Crystal and Molecular Structure of Methyltri(*p*-nitrophenoxy)phosphonium Chloride. Evidence for Hydrogen Bonds with a Methyl Group as Hydrogen Donor

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Abstract: The structure of methyltri(*p*-nitrophenoxy)phosphonium chloride has been determined by X-ray diffraction methods on a single crystal of symmetry $P\bar{1}$. There are two formula weights of the title compound, two molecules of *p*-nitrophenol, and one molecule of benzene in a unit cell having the parameters a = 11.940 (3) Å, b = 12,600 (3) Å, c = 10.471 (2) Å, α = 108.26 (2)°, β = 95.42 (3)°, γ = 84.58 (3)°. The structure was solved by direct methods and refined to $R = \Sigma|F_o| - |F_c|/\Sigma F_o = 0.077$ for 4382 reflections. The *p*-nitrophenol molecule has a strong O-H···Cl$^-$ hydrogen bond. Short nonbonding C-H···Cl$^-$ distances of 3.440 and 3.490 Å and C-H···O distances of 3.312 Å suggest the role of the methyl group as a proton donor.

Introduction

In a study of disproportionation among aryloxyphosphoranes, Sigal and Westheimer[1] obtained a compound of the empirical formula $CH_3P(OC_6H_4NO_2)_3{}^+Cl^-{\cdot}HOC_6H_4NO_2$ (I) from the reaction of CH_3PCl_2 and *p*-nitrophenol. The molecule of *p*-nitrophenol could not be removed by repeated recrystallization. This determination of crystal structure was undertaken to establish the connection between the molecule of *p*-nitrophenol and the salt, and the reason for the remarkable stability of the adduct.

Experimental Section

$CH_3P(OC_6H_4NO_2)_3{}^+Cl^-$ was prepared as described by Sigal and Westheimer.[1] Suitable crystals, which had approximate dimensions 0.3 × 0.3 × 0.3 mm, were obtained by recrystallization from CH_3CN/C_6H_6 solution. After the solvent was removed the surface of the crystals broke down rapidly, probably because of evaporation of the included solvent, but the thin layer that was destroyed apparently protected the rest of the crystal.

The crystals have triclinic symmetry, space group $P\bar{1}$. The unit cell, which has the parameter a = 11.940 (3) Å, b = 12.600 (3) Å, c = 10.471 (2) Å, α = 108.26 (2)°, β = 95.42 (3)°, γ = 84.58 (3)°, contains two molecules of 1, two molecules of *p*-nitrophenol, and one molecule of benzene. The solvent molecule was located in a difference-Fourier map, and when included yielded a calculated density of 1.51 g/cm^3. The data were measured on a Syntex $P2_1$ diffractometer (Cu Kα 1.541 78 Å) in the θ-2θ mode in the range $3.0° \leq 2\theta \leq 135°$ at scan speeds of 2.93-29.30°/min, depending on the intensity of the reflection. Lorentz and polarization factors were applied, but no absorption correction was made (μ = 21.56 cm^{-1} for Cu Kα radiation). After reduction of the data, 4382 independent reflections ($I \geq 2\sigma(I)$) were retained for the refinement of the structure.

All nonhydrogen atoms of the phosphonium salt could be located by direct methods (MULTAN 78).[2] A molecule of benzene was found at one of the symmetry centers. The hydrogen atoms could be clearly located in a difference Fourier synthesis and, together with isotropic temperature factors, were included in the refinement. For all other atoms anisotropic temperature factors were introduced. After several cycles, the refinement converged to a final value of R = 0.077. In the last cycle of the refinement for all parameters the shift divided by the standard deviation was smaller than 0.02. A final difference synthesis displayed no peak >0.53 e Å^{-3}.

Results

The atomic coordinates are shown in Tables I and II using the labeling scheme indicated in Figure 1.[3] Bond lengths and angles are given in Tables III and IV. Figure 3[3] provides a stereoview of the cation.

The salt crystallizes together with one molecule of *p*-nitrophenol and one-half molecule of benzene per formula weight (Figure 2).[3] The phenol hydrogen atom forms a strong hydrogen bond to the chloride ion (O···Cl 3.015 (5) Å, OH 0.82 (4) Å, H···Cl 2.19 Å). In addition there are certain short nonbonding distances, indicating the presence of i and ii hy-

Table I. Fractional Atomic Coordinates ×10^4

atom	x	y	z
P	3216(1)	1707(1)	8975(1)
Cl	5822(1)	−564(1)	7531(1)
C(1)	4500(3)	1654(3)	9851(4)
O(1)	2787(2)	533(2)	8216(2)
C(11)	2460(3)	−291(3)	8747(3)
C(12)	1765(4)	−21(3)	9783(4)
C(13)	1408(4)	−877(3)	10 175(4)
C(14)	1746(3)	−1964(3)	9493(4)
C(15)	2446(3)	−2234(3)	8450(4)
C(16)	2822(3)	−1367(3)	8077(4)
N(1)	1294(3)	−2880(3)	9837(4)
O(5)	616(4)	−2637(3)	10 696(4)
O(6)	1615(3)	−3833(3)	9252(4)
O(2)	2215(2)	2342(2)	9809(3)
C(21)	2227(3)	3251(3)	11 026(3)
C(22)	1609(3)	4234(3)	10 987(4)
C(23)	1602(3)	5122(3)	12 160(4)
C(24)	2188(3)	4996(3)	13 291(4)
C(25)	2773(3)	3993(3)	13 332(4)
C(26)	2774(3)	3102(3)	12 160(4)
N(2)	2237(3)	5944(3)	14 551(4)
O(7)	1732(4)	6830(3)	14 517(4)
O(8)	2754(4)	5805(3)	15 541(3)
O(4)	5843(3)	939(2)	4885(4)
O(3)	3395(2)	2236(2)	7865(2)
C(31)	2611(3)	2365(3)	6819(3)
C(32)	2583(3)	1517(3)	5600(4)
C(33)	1874(3)	1670(3)	4571(4)
C(34)	1214(3)	2660(3)	4758(4)
C(35)	1258(4)	3506(4)	5975(5)
C(36)	1969(4)	3363(3)	7005(4)
N(3)	483(3)	2809(4)	3606(5)
O(9)	452(3)	2054(4)	2547(4)
O(10)	−54(3)	3716(4)	3755(5)
C(41)	5698(3)	1977(3)	5752(4)
C(42)	5051(4)	2822(3)	5404(5)
C(43)	4934(4)	3883(3)	6345(5)
C(44)	5464(3)	4067(3)	7576(5)
C(45)	6109(4)	3243(4)	7956(5)
C(46)	6223(4)	2193(4)	7043(5)
N(4)	5348(3)	5195(3)	8540(4)
O(11)	5949(3)	5428(3)	9587(3)
O(12)	4660(3)	5882(3)	8235(4)
C(51)	−272(4)	−273(4)	3630(5)
C(52)	834(4)	−626(4)	5491(5)
C(53)	569(4)	−899(3)	4142(5)

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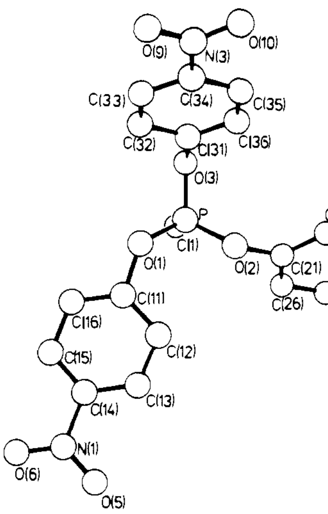
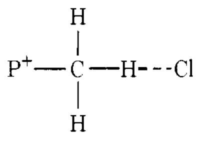


Figure 1. Labeling of atoms in methyltri(*p*-nitrophenoxy)phosphonium chloride.

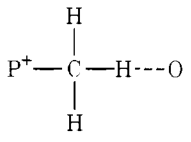
Table II. Hydrogen Coordinates $\times 10^3$

atom	*x*	*y*	*z*
H(101)	444(3)	149(3)	1062(4)
H(102)	475(3)	237(3)	1026(3)
H(103)	499(3)	128(3)	924(4)
H(12)	150(4)	64(4)	1016(5)
H(13)	92(4)	−75(4)	1094(5)
H(15)	270(5)	701(5)	797(6)
H(16)	325(3)	−151(3)	741(4)
H(22)	120(4)	419(4)	1007(5)
H(23)	118(5)	584(5)	1188(5)
H(25)	309(3)	393(3)	1418(4)
H(26)	323(4)	251(4)	1235(5)
H(4)	542(4)	78(4)	419(5)
H(32)	299(5)	85(5)	546(6)
H(33)	183(4)	119(4)	378(5)
H(35)	86(6)	410(6)	657(7)
H(36)	220(5)	389(4)	778(6)
H(42)	479(4)	264(4)	447(5)
H(43)	444(6)	461(6)	594(6)
H(45)	622(4)	341(4)	888(5)
H(46)	668(4)	166(4)	718(5)
H(51)	−52(3)	−46(3)	267(4)
H(52)	139(4)	−104(4)	582(5)
H(53)	96(4)	−150(4)	336(5)



$$P^{+}\text{—}CH_2\text{—}H\text{---}Cl$$

i



$$P^{+}\text{—}CH_2\text{—}H\text{---}O$$

ii

drogen bonds (Table V). This indication is strongly supported by the fact that the molecule makes no use of the freedom to increase the H···Cl and H···O distances by rotating the CH_3 group by approximately 60° around the P-C(1) axis. Instead the C-H···Cl and C-H···O angles are not far from 180° (Table V). A final remarkably short nonbonding distance is noticed: C(26)···Cl 3.560 (7), H(26)···Cl 2.63 Å.

The suggested hydrogen bonds are displayed in Figure 2, showing that the molecules participate in an extended intermolecular hydrogen bonded network.

The C_{methyl}-P-O-C_{Ph} torsion angles are C(1)-P-O(1)-C(11) 66°, C(1)-P-O(2)-C(21) 90°, and C(1)-P-O(3)-C(31) 174°.

Table III. Bonds Lengths (Å)

O(1)-P	1.553(2)	O(2)-P	1.553(3)
C(1)-P	1.718(4)	O(3)-P	1.549(3)
C(11)-O(1)	1.421(5)	C(12)-C(11)	1.367(6)
C(16)-C(11)	1.366(5)	C(13)-C(12)	1.381(7)
C(14)-C(13)	1.374(5)	C(15)-C(14)	1.375(6)
N(1)-C(14)	1.471(6)	C(16)-C(15)	1.394(7)
O(5)-N(1)	1.214(6)	O(6)-N(1)	1.209(4)
C(21)-O(2)	1.422(4)	C(22)-C(21)	1.390(5)
C(26)-C(21)	1.357(6)	C(23)-C(22)	1.378(5)
C(24)-C(23)	1.363(6)	C(25)-C(24)	1.396(5)
N(2)-C(24)	1.477(5)	C(26)-C(25)	1.380(5)
O(7)-N(2)	1.227(5)	O(8)-N(2)	1.207(6)
C(41)-O(4)	1.345(4)	C(31)-O(3)	1.412(4)
C(32)-C(31)	1.384(4)	C(26)-C(31)	1.378(5)
C(33)-C(32)	1.357(6)	C(34)-C(33)	1.381(6)
C(35)-C(34)	1.382(6)	N(3)-C(34)	1.471(6)
C(36)-C(35)	1.355(7)	O(9)-N(3)	1.213(6)
O(10)-N(3)	1.229(7)	C(42)-C(41)	1.378(6)
C(46)-C(41)	1.391(6)	C(43)-C(42)	1.393(5)
C(44)-C(43)	1.343(7)	C(45)-C(44)	1.371(6)
N(4)-C(44)	1.465(5)	C(46)-C(45)	1.372(6)
O(11)-N(4)	1.222(5)	O(12)-N(4)	1.231(6)
C(53)-C(51)	1.390(7)	C(53)-C(52)	1.359(7)
C(52)-C(51)′	1.378(12)		

Table IV. Bond Angles (deg)

O(2)-P-O(1)	103.9(1)	C(1)-P-O(1)	113.4(2)
C(1)-P-O(2)	116.7(2)	O(3)-P-O(1)	105.6(1)
O(3)-P-O(2)	110.4(1)	O(3)-P-C(1)	106.5(2)
C(11)-O(1)-P	129.3(2)	C(12)-C(11)-O(1)	121.7(3)
C(16)-C(11)-O(1)	114.8(3)	C(16)-C(11)-C(12)	123.3(4)
C(13)-C(12)-C(11)	118.5(3)	C(14)-C(13)-C(12)	118.9(4)
C(15)-C(14)-C(13)	122.5(4)	N(1)-C(14)-C(13)	118.9(4)
N(1)-C(14)-C(15)	118.5(3)	C(16)-C(15)-C(14)	118.4(3)
C(15)-C(16)-C(11)	118.4(4)	O(5)-N(1)-C(14)	118.2(3)
O(6)-N(1)-C(14)	118.5(4)	O(6)-N(1)-O(5)	123.4(5)
C(21)-O(2)-P	129.1(2)	C(22)-C(21)-O(2)	116.7(3)
C(26)-C(21)-O(2)	119.3(3)	C(26)-C(21)-C(22)	123.9(3)
C(23)-C(22)-C(21)	117.6(4)	C(24)-C(23)-C(22)	119.0(4)
C(25)-C(24)-C(23)	123.0(3)	N(2)-C(24)-C(23)	120.4(3)
N(2)-C(24)-C(25)	116.5(3)	C(26)-C(25)-C(24)	118.0(4)
C(25)-C(26)-C(21)	118.5(3)	O(7)-N(2)-C(24)	116.8(4)
O(8)-N(2)-C(24)	119.0(3)	O(8)-N(2)-O(7)	124.2(4)
C(31)-O(3)-P	127.5(2)	C(32)-C(31)-O(3)	118.5(3)
C(36)-C(31)-O(3)	119.1(3)	C(36)-C(31)-C(32)	122.2(3)
C(33)-C(32)-C(31)	118.4(3)	C(34)-C(33)-C(32)	119.7(3)
C(35)-C(34)-C(33)	121.4(4)	N(3)-C(34)-C(33)	118.1(3)
N(3)-C(34)-C(35)	120.5(4)	C(36)-C(35)-C(34)	119.3(4)
C(35)-C(36)-C(31)	119.0(3)	O(9)-N(3)-C(34)	119.5(5)
O(10)-N(3)-C(34)	117.8(4)	O(10)-N(3)-O(9)	122.7(5)
C(42)-C(41)-O(4)	122.3(4)	C(46)-C(41)-O(4)	118.2(4)
C(46)-C(41)-C(42)	119.5(3)	C(43)-C(42)-C(41)	119.7(4)
C(44)-C(43)-C(42)	119.3(4)	C(45)-C(44)-C(43)	122.4(4)
N(4)-C(44)-C(43)	118.4(4)	N(4)-C(44)-C(45)	119.2(4)
C(46)-C(45)-C(44)	118.8(4)	C(45)-C(46)-C(41)	120.2(4)
O(11)-N(4)-C(44)	119.5(4)	O(12)-N(4)-C(44)	117.9(4)
O(12)-N(4)-O(11)	122.6(3)	C(52)-C(53)-C(51)	120.3(4)
C(53)-C(51)-C(52)′	119.1(4)	C(53)-C(52)-C(51)′	120.6(4)

The bond lengths and angles in the *p*-nitrophenoxy groups are well within the expected range if compared, for example, with those for tris(*p*-nitrophenyl) phosphate.[4] The average P-O distance in I (1.552 Å) is shorter than in the phosphate (1.572 Å). That and the greater mean P-O-C angle of 128.6° compared with 123.5° in the phosphate are probably due to the fact that the phosphorus atom in I, because of its formal positive charge, can make better use of its d orbitals in dπ-pπ interactions with the oxygen atoms than can the phosphorus atom in a phosphate.

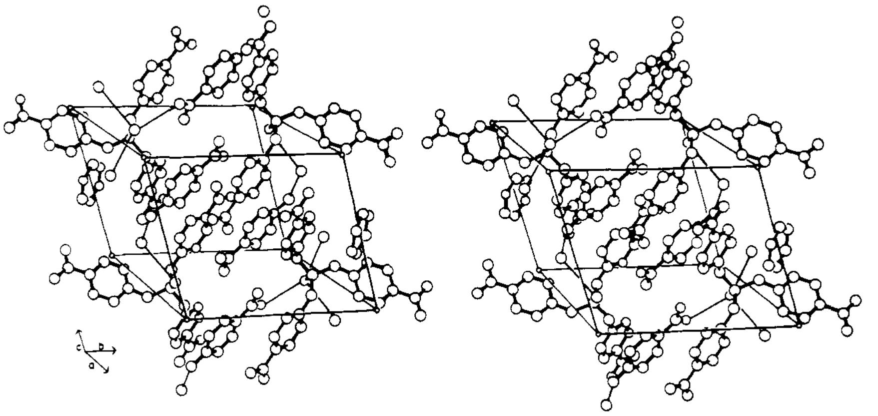


Figure 2. Stereoview of the unit cell. The long thin lines represent hydrogen bonds.

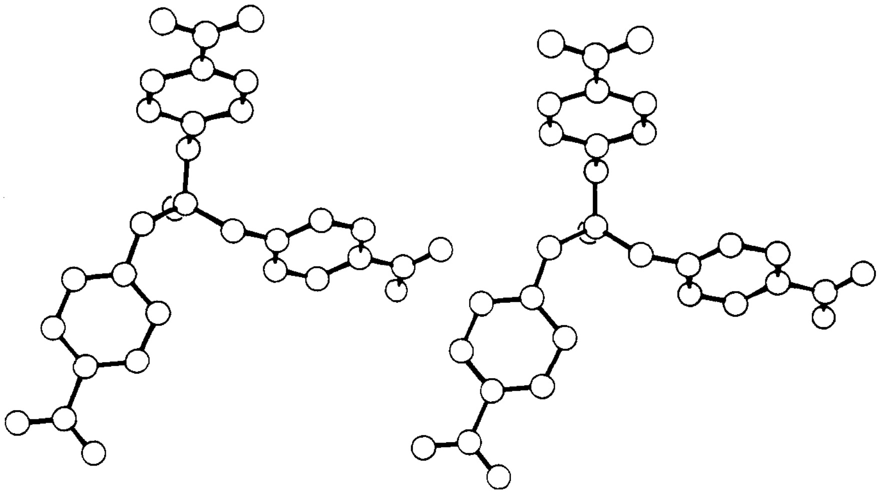


Figure 3. Stereoview of the molecule.

Table V. Hydrogen Bonds (Å)

	D-H···A[a,c]	$b_{DH} + r_H + r_A$[a,b]	Δ	H···A[a,c]	$r_H + r_{CL}$[b]	Δ
O(4)-H(4)···Cl	3.010	3.95	0.95	2.19	2.95	0.76
C(1)-H(101)···Cl	3.494	4.05	0.56	2.61	2.95	0.34
C(1)-H(103)···Cl	3.440	4.05	0.61	2.62	2.95	0 33
C(1)-H(102)···O(12)	3.312	3.82	0.51	2.39	2.72	0.33
C(26)-H(26)···Cl	3.560	4.05	0.49	2.63	2.95	0.32

[a] D = hydrogen donor, A = hydrogen acceptor. [b] *b* = bond lengths, *r* = van der Waals radii, Cl = 1.75, O = 1.52, H = 1.20.[15] In the X-ray structure, the observed bond lengths to hydrogen are generally shorter than the accepted C-H bond distance of 1.10 and the accepted O-H distance of 1.00; the latter values were here assumed as correct. [c] Observed values.

The P-C(1) bond distance of 1.718 (4) Å is very short if compared, for example, with the corresponding values in $CH_3P(C_6H_5)_3^+$ (1.825 (15) Å[5] or in CH_3PF_4 (1.780 (5) Å,[6] electron diffraction study). It is intermediate between these values and that for a formal P=C double bond, as in $(C_6H_5)_3P{=}CH_2$ (P=C 1.661 (8) Å).[7] The average C-P-O angle of 113.2° is significantly larger than the O-P-O angle of 106.6°.

The C-OH bond length in the *p*-nitrophenol molecule is considerably shorter than the comparable C-O bonds in the *p*-nitrophenoxy groups (1.345 compared with 1.417 Å) but is similar to the corresponding value in crystalline *p*-nitrophenol.[8,9]

The dihedral angles between the planar $C\text{-}NO_2$ groups and the attached phenyl rings are 4.7, 2.2, 2.9 and, 9.9°. The variation in these angles is probably due to packing effects.

Discussion

The most interesting feature of the crystal structure of I is without doubt the simultaneous enclosure of *p*-nitrophenol and benzene in the crystal. Probably the main reason is the very favorable packing which is made possible by this molecular arrangement. Some of the aromatic planes are nearly parallel (Figure 2); the angle between ring III [C(31)-C(36)] and IV [C(41)-C(46)] is 8.8°, between ring IV and II [C(21)-C(26)] 4.9°. In addition the *p*-nitrophenol ring is bound to the salt by a strong OH···Cl bond and a weak C-H···O bond.

In contrast the benzene molecule has no specific interactions with neighboring molecules (the closest intermolecular contact, H(51)···O(1), is 2.78 Å) and evaporates after removal of the solvent.

The other fascinating aspect of the crystal structure of the title compound is the hydrogen-bond network. Whereas X_3CH

groups as proton donors are found frequently, e.g., in CHCl$_3$,[10–12] the role of methyl groups as proton donors for hydrogen bonds is controversial. They were postulated by Sutor[13] for 1,3,7,9-tetramethyluric acid and caffeine, where C-H···O distances of 3.00 and 3.24 Å and C-H···O angles of 120.8 and 109.1° were observed. In contrast, the C-H···Cl and C-H···O groups of the title compound are nearly linear.

Recently methylene-hydrogen···O hydrogen bonds were found in Cl$_2$(O)PCH$_2$P(O)Cl$_2$.[14] The methyl group in I, however, differs from those in most methyl compounds; it is highly activated because it is bound directly to a phosphorus atom with a formal positive charge; furthermore, the phosphorus atom is additionally bound to three strongly electron-withdrawing groups. The strong influence that this environment exerts at phosphorus can also be seen in the extraordinarily short P-C(1) bond, one of the shortest phosphorus-carbon single bonds so far determined.

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Supplementary Material Available: Temperature factors and structure factor listing (26 pages). Ordering information is given on any current masthead page.

References and Notes

(1) I. S. Sigal and F. H. Westheimer, *J. Am. Chem. Soc.*, submitted.
(2) MULTAN: G. Germain, P. Main, and M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(3) Drawings were obtained using ORTEP-II: C. K. Johnson, "ORTEP-II, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Oak Ridge National Laboratory Report ORNL-5138 (1976).
(4) M. Ul. Haque and C. N. Caughlan, *Acta Crystallogr., Sect. B*, **26**, 1528 (1970).
(5) F. Sanz and J. J. Daly, *J. Chem. Soc., Perkin Trans. 1*, 1141 (1975).
(6) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).
(7) J. C. J. Bart, *J. Chem. Soc. B*, 350 (1969).
(8) P. Coppens and G. M. J. Schmidt, *Acta Crystallogr.*, **18**, 62 (1965).
(9) P. Coppens and G. M. J. Schmidt, *Acta Crystallogr.*, **18**, 654 (1965).
(10) G. C. Pimentel and A. L. McClellan, *Annu. Rev. Phys. Chem.*, **22**, 347 (1971).
(11) R. D. Green, "Hydrogen Bonding by C-H Groups", Macmillan, New York, 1974, pp 53–109.
(12) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand-Reinhold, Princeton, N.J., 1971.
(13) D. J. Sutor, *Nature (London)*, **195**, 68 (1962).
(14) W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 943 (1975).
(15) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

The Trindene Trianion

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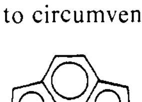
Abstract: The lithium salt of the trindene trianion (**6**) is synthesized in four steps from cyclopentanone. Bromination and debromination, as summarized in Scheme III, convert trindane (octahydro-1*H*-trindene, **14**) into the dihydro-1*H*-trindenes, **16a** and **16b**, and these with *n*-butyllithium in tetrahydrofuran give **6**. The formation of the trianion is evidenced by quenching with deuterated water yielding the required trideuterio derivatives of **16a,b**. When only 2 mol of *n*-butyllithium is used, the dianion **18** forms instead, as evidenced by reaction with deuterated water yielding molecules of **16a,b** containing two allylic deuterium atoms. Sandwich molecules, assigned structures **19a,b**, containing two irons, are produced when the dianion is combined with ferrous chloride, and only traces of sandwiches containing three iron atoms (presumably **9** with M = Fe) are detected in the corresponding reaction product of **6**. A product hoped for, polymer **5**, could not be identified. The trindene trianion, although it contains multiple charges in one π-electron system, is a favorable species because its rings are all five and six membered, because its highest occupied molecular orbital is low in energy, and because its lowest unoccupied molecular orbital is high in energy.

Introduction

With proper control of the hydrocarbon, it should be possible to circumvent the tendency of ions like **1**,[1] **2**,[2] and **3**,[3] when mixed with transition-metal salts, from giving dimers like **4** (here M is the metal) rather than the novel polymeric structures **5**. One way is to cause the hydrocarbon to react with metals on opposite faces, at b rather than a in Scheme I, a possibility considered in another publication.[4] The other is to constrain the hydrocarbons bonded by the metals to anti conformations, in which dimerization is impossible whether the metals attach to the same or to opposite faces of a one ring system (Scheme II), a possibility considered here.



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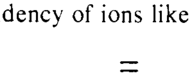

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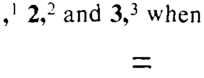

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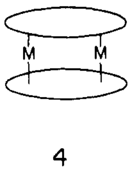

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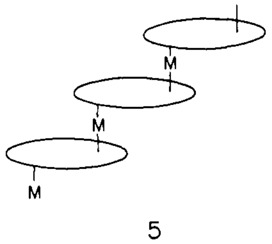

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At first the means by which the hydrocarbons could be strapped together appropriately appeared obscure and the task seemed formidable, but motivating the work below was the thought that the trindene trianion, **6**, could provide a simple

Scheme I