to this quadrupole moment due to HCl depends on the effective dipole moment of HCl in the complex. The Q_{cc} components will be less dependent on the vibrational angle of acetylene. Using this second method, we get $Q(\text{acetylene}) = 7.6 \times 10^{-26}$ esu cm^2. These results are in reasonably good agreement with calculated values[15,17] of $Q(\text{acetylene}) = 7.34$ or 7.2×10^{-26} esu cm^2.

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(17) A. D. McLean and M. Yoshimine, *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **438**, 67 (1967).

Acknowledgment. The support of the National Science Foundation and the University of Illinois School of Chemical Sciences is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, for partial support of this research. One of us (S.G.K.) thanks the University of Illinois Research Board for support. We wish to thank Peter Aldrich for the use of his computer programs for part of the data analysis.

Registry No. Acetylene–hydrochloric acid, 52218-20-9.

Rotational Barriers in Diphenylmethyl Anions Stabilized by Trimethylsilyl and Tricarbonylchromium(0) Moieties

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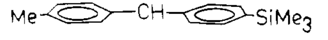
Abstract: A series of diphenylmethyl anions has been prepared in which the phenyl rings bear π-bonded $Cr(CO)_3$ groups and/or a trimethylsilyl moiety. Variable-temperature ^{13}C NMR studies on these compounds have allowed the evaluation of the barriers to phenyl rotation. It is shown that a π-bonded $Cr(CO)_3$ group stabilizes the negative charge much more efficiently than does a p-$SiMe_3$ functionality. However, when the Me_3Si substituent is bonded directly to the α-carbon atom, the charge preferentially resides on the silicon, allowing the (π-$Cr(CO)_3$–C_6H_5) groups to rotate apparently unhindered.

The delocalization of negative charge from carbanionic centers is of paramount importance in many reaction sequences.[1,2] It is well established that adjacent carbonyl functions,[3] cyano[4] or nitro[5] groups, etc., very significantly stabilize carbanions such that the carbon formally bearing the negative charge is probably best regarded as being in an sp^2-hybridized, trigonal-planar environment. In contrast, carbanions lacking neighboring groups that facilitate charge dispersal are presumably pyramidal and mimic amines in their behavior.

The interactions of trimethylsilyl groups with carbanions have been the subject of some debate;[6] however, it was quickly recognized that such moieties, when directly bonded to the carbanionic center, lead to marked stabilization of the anion.[7] A quantitative assessment of the stabilizing effect of a remote trimethylsilyl substituent was attempted via an ingenious NMR experiment described recently.[8] In this study, the authors used DNMR to show conclusively that in the 4-methyl-4′-(trimethylsilyl)diphenylmethyl anion, **1**, the ortho carbons (and protons) of the two phenyl rings are equilibrated via phenyl rotation at quite different rates. Indeed, the 4-methylphenyl ring is rotating faster than the 4′-(trimethylsilyl)phenyl moiety by a factor of 200 at 255 K. These data allowed the evaluation of the rotational barriers, which are ~10 kcal mol^{-1} for the methyl-substituted ring and ~12.7 kcal mol^{-1} for the silylated ring. The conclusions drawn were that the anion was essentially coplanar and that, assuming that the barrier was determined exclusively by the strength of π bonding to the benzylic carbon, the π interaction with the silylated ring was enhanced relative to that in the other ring. One possible rationale would involve pπ–dπ overlap, as in **2**, between the arene ring and a vacant d orbital on silicon.[6] Others prefer to attribute this stabilization to a polarization effect or to hyperconjugation.[7]



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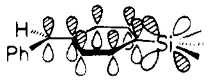

2

For some years now we have concerned ourselves with the capacity of the tricarbonylchromium(0) moiety to stabilize anions[9] or cations[10] at the benzylic position. Indeed, we have demonstrated the viability of a number of reactions for the (arene)$Cr(CO)_3$ complexes not readily achieved for the noncomplexed arenes.[11,12] We now report the syntheses and variable-temperature NMR spectra of diphenylmethyl anions bearing trimethylsilyl and/or tricarbonylchromium(0) substituents; this allows a direct comparison of the relative stabilizing effects of the two moieties.

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[‡] McMaster University.

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(5) Reference 2, p 52.

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(10) (a) Top, S.; Jaouen, G.; McGlinchey, M. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1110. (b) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1980**, *197*, 199

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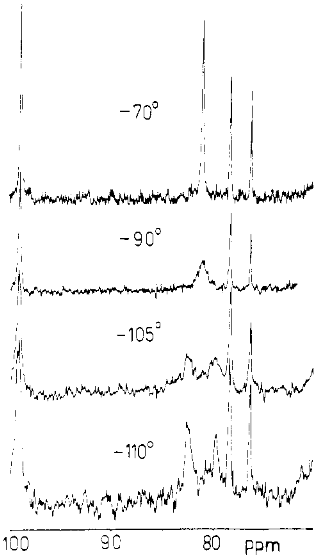
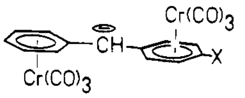


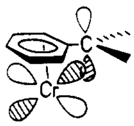
Figure 1. Section of the 100.6-MHz ^{13}C NMR spectrum of **4**, at various temperatures.

Results and Discussion

The barrier to phenyl rotation in the diphenylmethyl anion **3** has been measured as 11.2 kcal mol^{-1}.[13] We have previously reported[9] the synthesis of **4**, the bis(chromium(0)tricarbonyl) complex of **3**, and demonstrated that there is extensive delocalization of the carbanionic charge onto the Cr(CO)$_3$ group. In contrast to the stabilization of benzylic cations by the Cr(CO)$_3$ group—a phenomenon[14] that seems to involve direct overlap of a filled chromium 3d orbital with the vacant 2p orbital at the α-carbon as in **5**—the stabilization of the benzylic anion is indirect; indeed, such an overlap between the Cr d orbital and the orbital on the α-carbon would be destabilizing since both orbitals are filled. Taking a simple valence bond viewpoint, one could visualize a resonance structure wherein the Cr(CO)$_3$ is bonded to the ring in a pentahapto manner and there is essentially a double bond between the C$_1$ phenyl carbon and the benzylic carbon. Such a picture gains some support from X-ray crystallographic data on (fluorene)Fe(C$_5$H$_5$).[15] In any event, the occurrence of charge delocalization into the metal carbonyls is unquestionable. The decrease in metal-carbonyl stretching frequencies and deshielding of the carbonyl ^{13}C NMR peaks in **4** relative to the diphenylmethane precursor are comparable, but of opposite sign, to those observed for the corresponding cation.[9,14a] Interestingly, a recent X-ray crystallographic study of (*N*,*N*-diethylaniline)tricarbonylchromium(0) revealed a planar geometry for the exocyclic diethylamino group. Furthermore, the N–C(arene) bond was short, supporting the picture of delocalization of the nitrogen lone pair onto the arene and thence to the Cr(CO)$_3$ group.[16] Now, since the noncomplexed anions **1** and **3** are postulated to be planar,[8] the enhanced charge delocalization onto the ring and thence to the Cr(CO)$_3$ groups, together with the bulk of the π-complexed moieties, would be expected to considerably hinder phenyl group rotation; we thus expected an increased $\Delta G^{\ddagger}$ relative to the 11.2 kcal mol^{-1} barrier previously reported[13] for **3**.



4 X = H
6 X = SiMe$_3$



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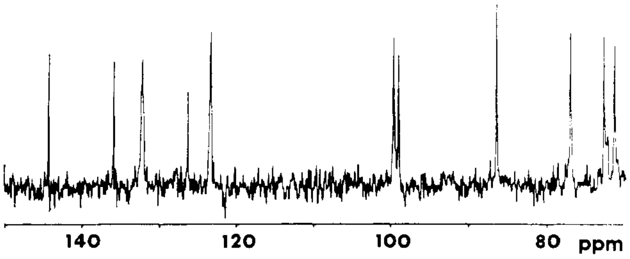

Figure 2. Section of the 100.6-MHz ^{13}C NMR spectrum of **7**, at −40 °C.

The ^{13}C NMR spectra of **4** in THF at various temperatures are shown in Figure 1. The particular features to focus on are the resonances at δ 82 and 99, which are assigned to the ortho (2, 6) and meta (3, 5) carbons, respectively.[17] We see that it is necessary to cool the anion **4** to −110 °C at 9.4 T (100.614 MHz for ^{13}C) to obtain the limiting spectrum; these data yield a barrier $\Delta G^{\ddagger}_{178}$ of 8.1 ± 0.5 kcal mol^{-1}. It is difficult to rationalize a diminution of the barrier by such a large amount as 3 kcal mol^{-1} purely on the basis of an electronic effect; indeed it would suggest that the Cr(CO)$_3$ groups destabilize the anion—an interpretation that would contradict all previous evidence on these systems! A more plausible explanation requires a major portion of the barrier in the noncomplexed anions to be steric in origin.[18] Clearly, to maximize p-orbital overlap and minimize the steric interactions between the bulky Cr(CO)$_3$ groups, the anion should be planar, but such considerations suggest that the assumption of planarity for the noncomplexed anion **3** is invalid. Clearly, in the absence of X-ray crystallographic data on the anion **3** and its bis(chromium(0)tricarbonyl) analogue **4**, it is difficult to separate the steric and electronic components of the barrier to rotation. Furthermore, at some point one reaches a limit to the ability of the α-carbon atom to delocalize its charge, and it is conceivable that the presence of two Cr(CO)$_3$ units each competing for back-donated electron density actually has a bond-weakening effect on the other. Such a trans influence is frequently encountered with strong π-acid ligands such as CO or PF$_3$.[19] Nevertheless, the results of Bank et al.[8] unequivocably demonstrated the preference for electronic delocalization into a trimethylsilyl-substituted aryl ring and so, to make a meaningful comparison, the bis(chromium(0)tricarbonyl) complex of the 4-(trimethylsilyl)diphenylmethyl anion, viz. **6**, was synthesized. In this case, as for **4**, it was necessary to use a very high-field spectrometer; at −120 °C the silylated aryl ring resonances are separated while the phenyl ring rotation is still rapid on the NMR time scale. The barrier to rotation is 8.5 ± 0.5 kcal mol^{-1} and so, while acknowledging the limits of experimental error, the introduction of a 4-trimethylsilyl group stabilizes the negative charge but only to a minimal extent. Apparently, the Me$_3$Si group exerts only a second-order effect and merely perturbs the much stronger influence of the Cr(CO)$_3$ group.

To test this hypothesis, the anion of (4′-(trimethylsilyl)diphenylmethane)tricarbonylchromium(0), **7**, was prepared to allow a direct comparison between a p-Me$_3$Si group and a π-complexed

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(13) Bank, S.; Sturges, J.; Bushweller, C. H. In "Stereodynamics of Molecular Systems"; Sarma, R. H.; Ed.; Pergamon Press: New York, 1979; p 147.

(14) (a) Seyferth, D.; Merola, J. S.; Eschbach, C. S. *J. Am. Chem. Soc.* **1978**, *100*, 4124. (b) Acampora, M.; Ceccon, A.; Dal Farra, M.; Giacometti, G.; Rigatti, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 483.

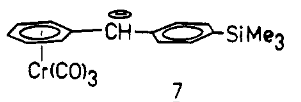
(15) Johnson, J. W.; Treichel, P. M. *J. Am. Chem. Soc.* **1977**, *99*, 1427.

(16) Saillard, J. Y.; Grandjean, D.; LeMaux, P.; Jaouen, G. *Nouv. J. Chim.* **1981**, *5*, 153.

(17) In a preliminary communication (ref 9) these assignments were reversed. However, in the present case the data were remeasured on a 400-MHz spectrometer and the assignments confirmed by single-frequency off-resonance decoupling.

(18) While it is true that the data in ref 8 are for the lithium salt and the present results are for the potassium salt, this does not invalidate the conclusions. Indeed, comparisons between analogous Li and K salts show that aryl rotation in the lithium salts is actually faster: Staley, S. W. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, p 202.

(19) Typically, in W(CO)$_6$ it is relatively easy to displace three facially disposed carbonyl groups since each is trans to another carbonyl. However, further replacement of carbonyls is much more difficult: King, R. B. "Transition-Metal Organometallic Chemistry"; Academic Press: New York, 1969; pp 73–75.



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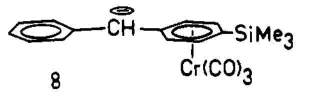
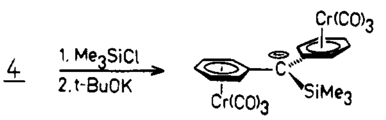


8

$Cr(CO)_3$ substituent. The results were a striking confirmation of the previous observation. A typical spectrum appears as Figure 2 but, in fact, the spectrum scarcely changes over the temperature range −100 °C to room temperature, above which thermal decomposition is observed. In an attempt to observe coalescence of the peaks due to the ortho and meta carbons of the chromium-complexed ring, the spectra were also obtained on 250- and 90-MHz spectrometers (at 62.86 and 22.62 MHz, respectively), but the results were unchanged. As the 4-(trimethylsilyl)phenyl rotation cannot be made slow on the NMR time scale, it is not possible to deduce a rotational barrier but, assuming similar chemical shift differences to those seen in the other anions studied, $\Delta G^{\ddagger}$ is probably somewhat less than 8 kcal mol^{-1}. In contrast, the $-C_6H_5Cr(CO)_3$ rotation has a barrier of at least 15 kcal mol^{-1} and may be much higher. Not surprisingly, the same behavior is observed for **8** in which both the Me_3Si and π-$Cr(CO)_3$ moieties are in the same ring.

The facility with which the anion **4** could be prepared prompted us to treat this ion with chlorotrimethylsilane and then deprotonate a second time to give the anion **9** in which the carbanionic center



9

was directly bonded to the silicon. This particular anion is thermally stable at room temperature for several hours—even in air! Furthermore, the α-Me_3Si group in **9** provides much more severe competition to the π-complexed rings in its capacity to tolerate negative charge. Indeed, the ^{13}C NMR spectrum of **9** shows no separation of the ortho-carbon resonances even at −110 °C. It is thus clear that very extensive delocalization of the carbanionic charge onto silicon has occurred. This is also reflected in the large shielding of the ^{29}Si NMR signal in **9** relative to the other ^{29}Si shifts that appear in Table I.

Another important factor here is the steric crowding around the α-carbon when it is four-coordinate. Thus, the reaction of the anion **4** with Me_3SiCl is a surprisingly slow process, and the ^{13}C NMR spectrum of the product, viz. $(C_6H_5Cr(CO)_3)_2CHSiMe_3$, shows five distinct proton-bearing aromatic carbons demonstrating that aryl rotation is severely hindered even at elevated temperatures. Thus the relief of steric strain favors the formation of the anion **9** in which aryl rotation proceeds without hindrance.

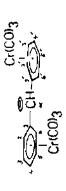
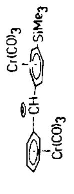
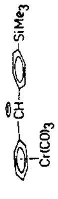
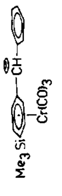
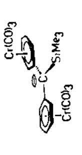
Conclusions

DNMR studies on a series of diphenylmethyl anions reveal that complexation by $Cr(CO)_3$ groups lowers the barriers to phenyl rotation relative to those found for the noncomplexed anions. It is proposed that the free anions are pyramidal but that complexation renders them planar. Delocalization of the charge on the α-carbon is much better accommodated on the $Cr(CO)_3$ moiety than on the p-Me_3Si group. However, attachment of the Me_3Si grouping directly to the α-carbon yielded an air- and temperature-stable anion in which very extensive delocalization onto silicon has occurred.

Experimental Section

All manipulations involving the organometallic anions were performed under an atmosphere of nitrogen. Solvents were dried over sodium and freshly distilled just prior to use. ^{13}C NMR spectra were obtained on a Bruker WM 400 spectrometer operating at 100.614 MHz; ^{29}Si NMR

Table I. ^{13}C, ^{29}Si NMR Spectra (ppm) and ν_{CO} Values for Complexes 4 through 8

	C_1	$C_{2,6}$	$C_{3,5}$	C_4	C_α	C'_1	$C'_{2,6}$	$C'_{3,5}$	C'_4	CO	CH_3	^{29}Si	ν_{CO}, cm^{-1}	NMR solvent
	112.1[a] *134.2*[b]	95.1 *81.2*[c]	94.9 *98.7*[d]	93.4 *78.4*	38.6 *76.4*	112.1 *134.2*	95.1 *81.2*[c]	94.9 *98.7*[d]	93.4 *78.4*	233.8 *237.4*			1975, 1901 *1941, 1858*	THF THF
	113.6[a] *136.4*[b]	94.7[e] *82.3*	94.5[e] *98.7*	93.1 *78.3*	39.8 *77.0*	111.6 *133.5*	92.7 *81.1*[f]	101.1 *103.4*[g]	99.4 *79.4*	234.1, 233.8 *237.7, 237.3*	−1.9 *−1.5*	0.4 *−2.7*	1978, 1970, 1900 *1949, 1936, 1860*	acetone THF
	112.9[a] *136.0*[b]	93.9[e] *86.4/77.0*	93.4[e] *99.6/99.0*	90.0 *72.8*	41.3 *71.4*	139.9 *144.4*	129.0 *123.5*	134.6 *132.3*	139.6 *126.4*	234.1 *239.4*	−0.6 *−1.5*	−4.6 *−7.4*	1970, 1896 *1921, 1822*	benzene THF
	114.9[a] *135.9*[b]	92.1 *87.6/78.8*	100.4 *103.3/102.5*	97.8 *76.6*	41.7 *73.4*	139.6 *143.1*	129.8 *124.3*	129.8 *127.1*	127.8 *118.4*	234.5 *239.9*	−0.7 *−1.1*	0.1 *−3.1*	1970, 1896 *1921, 1822*	benzene THF
	113.5[a] *135.8*[b]	94.6/90.3 *86.1*	96.4/95.5 *97.5*	89.3 *80.5*	41.1 *98.9*	113.5 *135.8*	94.6/90.3 *86.1*	96.4/95.5 *97.5*	89.3 *80.5*	233.2 *237.2*	−0.4 *+1.7*	−4.0 *−10.4*	1955, 1895 *1945, 1840*	chloroform THF

[a] Data for the diphenylmethane complexes. [b] Data for the diphenylmethyl anion complexes (in italics). [c] 82.5/79.6 at −110 °C. [d] 99.4/99.2 at −110 °C. [e] Assignments may be interchanged. [f] 83.5/81.3 at −110 °C. [g] 103.6/103.3 at −120 °C.

spectra were obtained on a Bruker WM 250 spectrometer operating at 49.964 MHz; shifts are reported relative to tetramethylsilane and positive shifts are to high frequency.

Synthesis of 4-(Trimethylsilyl)diphenylmethane. 4-Chlorobenzophenone (22 g, 0.1 mol) dissolved in anhydrous ether was added to $LiAlH_4$ (6.6 g, 0.18 mol) and $AlCl_3$ (48 g, 0.36 mol) in 100 mL of ether, and the mixture was heated under reflux for 1.5 h according to the method of Blackwell and Hickinbottom.[20] Excess of the reagent was destroyed by adding ethyl acetate, and the mixture was poured into 20% aqueous H_2SO_4. Ether extraction, solvent evaporation, and vacuum distillation (160 °C/11 torr) gave 4-chlorodiphenylmethane (18 g, 0.089 mol; 89%). This latter product (8 g, 0.04 mol) was stirred with magnesium (3.6 g, 0.15 mol) in THF at 50 °C over a 12-h period. Chlorotrimethylsilane (15 g, 0.138 mol) was added and the mixture heated at 90 °C for 48 h. Addition to water, ether extraction, and removal of solvent in vacuo gave 4-(trimethylsilyl)diphenylmethane (9.5 g) as a pale yellow, slightly viscous liquid, which was not further purified. This product gave a ^{29}Si NMR peak at −5.2 ppm.

Syntheses of the (Diphenylmethane)tricarbonylchromium(0) Complexes. (Diphenylmethane)bis(tricarbonylchromium(0)) was prepared as described previously.[21,22] 4-(Trimethylsilyl)diphenylmethane (3 g, 12.5 mmol), $Cr(CO)_6$ (2.2 g, 10 mmol), dibutyl ether (100 mL), and THF (10 mL) were heated under reflux in a nitrogen atmosphere for 24 h. After filtration and evaporation of the solvent, the residual oil was chromatographed on a silica gel column by using ether/petroleum ether (1:10) as eluent. The first product was recrystallized from ether/petroleum ether to give yellow crystals of (4-(trimethylsilyl)diphenylmethane)tricarbonylchromium(0) (700 mg, 1.86 mmol; 19%), mp 80 °C. Anal. Calcd for $C_{19}H_{20}CrO_3Si$: C, 60.6; H, 5.3. Found: C, 60.9; H, 5.4.

The second product eluted was recrystallized from ether/petroleum ether to give yellow crystals of (4′-(trimethylsilyl)diphenylmethane)tricarbonylchromium(0) (150 mg, 0.4 mmol; 4%), mp 123 °C. Anal. Calcd for $C_{19}H_{20}CrO_3Si$: C, 60.6; H, 5.3. Found: C, 60.4; H, 5.4.

4-(Trimethylsilyl)diphenylmethane (1.7 g, 7.1 mmol), $Cr(CO)_6$ (4.4 g, 20 mmol), dibutyl ether (100 mL), and THF (10 mL) were heated under reflux in a nitrogen atmosphere for 48 h. After filtration the solution was cooled in a refrigerator overnight. Yellow crystals precipitated and were recrystallized from ether/petroleum ether to give (4-(trimethylsilyl)diphenylmethane)bis(tricarbonylchromium(0)) (2 g, 3.9 mmol; 55%), mp 144 °C. Anal. Calcd for $C_{22}H_{20}Cr_2O_6Si$: C, 51.6; H, 3.9. Found: C, 51.5; H, 4.1.

Synthesis of (α-(Trimethylsilyl)diphenylmethane)bis(tricarbonylchromium(0)). (Diphenylmethane)bis(tricarbonylchromium(0)) (220 mg, 0.5 mmol) was dissolved in THF (4 mL) and was treated with potassium *tert*-butoxide (280 mg, 2.5 mmol) at 0 °C. After 5 min the solution was filtered and treated with anhydrous hexane to precipitate the anion **4**. After decantation and removal of liquid by using a syringe, the anion was redissolved in THF (6 mL). Immediately, chlorotrimethylsilane (1 mL) was added and the initially orange solution gradually became yellow. After 30 min the reaction was quenched with water. After ether extraction and removal of solvent in vacuo, the crude residue was chromatographed on a silica gel column and was eluted with ether/petroleum ether (3:2) to give yellow crystals of (α-(trimethylsilyl)diphenylmethane)bis(tricarbonylchromium(0)) (30 mg, 0.06 mmol), mp 168 °C. Anal. Calcd for $C_{22}H_{20}Cr_2O_6Si$: C, 51.6; H, 3.9. Found: C, 51.8; H, 3.8. Some starting material, viz. $(PhCH_2Ph)[Cr(CO)_3]_2$, was also recovered (80 mg); the global yield of the α-silylated complex was thus 19%.

Generation of the Anions for the NMR Study. Freshly distilled THF was added to a mixture of the appropriate complex and a 5-fold quantity of potassium *tert*-butoxide at 0 °C. (For the two monocomplexed compounds this was done at −30 °C since their anions are thermally sensitive.) After stirring for 5 min the anion was filtered directly into the NMR tube and sealed in vacuo. The anions were kept frozen in liquid nitrogen until required for the NMR studies. The data pertaining to the anions listed in Table I were obtained at −40 °C except where stated.

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Registry No. 4, 32823-67-9; **4⁻**, 75983-29-8; **6**, 86969-84-8; **6⁻**, 86969-78-0; **7**, 86969-82-6; **7⁻**, 86969-79-1; **8**, 86969-83-7; **8⁻**, 86969-80-4; **9**, 86969-85-9; **9⁻**, 86969-81-5; 4-chlorobenzophenone, 134-85-0; 4-chlorodiphenylmethane, 831-81-2; 4-(trimethylsilyl)diphenylmethane, 17964-29-3.

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Sapphyrins: Novel Aromatic Pentapyrrolic Macrocycles

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Abstract: Sapphyrins are pentapyrrolic macrocycles containing one direct link and four bridging methine groups between the five pyrrolic subunits. The syntheses of decamethylsapphyrin, other peripherally alkylated derivatives, and metal complexes are described. The physical and chemical properties of sapphyrins show them to be aromatic like porphyrins and corroles. This aromaticity is reflected in the large shielding of the methine and deshielding of the NH protons in the NMR spectra and by their optical spectra, which exhibit Soret and visible bands similar to porphyrins but all bathochromically shifted.

The chemistry described here was performed under the guidance and encouragement of the late R. B. Woodward and began two decades ago following a report by Johnson and Price[1] claiming the synthesis of metallocorroles (**1**). These complexes were supposedly prepared by treating the palladium complex of 5,5″-bi(5′-bromo-3,3′-diethyl-4,4′-dimethyldipyrromethene) (**2**), originally prepared by Fischer and Stachel,[2] with formaldehyde and hydrochloric acid in refluxing ethanol. However, it was shown that this reaction gave the metallooxocorroles (**3**) instead.[3] Since the original claim for a corrole synthesis had not been fulfilled, Woodward and Bauer directed their efforts toward such a synthesis

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