selective detector (MSD) using a 0.25-mm by 30-m DB-5 (95% dimethyl, 5% diphenylpolydisiloxane, J&W) capillary column. High-resolution mass spectrometry (HRMS) analyses were performed by the Midwest Center for MS Spectrometry, Lincoln, NE, and recorded as electron impact spectra. Elemental analyses were done by M-H-W Laboratories, Phoenix, AZ. Reactions run at temperatures lower than ambient were maintained by liquid nitrogen–acetone (–96 °C) and dry ice–acetone (–78 °C).

Chromium Tricarbonyl Complexes. General. Chromium tricarbonyl complexes (unless noted otherwise) were prepared by refluxing the arene substrate and chromium hexacarbonyl ($Cr(CO)_6$) in an appropriate solvent under N_2 or Ar.[29-31] Sublimed $Cr(CO)_6$ was mechanically returned to the reaction flask with a glass rod.

(Tetralin)chromium Tricarbonyl (1). $Cr(CO)_6$ (44.8 mmol) and tetralin (184 mmol) were refluxed in THF for 5 days. Excess tetralin and THF were removed by distillation at reduced pressure leaving crude complex 1. The crude material in CH_2Cl_2 was filtered through silica; the solvent was removed, and the resulting solid washed with hexane on a Schlenk frit to give fine yellow needles of 1 (2.26 g, 19%), mp (st) 112–114 °C (lit.[32] mp 114.5–115.5 °C). IR ($CHCl_3$): 1981, 1963, 1888 cm^{-1}. ^1H NMR: δ 1.77 (m, 4 H, b-CH_2), 2.64 (t, 4 H, a-CH_2), 5.26 (s, 4 H, Ar-H).[32] ^{13}C NMR: δ 21.96 (C-2,3), 28.09 (C-1,4), 91.83 (C-6,7), 93.90 (C-5,8), 109.63 (C-4a,8a), 233.76 (CO).[32]

(Diphenylmethane)chromium Tricarbonyl (2). $Cr(CO)_6$ (45.5 mmol) and diphenylmethane (131 mmol) were refluxed in a di-*n*-butyl ether (80 mL)/THF (18 mL) mixture for 4 days followed by distillation at reduced pressure. The residue was collected on a Schlenk frit and washed several times with hexane to give bright yellow crystals of complex 2 (1.3 g, 10%), mp (st) 95–97 °C (lit.[33] mp 97–98 °C). IR: 1948, 1865 cm^{-1}. ^1H NMR: δ 3.73 (s, 2 H, CH_2), 5.19 (m, 3 H, J_{24} = 3.1 Hz, H-2,4,6), 5.36 (t, 2 H, J_{23} = 6.33 Hz, H-3,5), 7.40–7.20 (m, 5 H, H-8,9,10,11,12).[33] ^{13}C NMR: δ 40.77 (CH_2), 90.70 (C4), 92.97 (C2,6), 93.50 (C3,5), 112.39 (C1), 127.10 (C10), 128.82 (C8,9,11,12), 138.23 (C7), 233.01 (CO).[34]

(Diphenylmethane)bis(chromium tricarbonyl) (3). $Cr(CO)_6$ (64 mmol) and DPM (30 mmol) were refluxed in a di-*n*-butyl ether (80 mL)/THF (13 mL) mixture for 4 days. Chromatography with a 5:2 cyclohexane–chloroform mixture eluted the monoadduct 2 followed by 3. After solvent removal, complex 3 was isolated as bright yellow crystals, mp (st) 153–156 °C (lit.[35,36] mp 158 °C). IR: 1956, 1880 cm^{-1}. ^1H NMR: δ 3.45 (s, 2 H, CH_2), 5.40–5.24 (m, 10 H, Ar-H).[36] ^{13}C NMR: δ 39.49 (CH_2), 91.61 (C-4,10), 92.62 (C-3,5,9,11), 92.93 (C-2,6,8,12), 108.52 (C-1,7), 232.39 (CO).[36] The reaction yield was not determined because several reaction mixtures were combined before isolation.

(Naphthalene)chromium Tricarbonyl (4). To a cold (0 °C) ether solution (40 mL) of $[(NH_3)_3Cr(CO)_3]$[37] (11.1 mmol) and naphthalene (11.2 mmol) was added BF_3·OEt_2 (44.7 mmol).[38] The mixture was then allowed to warm to ambient temperature and stir for 8 days. Excess BF_3·OEt_2 was quenched with 1 M HCl solution. The solvent was removed from the dired organic layer and the residual naphthalene sublmimed from the crude mixture at ca. 40 °C (0.5 mm) to give dark orange crystals of complex 4 which did not require further purification (2.05 g, 70%), mp (st) 134–136 °C (lit.[17] mp 135–137 °C). IR: 1941, 1864 cm^{-1}. ^1H NMR: δ 5.53 (bs, 2 H, H-2,3), 6.15 (bs, 2 H, H-1,4), 7.60–7.35 (m, 4 H, H-5,6,7,8).[14,39] ^{13}C NMR: δ 90.70 (C-1,4), 92.34 (C-2,3), 105.69 (C-4a,8a), 128.70 (C-6,7), 128.77 (C-5,8).[14,39]

(Anthracene)chromium Tricarbonyl (5). Anthracene (2.08 mmol) and $(NH_3)_3Cr(CO)_3$ (2.14 mmol) were treated at 0 °C in ether (10 mL) with BF_3·OEt_2 (8.13 mmol). After warming to ambient temperature the mixture was stirred for 4 days. The solvent was then removed, and the purple solid was kept at 1 mmHg for several hours at ambient temperature. The integrated ^1H NMR spectrum indicated that the reaction produced approximately 40% complexed material. This was done by comparing the areas of the 1,4 protons (δ 6.28, m) and the 5,8 protons (δ 7.73, m) of the complexed material with that of the uncomplexed 1,4,5,8 protons (δ 7.91, m) (lit.[14] ^1H NMR). Attempted isolation and purification of complex 5 by either sublimation or column chromatography resulted in rapid decomposition. Therefore, the crude mixture was used without further purification. IR: 1935, 1861 cm^{-1}.

(Pyrene)chromium Tricarbonyl (7). $(NH_3)_3Cr(CO)_3$[37] (5.56 mmol) and pyrene (5.90 mmol) were treated with BF_3·OEt_2 (22.5 mmol) at 0 °C in ether (40 mL). After being warmed to ambient temperature, the mixture was stirred for 4 days. The precipitate was collected on a Schlenk frit, dissolved in CH_2Cl_2, washed quickly with 1 M HCl solution, and dried; the solvent was removed to give bright red crystals of complex 7 (0.78 g, 41.5%), mp (st) 202–204 °C. The original filtrate was chromatographed, eluting with petroleum ether to remove pyrene and then CH_2Cl_2 to remove 7 (0.31 g, total reaction yield of 58.5%). IR: 1949, 1869, 1844 (sh) cm^{-1}. ^1H NMR: δ 5.58 (t, 1 H, J_{12} = 6.3 Hz, H-2), 6.02 (d, 2 H, H-1,3), 7.51 (d, 2 H, J_{45} = 9.27 Hz, H-4,10), 7.79 (d, 2 H, H-5,9), 7.95–7.87 (m, 3 H, H-6,7,8).[16] ^{13}C NMR: δ 90.11 (C-1,3), 92.08 (C-2), 99.78 (C-15), 101.50 (C-11,12), 126.66 (C-16), 127.10 (C-4,10), 127.22 (C-5,9), 128.39 (C-7), 129.93 (C-6,8), 131.24 (C-13, 14), 233.37 (CO).[40]

(Fluoranthene)chromium Tricarbonyl (8). $Cr(CO)_6$ (10.14 mmol) and fluoranthene (10.52 mmol) were refluxed in 1,2-dimethoxyethane (80 mL) for 3 days followed by filtration through Celite and then solvent distillation. Flash chromatography[41] with 2.5% ethyl acetate in petroleum ether removed unreacted fluoranthene; complex 8 was removed with CH_2Cl_2. Solvent removal and recrystallization from a $CHCl_3$/hexane mixture gave pure 8 as purple-red needles (1.14 g, 32%), mp (st) 204–205 °C (lit.[14] mp 180 °C). IR: 1953, 1883 cm^{-1}. ^1H NMR: δ 5.55–5.53 (m, 2 H, H-2,3), 6.29–6.27 (m, 2 H, H-1,4), 7.61 (t, 2 H, J_{67} = 7.6 Hz, H-6,9), 7.86–7.78 (m, 4 H, H-5,7,8,10).[14] ^{13}C NMR: δ 87.81, 90.37, 106.37, 119.98, 127.45, 128.25, 130.13, 134.73, 233.31.

Aromatic Ring Hydroxylation with $(BuO)_3B$. General.[42] The chromium complex was deprotonated by base in the presence of $(BuO)_3B$ with stirring under an inert atmosphere; the resulting "ate" complex was directly decomposed to the phenolic derivative with acidic (HOAc) H_2O_2. The dry ice–acetone bath used in reactions run at –78 °C was removed after acetic acid addition; the reaction mixture was stirred for several minutes until it became homogeneous and then was cooled with an ice–water bath prior to H_2O_2 addition.

5,6,7,8-Tetrahydro-2-naphthol. Complex 1 (0.276 mmol), THF (2 mL), and $(BuO)_3B$ (0.826 mmol) were cooled to 0 °C and a solution of LDA (0.9 M in cyclohexane, 1.39 mmol) added. After 3.5 h at 0 °C, the resulting solution was quenched with chilled acetic acid (2.62 mmol) followed by the careful dropwise addition of cold 30% H_2O_2 (2.90 mmol). The solution turned dark purple as it was slowly allowed to warm to ambient temperature. After the solution was stirred for 0.5 h at ambient temperature, excess H_2O_2 was quenched with excess 10% ferrous ammonium sulfate, and most of the solvent was removed in vacuo. The residue was then acidified with a 1 M HCl solution and extracted with ether (3 × 10 mL), and the combined extracts were washed with 5% $NaHCO_3$ (1 × 10 mL) followed by a saturated sodium chloride

(29) Fischer, E. O.; Ofele, K.; Essler, H.; Frohlich, W.; Mortensen, P.; Semmlinger, W. *Chem. Ber.* **1958**, *91*, 2763–2772.
(30) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1975**, *19*, 154–158.
(31) Strohmeier, W. *Chem. Ber.* **1961**, *94*, 2490–2493.
(32) Cambie, R. C.; Clark, G. R.; Gallagher, S. R.; Rutledge, P. S.; Stone, M. J.; Woodgate, P. D. *J. Organomet. Chem.* **1988**, *342*, 315–337.
(33) von Rosenberg, J. L.; Pinder, A. R. *J. Chem. Soc., Perkin Trans.* **1987**, *1*, 747–752.
(34) Ceccon, A.; Gambaro, A.; Venzo, A. *J. Organomet. Chem.* **1984**, *275*, 209–222.
(35) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1979**, *182*, 381–392.
(36) Jaouen, G.; Top, S.; McGlinchey, M. J. *J. Organomet. Chem.* **1980**, *195*, C5–C8.
(37) Razuvaev, G. A.; Artemov, A. N.; Aladjin, A. A.; Sirotkin, N. I. *J. Organomet. Chem.* **1976**, *111*, 131–135.
(38) Ofele, K. *Chem. Ber.* **1966**, 1732–1736.
(39) Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288–1297.
(40) Hansen, P. E.; Poulsen, O. K. *Org. Magn. Reson.* **1975**, *7*, 475.
(41) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
(42) Harvey, R. G. *Synthesis* **1986**, 605–619.

solution wash. The ether layer was extracted with a 3 N NaOH solution until no hydroxylated material could be detected in the neutral ether layer by TLC. The combined base extracts were back-extracted with ether, acidified with concentrated HCl, and finally extracted with CH_2Cl_2 to give the naphthol (0.034 g, 83%). ^1H NMR: δ 1.84–1.79 (m, 4 H), 2.80–2.64 (m, 4 H), 6.67–6.59 (m, 2 H), 6.97 (d, 1 H, J = 8.1 Hz). ^{13}C NMR: δ 23.67, 23.98, 29.14, 30.07, 113.43, 115.90, 129.99, 130.68, 139.06, 153.53. The naphthol was found (GLC and NMR) to be contaminated with 3% of the 1-isomer, 5,6,7,8-tetrahydro-1-naphthol. ^1H NMR, 5,6,7,8-tetrahydro-1-naphthol: δ 1.99–1.80 (m, 4 H), 2.71 (t, 2 H), 2.84 (t, 2 H), 4.83 (s, 1 H), 6.68 (d, 1 H, J = 7.8 Hz), 6.77 (d, 1 H, J = 7.2 Hz), 7.06 (t, 1 H, J = 7.6 Hz). ^{13}C NMR, 5,6,7,8-tetrahydro-1-naphthol: δ 23.27, 23.31, 23.34, 30.14, 112.35, 122.16, 123.85, 126.55, 139.51, 153.94. Both compounds were identified by comparison of their spectroscopic properties to those of authentic samples.

Benzylphenols. LDA (1.17 mmol) was added to a cold (–78 °C) THF (3 mL) solution of complex **2** (0.230 mmol) and $(BuO)_3B$ (0.710 mmol); the solution was stirred 0.5 h at –78 °C. Base extraction gave a 90% yield of a 3.5:1 mixture of 3-benzylphenol to 4-benzylphenol. The isomeric ratio was determined by NMR spectral comparison to authentic 4-benzylphenol and 3-benzylphenol (see below).

3-Benzylphenol. 3-Methoxybenzoic acid (7.70 g, 50.7 mmol) and freshly distilled thionyl chloride (96.0 mmol) were refluxed for 40 min under N_2.[43] The resulting light brown solution was vacuum distilled to give 3-methoxybenzoyl chloride as a colorless liquid (6.48 g, 75%). IR (neat): 3081, 3011, 2951, 2841, 1764, 1601, 1489, 1266, 1159, 799, 776, 699, 667 cm^{-1}. ^1H NMR: δ 3.86 (s, 3 H), 7.22 (q of d, 1 H, J = 1.0, 2.6, 8.3 Hz), 7.41 (t, 1 H, J = 8.0 Hz), 7.57 (dd, 1 H, J = 1.7, 2.5 Hz), 7.73 (q of d, 1 H, J = 1.0, 1.7, 7.8 Hz). ^{13}C NMR; δ 55.42, 115.32, 121.88, 124.07, 129.84, 134.42, 159.81, 168.21.

To 3-methoxybenzoyl chloride (4.86 g, 28.5 mmol), benzene (11.36 g, 145.7 mmol), and 25 mL nitroethane at 0 °C was added slowly aluminum chloride (8.30 g, 62.2 mmol).[44] The resulting dark red solution was stirred 35 min at 0 °C followed by 6 h at ambient temperature. The reaction mixture was then poured onto 75 mL of ice water, acidified with concentrated HCl, and extracted into ether. The ether extracts were washed with 5% $NaHCO_3$ and dried, and the solvent was removed to give a orange-red oil (4.06 g). Phenolic impurities were removed by base extraction with a 1 M KOH solution to give 3-methoxybenzophenone (3.02 g, 50%). IR ($CHCl_3$): 1667 cm^{-1}. MS m/e (rel abund): 212 (77.3, M^+), 213 (12.7, M + 1), 181 (12.9) 135 (100), 107 (17.8), 105 (58), 92 (16.8), 77 (79.8). ^1H NMR: δ 3.90 (s, 3 H, OCH_3), 7.89–7.15 (m, 9 H, Ar-H). ^{13}C NMR: δ 55.36, 114.30, 118.78, 122.80, 128.19, 129.50, 130.00, 132.36, 137.57, 138.50, 159.50, 196.43.

3-Methoxybenzophenone (2.00 g, 9.40 mmol) was reduced with hydrazine hydrate (ca. 0.1 mol) and KOH (3.43 g, 6.13 mmol) under modified Wolff–Kishner conditions[45,46] to give crude 3-benzylanisole (1.41 g, 75%). Chromatography on silica gel with a 9/1 hexane/ether gave pure 3-benzylanisole (1.03 g, 55%). MS m/e (rel abund): 198 (100, M^+), 199 (14.7, M + 1), 183 (23.7), 167 (50.9), 165 (51.4), 91 (17.7). ^1H NMR: δ 3.69 (s, 3 H), 3.91 (s, 2 H), 6.78–6.69 (m, 3 H), 7.28–7.12 (m, 6 H). ^{13}C NMR: δ 41.90, 54.97, 111.25, 114.75, 121.31, 126.03, 128.39, 128.85, 129.34, 140.86, 142.63, 159.69.

The 3-benzylanisole (0.75 g, 3.79 mmol) was added to a solution of excess MgI (prepared fresh by stirring MeI (2.96 g, 20.9 mmol) with Mg turnings (0.47 g, 19.3 mmol) in 30 mL of dry ether for 1 h).[47] The solvent was removed, and then the residue was heated to 160 °C until the evolution of ethane ceased (4 h). After cooling, the resulting paste was dissolved in acetic acid (75 mL) and extracted with ether (3 × 75 mL). The combined ether extracts were washed with 5% $NaHCO_3$ (1 × 75 mL) and then extracted with a 3 M KOH solution until no more phenol remained in the neutral ether phase (TLC). Acidification of the base extract, followed by ether extraction, drying, and solvent removal gave the phenol (0.510 g, 73%). Recrystallization (ethanol/hexane) gave pure 3-benzylphenol (0.31 g, 44%), mp 51–52 °C (lit.[48] mp 55 °C). MS m/e (rel abund): 184 (100, M^+), 185 (13.5, M + 1), 183 (47.6, M – 1), 167 (16.3), 165 (54.9), 91 (16.4). ^1H NMR: δ 3.91 (s, 2 H, CH_2), 4.82 (bs, 1 H, OH), 6.79–6.60 (m, 3 H, H-2,4,6), 7.3–7.1 (m, 6 H, H-5,8,9,10,11,12). ^{13}C NMR: δ 41.73 (CH_2), 113.05 (C-4), 115.85 (C-2), 121.50 (C-6), 126.15 (C-10), 128.48 (C-8,12), 128.96 (C-9,11), 129.64 (C-5), 140.76 (C-7), 143.06 (C-1), 155.52 (C-3).

Dihydroxydiphenylmethanes. LDA (1.44 mmol) was added to a cold (0 °C) THF (3 mL) solution of complex **3** (0.136 mmol) and $(BuO)_3B$ (0.913 mmol). The resulting solution was stirred 5 h at 0 °C. Base extraction gave a 95% yield of a 2:1.3:1 mixture of 3,3′-dihydroxydiphenylmethane, 3,4′-dihydroxydiphenylmethane, and 4,4′-dihydroxydiphenylmethane, respectively. The individual compounds were not isolated; the isomeric ratio was determined by ^1H and ^{13}C NMR. The ^1H NMR chemical shifts for the methylene bridging groups were assigned as follows: 3,3′-dihydroxydiphenylmethane, δ 3.85; 3,4′-dihydroxydiphenylmethane, δ 3.86; 4,4′-dihydroxydiphenylmethane, δ 3.83. ^{13}C NMR, 3,3′-dihydroxydiphenylmethane: δ 40.81, 113.15, 115.86, 121.39, 129.64, 142.68, 155.66. ^{13}C NMR, 3,4′-dihydroxydiphenylmethane: δ 112.99, 115.28, 115.71, 121.25, 129.59, 129.91, 132.97, 142.65, 153.76, 155.61. The methylene bridge carbon for 3,4′-dihydroxydiphenylmethane was buried beneath that of the methylene bridge for the 4,4′-isomer. ^{13}C NMR, 4,4′-dihydroxydiphenylmethane: δ 41.53, 115.33, 130.08, 133.00, 153.88. MS m/e (rel abund): 200 (100, M^+), 201 (69.9, M + 1), 202 (11.0, M + 2), 199 (25.0, M – 1), 184 (12.0), 183 (16.0), 107 (71.0), 94 (17.0).

2-Naphthol. (2,2,6,6-Tetramethylpiperidyl)lithium [LiTMP, prepared by the addition of n-BuLi (2.25 M solution in hexanes, 2.52 mmol) to a cold (–78 °C) THF (4 mL) solution of 2,2,6,6-tetramethylpiperidine (2.55 mmol) for 15 min] was added to a cold (–78 °C) solution of complex **4** (0.485 mmol) and $(BuO)_3B$ (1.56 mmol) in THF (5 mL) followed by stirring for 0.5 h. Base extraction and chromatography with ether gave pure 2-naphthol (0.042 g, 94%), mp 121–123 °C (lit.[49] mp 119–120 °C). MS m/e (rel abund): 144 (100, M^+), 145 (9.9, M + 1), 116 (24.2), 115 (75.0). ^1H NMR: δ 5.50 (bs, 1 H, OH), 7.08 (dd, 1 H, J_{13} = 2.5 Hz, J_{34} = 8.7 Hz, H-3), 7.12 (d, 1 H, H-1), 7.31 (dt, 1 H, J_{57} = 1.3 Hz, J_{67} = 7.0 Hz, H-7), 7.41 (dt, 1 H, J_{68} = 1.3 Hz, H-6), 7.65 (d, 1 H, H-4), 7.74 (m, 2 H, H-5,8).[50] ^{13}C NMR: δ 109.50 (C-1), 117.70 (C-3), 123.57 (C-6), 126.34 (C-8), 126.48 (C-7), 127.72 (C-5), 128.90 (C-10), 129.81 (C-4), 134.55 (C-9), 153.30 (C-2).[50]

2-Hydroxy-9,10-anthraquinone. Crude complex **5** (0.332 mmol, estimated by ^1H NMR to be 40% complexed) and $(BuO)_3B$ (1.74 mmol) were cooled to –78 °C. To this was added cold (–78 °C) THF (3 mL) followed by LiTMP (2.91 mmol in 3 mL of THF), and the resulting solution was stirred 0.5 h at –78 °C. Base extraction gave the quinone (0.021 g, 71%), mp (st) 308–310 °C (lit.[51] mp 302–303 °C). A mixture melting point with authentic 2-hydroxy-9,10-anthraquinone[51] was not depressed. IR: 3228, 1713, 1617, 1302, 1261, 1093, 1020, 800 cm^{-1}. ^1H NMR (acetone-d_6) δ 7.36 (dd, 1 H, J_{13} = 2.6 Hz, J_{34} = 8.5 Hz, H-3), 7.66 (d, 1 H, H-1), 7.90 (m, 2 H, H-6,7), 8.19 (d, ^1H, H-4), 8.28–8.23 (m, 2 H, H-5,8) (the peak assignments were confirmed by a COSY experiment). ^{13}C NMR (acetone-d_6): δ 113.11 (C-3), 122.16 (C-1), 127.08 (C-4a), 127.54 (C-5,8), 130.73 (C-4), 134.47 (C-5a,8a), 134.60 (C-7), 135.10 (C-6), 136.63 (C-1a), 163.66 (C-2), 182.14 (C-10), 183.48 (C-9).[51]

In an alternate procedure, ether (10 mL), anthracene (2.08 mmol), $(NH_3)_3Cr(CO)_3$ (2.14 mmol), and $BF_3{\cdot}OEt_2$ (8.13 mmol) were stirred for 4 days at ambient temperature. The ether was then removed and THF (2 mL) was added. The resulting solution was cooled to –78 °C, and $(BuO)_3B$ (10.75 mmol) and LiTMP (17.81 mmol) were added. After being stirred for 3.5 h at –78 °C the reaction mixture was worked up as before. Base extraction gave 2-hydroxy-9,10-anthraquinone (0.029 g, 6.2%).

Phenanthrols. LiTMP (1.28 mmol in 1.6 mL of THF) was

(43) Marsh, J. T.; Stephen, H. *J. Chem. Soc.* **1925**, *127*, 1633–1637.
(44) Rubidge, C. R.; Qua, N. C. *J. Am. Chem. Soc.* **1914**, *36*, 732–737.
(45) Huang-Minlong, M. *J. Am. Chem. Soc.* **1946**, *68*, 2487–2488.
(46) Huang-Minlong, M. *J. Am. Chem. Soc.* **1949**, *71*, 3301–3303.
(47) Oki, M.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 681–684.
(48) Blackwell, J.; Hickinbottom, W. J. *J. Chem. Soc.* **1961**, 1405–1407.
(49) Brown, R. F. C.; McMullen, G. L. *Aust. J. Chem.* **1974**, *27*, 2385–2391.
(50) Ernst, L. *Chem. Ber.* **1975**, *108*, 2030–2039.
(51) Mahai, G. G.; Tarassoff, P. G.; Filipescu, N. *J. Chem. Soc., Perkin Trans.* **1975**, *1*, 1374–1376.

added to a cold (−78 °C) THF (3 mL) solution of complex 6 (0.245 mmol) and $(BuO)_3B$ (0.696 mmol). The resulting solution was stirred 0.5 h at −78 °C. Base extraction gave a 93% yield of a 2.5:1 mixture of 2-phenanthrol to 3-phenanthrol. The isomeric ratio was determined by ^{13}C NMR analysis of the mixture as compared to authentic materials prepared by alkali fusion of the corresponding 2- and 3-phenanthrene sulfonic acids. The individual sulfonic acids were prepared by treating phenanthrene with concentrated sulfuric acid at 120 °C and then identified as their *p*-toluidine salts:[25] 2-phenanthrenesulfonic acid *p*-toluidine salt, mp 276–279 °C (lit.[25] mp 291 °C); 3-phenanthrenesulfonic acid *p*-toluidine salt, mp 219–222 °C (lit.[25] mp 222 °C). ^{13}C NMR (acetone-d_6) 2-phenanthrol: δ 107.22, 117.99, 123.51, 124.49, 126.88, 127.37, 127.45, 127.49, 129.21, 130.42, 130.89, 132.77, 133.32, 157.32. ^{13}C NMR (acetone-d_6) 3-phenanthrol: δ 112.31, 118.05, 122.86, 124.68, 125.26, 126.19, 127.07, 127.51, 128.07, 129.32, 131.51, 131.76, 134.73, 157.13.

2-Pyrenol. LiTMP (1.66 mmol in 4.1 mL of THF) was added to a cold (−78 °C) THF (3 mL) solution of complex 7 (0.254 mmol) and $(BuO)_3B$ (1.01 mmol). The resulting solution was stirred for 35 min at −78 °C. Base extraction gave 2-pyrenol (0.033 g, 59%), mp (st) 205–206 °C (lit.[52,53] mp 206–207 °C). MS *m/e* (rel abund): 218 (100, M^+), 219 (14.5, M + 1), 189 (44.9), 187 (11.5), 94 (10.3). ^1H NMR (acetone-d_6): δ 7.75 (s, 2 H, H-1,3), 7.93 (t, 1 H, J_{67} = 7.6 Hz, H-7), 8.01 (d, 2 H, J_{45} = 8.8 Hz, H-4,10), 8.09 (d, 2 H, H-5,9), 8.19 (d, 2 H, H-6,8), 8.97 (bs, 1 H, OH).[2] ^{13}C NMR (acetone-d_6): δ 112.70 (C-1,3), 120.11 (C-15), 125.48 (C-16), 125.59 (C-7), 126.00 (C-6,8), 127.51 (C-4,10), 128.65 (C-5,9), 130.94 (C-13,14), 133.76 (C-11,12), 156.84 (C-2).

In an alternate procedure, THF (6 mL), pyrene (0.743 mmol), $(NH_3)_3Cr(CO)_3$ (0.749 mmol), and BF_3-OEt_2 (2.28 mmol) were stirred for 3 days at ambient temperature. After the mixture was cooled to −78 °C, $(BuO)_3B$ (2.22 mmol) and LDA (3.78 mmol) were added. After 45 min of stirring the reaction mixture was worked up as before. Base extraction of the resulting mixture gave 2-pyrenol (0.032 g, 20%).

8-Hydroxyfluoranthene. LiTMP (1.22 mmol in 3 ml of THF) was added to a cold (−78 °C) THF (3 mL) solution of complex 8 (0.243 mmol) and $(BuO)_3B$ (0.737 mmol). The resulting solution was stirred 35 min at −78 °C and worked up as before (without the base extraction). Chromatography with a 25% ethyl acetate in hexanes gave 8-hydroxyfluoranthene (0.041 g, 78%). Recrystallization from benzene gave light yellow crystals, mp 158–159 °C (lit.[23] mp 155–157.5 °C). MS *m/e* (rel abund): 218 (100, M^+), 219 (18.3, M + 1), 190 (18.2), 189 (75.6), 109 (10.7). ^1H NMR: δ 4.95 (bs, 1 H, OH), 6.83 (dd, 1 H, J_{79} = 2.37 Hz, $J_{9,10}$ = 8.16 Hz, H-9), 7.38 (d, 1 H, H-7), 7.59 (t, 1 H, *J* = 6.87 Hz, H-2 (5)), 7.61 (t, 1 H, *J* = 6.86 Hz, H-5 (2)), 7.75 (d, 1 H, H-10), 7.89–7.75 (m, 4 H, H-1,3,4,6). ^{13}C NMR: δ 109.10, 114.21, 118.99, 120.06, 122.37, 125.52, 126.99, 127.76, 128.03, 129.94, 132.63, 132.81, 136.56, 136.86, 141.52, 155.69.

In an alternate procedure, complex 8 (0.222 mmol) and $(BuO)_3B$ (0.668 mmol) were treated as above with potassium 2,2,6,6-tetramethylpiperidine [KTMP, prepared by the addition of *n*-BuLi (1.10 mmol) to a cold (−78 °C) THF solution of potassium *tert*-butoxide (1.12 mmol) and 2,2,6,6-tetramethylpiperidine (1.13 mmol) with stirring for 10 min]. Chromatography with 25% ethyl acetate in hexanes gave 8-hydroxyfluoranthene (0.018 g, 37%) and 7,9-dihydroxyfluoranthene (0.011 g, 21%), a dark yellow-brown oil: IR: 3564, 3116, 3090, 3004, 1261, 1102, 1090, 1019, 819 cm^{-1}. ^1H NMR: δ 5.2 (bs, 1 H, OH), 5.4 (bs, 1 H, OH), 6.33 (d, 1 H, *J* = 1.5 Hz), 7.03 (d, 1 H, *J* = 1.5 Hz), 7.62–7.56 (m, 2 H), 7.73 (d, 1 H, *J* = 8.2 Hz), 7.87–7.82 (m, 2 H), 7.95 (d, 1 H, *J* = 6.8 Hz). ^{13}C NMR: δ 102.57, 102.61, 118.69, 120.35, 121.50, 124.80, 127.18, 127.51, 128.29, 129.79, 132.32, 135.69, 136.68, 142.78, 152.87, 156.80. HRMS calcd for $C_{16}H_{10}O_2$ 234.0681, found (EI) 234.0682.

2-(Trimethylsilyl)naphthalene. Complex 4 (0.322 mmol) and TMSCl (1.02 mmol) were placed in a 25-mL flask equipped with a magnetic stir bar and a rubber septum. The flask was cooled to −78 °C, cold (−78 °C) THF (4 mL) was added, followed by the rapid addition (syringe) of cold (−78 °C) LiTMP (1.61 mmol in 2.0 mL of THF). After stirring 35 min at −78 °C, the resulting solution was quenched with an excess of a 0.3 M DCl solution, allowed to warm to ambient temperature, and diluted with ether, and the complex was decomposed with an excess of a 0.2 N Ce(IV) solution. After stirring overnight, the reaction mixture was acidified with a 1 M HCl solution, extracted into ether (2 × 15 mL), and dried over Na_2SO_4, and the solvent was removed to give crude 2-(trimethylsilyl)naphthalene as a yellow oil (0.052 g, 81%).[54] Chromatography on silica gel (1% EtOAc in petroleum ether) gave pure material as a yellow oil (0.043 g, 67%). MS *m/e* (rel abund): 200 (18.4, M^+), 201 (3.8, M + 1), 202 (1.0, M + 2), 185 (100, M − 15), 186 (16.8), 155 (8.2). ^1H NMR ($CDCl_3$): δ .34 (s, 9 H, Si-CH_3), 7.49–7.43 (m, 2 H, H-6,7), 7.60 (dd, 1 H, J_{13} = 1.2 Hz, J_{34} = 8.2 Hz, H-3), 7.86–7.77 (m, 3 H, H-4,5,8), 8.00 (bs, 1 H, H-1) (109). ^{13}C NMR ($CDCl_3$); δ −1.08 (Si-CH_3), 125.85 (C-7), 126.18 (C-6), 126.90 (C-4), 127.68 (C-8), 127.99 (C-5), 129.77 (C-3), 132.93 (C-9), 133.62 (C-10), 133.74 (C-1), 137.88 (C-2).[56] Also found, but not fully characterized, was 1,3-bis(trimethylsilyl)naphthalene (eluted with ether after 2-(trimethylsilyl)naphthalene; 9%). MS *m/e* (rel abund): 272 (28.9, M^+), 273 (7.8, M + 1), 274 (3.3, M + 2), 257 (100, M − 1), 258 (22.2).

2-(Trimethylsilyl)pyrene. Complex 7 (0.243 mmol), THF (3 mL), and TMSCl (0.733 mmol) were cooled to −78 °C and a cold (−78 °C) solution of LiTMP (1.22 mmol in 2.5 mL of THF) was added by syringe. After stirring 1 h at −78 °C, the reaction mixture was worked up and decomplexed as above to give 2-(trimethylsilyl)pyrene as a pale yellow solid (0.065 g, 98%). Recrystallization from ethanol/hexane gave pure material as light yellow crystals, mp 91.5–92.5 °C. MS *m/e* (rel abund): 274 (70.1, M^+), 275 (21.0, M + 1), 276 (4.6, M + 2), 259 (100, M − 15), 260 (22.2), 229 (11.1), 201 (8.9). ^1H NMR ($CDCl_3$): δ .473 (s, 9 H, Si-CH_3), 7.99 (t 1 H, J_{67} = 7.60 Hz, H-7), 8.07 (m, 4 H, H-4,5,9,10), 8.16 (d, 2 H, H-6,8), 8.32 (s, 2 H, H-1,3). ^{13}C NMR ($CDCl_3$): δ −0.779 (Si-CH_3), 124.61 (C-15), 124.76 (C-6,8), 124.91 (C-16), 125.91 (C-7), 127.26 (C-4,10), 127.44 (C-5,9), 129.91 (C-1,3), 130.28 (C-13,14), 131.27 (C-11,12), 137.96 (C-2). COSY and HETOR 2-D NMR experiments were used to make ^1H and ^{13}C NMR peak assignments. HRMS calcd for $C_{19}H_{18}Si$ 274.1178, found (EI) 274.1179.

2-Carbethoxynaphthalene. Complex 4 (0.218 mmol) and cold (−78 °C) THF (2 mL) were stirred as cold (−78 °C) LiTMP (0.220 mmol in 1.2 mL of THF) was added. After 40 min at −78 °C, the reaction was quenched with ethyl chloroformate (0.336 mmol) and stirred for 10 min, and the dry ice–acetone bath replaced with an ice–water bath. After 2 h at 0 °C, more ethyl chloroformate (0.116 mmol) was added and stirring continued. The reaction mixture was quenched after 3.5 h at ca. 0 °C with an excess of a saturated NH_4Cl solution and excess I_2 to decompose the complex. Stirring was continued for 1 h at which time the solution was washed with 5% $NaHSO_3$, acidified with a 1 M HCl solution, extracted with ether (3 × 10 mL), and dried over Na_2SO_4, and the solvent was removed. The remaining naphthalene was removed by sublimation to give crude 2-carbethoxynaphthalene (56%, GLC). Chromatography on silica gel (petroleum ether, followed by 5% EtOAc in petroleum ether) gave the pure ester as a light yellow oil (0.021 g, 48%). FT-IR (KBr): 3058, 2974, 1714, 1284, 1095, 778, 761 cm^{-1}. MS *m/e* (rel abund): 200 (47.3, M^+), 201 (6.6, M + 1), 172 (27.2), 155 (100), 127 (91.9), 126 (19.9). ^1H NMR ($CDCl_3$): δ 1.44 (t, 3 H, CH_3), 4.44 (q, 2 H, CH_2), 7.55 (m, 2 H, H-6,7), 7.86 (m, 2 H, H-4,5), 7.93 (d, 1 H, J_{78} = 7.84 (Hz, H-8), 8.03 (dd, 1 H, J_{13} = 1.70 Hz, J_{34} = 8.6 Hz, H-3), 8.60 (bs, 1 H, H-1). ^{13}C NMR ($CDCl_3$): δ 14.36 (CH_3), 61.04 (CH_2), 125.21 (C-3), 126.53 (C-7), 127.70 (C-5), 128.02 (C-4), 128.09 (C-6), 129.28 (C-8), 130.89 (C-1), 132.46 (C-8a), 135.43 (C-4a), 166.72 (C-9). C-2 was buried under a peak or not detected. The ester prepared[55] by acid-catalyzed esterification of 2-naphthoic acid with ethanol exhibited identical spectral properties. Co-injection of the two

(52) Vollman, H.; Becker, H.; Corell, M.; Streeck, H. *Liebigs Ann. Chem.* **1937**, *531*, 1–159.

(53) Harvey, R. G.; Schmolka, S.; Cortez, C.; Lee, H. *Synth. Commun.* **1988**, *18*, 2207.

(54) Benkeser, R. A.; Schroeder, W.; Thomas, O. H. *J. Am. Chem. Soc.* **1958**, *80*, 2283.

(55) Cf.: Vogel, A. I. *A Textbook of Practical Organic Chemistry*; Longmans, Green and Co.: London, **1948**, p 739.

(56) Kitching, W.; Bullpitt, M.; Gartsore, D.; Adcock, W.; Khor, T. C.; Doddrell, D.; Rae, I. D. *J. Org. Chem.* **1977**, *42*, 2411–2418.

esters on two different GC column packings gave one peak in each case.

2-Carbethoxypyrene (11). Complex **7** (0.135 mmol), THF (3 mL), and ethyl chloroformate (0.401 mmol) were cooled to −78 °C, transferred by a cannula to a cold (−78 °C) dropping funnel, and added dropwise over 4 min to a cold (−78 °C) THF (3 mL) solution of KTMP (0.660 mmol in 3 mL of THF). After being stirred for 1 h at −78 °C, the reaction mixture was quenched with H_2O and decomplexed by stirring overnight with excess of a 0.2 N Ce(IV) solution. The resulting solution was filtered through Celite, acidified with a 1 M HCl solution, extracted with ether (3 × 10 mL), and dried. GLC analysis of the mixture showed it to contain 73% of **11** and 27% 1,2,3-tricarbethoxypyrene (**13**). Chromatography on silica gel (2.5% ethyl acetate in petroleum ether) and recrystallization from ethanol gave pure **11** as light yellow flakes (0.023 g, 62%), mp 114.5–115.0 °C (lit.[52,57] mp 117 °C). FT-IR (KBr): 3037, 2980, 2929, 1720 (split, also see band at 1711), 1296, 1227, 1209, 1037, 840, 693 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.52 (t, 3 H, CH_3), 4.55 (q, 2 H, CH_2), 8.05 (t, 1 H, J_{67} = 7.65 Hz, H-7), 8.09 (d, 2 H, J_{45} = 9.03 Hz, H-5,9), 8.13 (d, 2 H, H-4,10), 8.20 (d, 2 H, H-6,8), 8.83 (s, 2 H, H-1,3).[58] ^{13}C NMR ($CDCl_3$): δ 14.48 (CH_3), 61.31 (CH_2), 124.29 (C-16), 125.36, (C-1,3), 125.65 (C-6,8), 126.86 (C-15), 126.94 (C-7), 127.53 (C-2), 127.73 (C-4,10), 128.09 (C-5,9), 130.88 (C-11,12), 131.73 (C-13,14), 167.19 (CO).

1,2-Dicarbethoxypyrene (12). Complex **7** (0.128 mmol), ether (3 mL), and ethyl chloroformate (0.384 mmol) were cooled to −78 °C, and cold (−78 °C) LiTMP (0.630 mmol in 1.65 THF) was added by syringe. The resulting solution was stirred at −78 °C for 1.5 h, quenched with excess H_2O, decomplexed, and worked up as above. GLC analysis of the reaction mixture showed it to contain 36% 1,2-dicarbethoxypyrene along with 28% of the monoester. The remainder was pyrene. Chromatography on silica gel with petroleum ether removed the pyrene. Further elution with 2.5% ethyl acetate in petroleum ether removed the monoester. The diester was eluted with 7% ethyl acetate in petroleum ether. Recrystallization from ethanol gave **12** as light brown crystals (0.012 g, 27%), mp 138.5–140.0 °C. FT-IR (KBr): 3035, 2985, 1723, 1298, 1253, 1215, 1060 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.500 (t, 3 H, CH_3), 1.504 (t, 3 H, CH_3), 4.52 (q, 2 H, CH_2), 4.64 (q, 2 H, CH_2), 8.10 (t, 1 H, J_{67} = 7.6 Hz, H-7), 8.20–8.11 (m, 4 H, H-4,5,9,10), 8.28–8.24 (m, 2 H, $J_{6,8}$ = 1.6 Hz, H-6,8), 8.79 (s, 1 H, H-3).[59] ^{13}C NMR ($CDCl_3$): δ 14.22 (CH_3), 14.32 (CH_3), 61.80 (CH_2), 62.00 (CH_2), 123.93 (C-1), 124.20 (C-10), 125.41 (C-16), 125.76 (C-3), 126.00 (C-6), 126.20 (C-8), 126.27 (C-2), 127.32 (C-7), 127.36 (C-4), 128.16 (C-11), 129.08 (C-9), 129.37 (C-5), 129.60 (C-15), 131.12 (C-14), 131.30 (C-13), 131.70 (C-2), 166.47 (CO), 169.46 (CO). COSY and HETCOR 2-D NMR experiments were used to make ^1H and ^{13}C NMR peak assignments. Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 75.93; H, 5.45.

1,2,3-Tricarbethoxypyrene (13). Complex **7** (0.193 mmol), THF (3 mL), and ethyl chloroformate (1.16 mmol) were cooled to −78 °C, and KTMP (1.89 mmol in 7.0 mL of THF) was added via cannula. The resulting solution was stirred at −78 °C for 3 h, quenched, decomposed, and worked up as above. Chromatography on silica gel with petroleum ether removed traces of pyrene. Gradual increase of solvent polarity to a 15% EtOAc in petroleum either mixture removed the triester (0.057 g, 71%). Recrystallization from ethanol/hexane gave pure **13** as light yellow flakes, mp 94.5–95.5 °C. FT-IR (KBr): 3036, 2985, 1728, 1300, 1247, 1198, 1032 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.50 (m, 9 H, CH_3), 4.47 (q, 2 H, CH_2), 4.57 (q, 4 H, CH_2), 8.13 (t, 1 H, J_{67} = 7.2 Hz, H-7), 8.24 (d, 2 H, J_{45} = 9.42 Hz, H-5,9), 8.30 (d, 2 H, H-6,8), 8.33 (d, 2 H, H-4,10). A COSY 2D NMR experiment was used to make ^1H NMR peak assignments. ^{13}C NMR ($CDCl_3$): δ 14.08 (CH_3; 2-position), 14.17 (CH_3; 1,3-position), 62.18 (CH_2; 1,3-position), 62.31 (CH_2; 2-position), 123.66 (C-16), 124.10 (C-4,10), 125.35 (C-15), 126.98 (C-6,8), 127.40 (C-2), 127.53 (C-7), 127.63 (C-1,3), 129.33 (C-11,12), 130.59 (C-5,9), 130.95 (C-13,14), 167.19 (CO; 2-position), 168.10 (CO; 1,3-position). HRMS calcd for $C_{25}H_{22}O_6$ 418.1417, found (EI) 418.1417.

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(57) Vollman, H. *Justus Liebigs Ann. Chem.* **1983**, *48*, 2360.
(58) Reynders, P.; Kühnle, W.; Zachariasse, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3929–3939.
(59) Murata, I.; Nakasuji, K.; Kume, H. *Tetrahedron Lett.* **1973**, 3401–3404.