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Dibenzouranocene and Related Compounds

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Bis(benzo[8-annulene])uranium(IV) (dibenzouranocene), 4, and the thorium analogue 5 have been prepared from benzocyclooctatetraene dianion and the metal tetrachlorides. The Diels–Alder product from cyclooctatrienyne and butadiene, 7,10-dihydrobenzocyclooctatetraene, 2, gave a uranocene derivative, 6, which could not be dehydrogenated to 4. Catalytic hydrogenation, however, did gave the uranium derivative 7 of tetrahydrobenzocyclooctatetraene. The corresponding deuterogenation gave 70% exo and 30% endo incorporation of deuterium. Reaction of cyclooctatetraene dianion with 1,4-dibromobutane gave *cis*-bicyclo[6.4.0]dodeca-2,4,6-triene, 8, which on deprotonation with KNH_2/NH_3 and treatment with UCl_4 also gave 7. Analysis of NMR spectra of 4 indicates a spin density distribution closely related to that in the radical anion of benzocyclooctatetraene. The ligand exchange equilibrium between 4 and uranocene has been determined and found to favor the mixed-sandwich compound.

The nature of the bonding in uranocenes has been a matter of interest and controversy for some years.[2] Structural data fit an ionic model,[3,4] but photoelectron spectra,[5] NMR studies,[6] $X\alpha$ calculations,[7] and Mössbauer spectroscopy[8] suggest substantial covalency. A large number of substituted uranocenes have been prepared for such studies, but most substituents (e.g., alkyl groups) constitute a relatively small perturbation of the electronic system of the [8]annulene ring. For this reason the benzo[8]annulene system is of special interest; in the benzocyclooctatetraene radical anion, for example, a substantial fraction of the spin density is delocalized into the benzene ring.[9] In this paper we report the preparation of benzo[8]annulene sandwich compounds of uranium and thorium, some related compounds, some aspects of their chemistry, and spectral characterization.

Benzocyclooctatetraene, 1, has been prepared several times, but none of the reported syntheses is satisfactory. Wittig's original preparation, for example, gave an overall yield of less than 0.01%.[10] Similarly, other preparations were not considered as practical syntheses.[11-16] The most promising route appeared to be that of Elix and Sargent[17] involving dehydrogenation of 7,10-dihydrobenzocyclooctatetraene, 2, derived from trapping with butadiene the cyclooctatrienyne intermediate produced by reaction of bromocyclooctatetraene with potassium *tert*-butoxide. Unfortunately, a number of attempts to repeat their preparation, even with the help of personally communicated additional experimental details,[18] gave principally *tert*-butoxycyclooctatetraene. It was clear that in our hands the intermediate reacted with the *tert*-butoxide ion rather than undergoing the Diels–Alder reaction with butadiene. Fortunately, when potassium *tert*-butoxide was replaced with sodium amide, we obtained the desired adduct in yields of about 50%. Oxidation of 2 with dichlorodicyanobenzoquinone (DDQ) proceeded normally to give benzocyclooctatetraene in 85% yield.

The dianion of 1 has been described.[19,20] Benzo[8]-annulene dianion, 3, is produced by reduction of 1 with potassium or potassium naphthalide in THF. The reaction of 3 with uranium tetrachloride, however, did not follow the usual course. Generally, all cyclooctatetraene (COT) dianions that form a uranocene react immediately to give an intense green color. In this case, however, the initial result was a dark muddy gray color, which turned to a dark purple after 2 days at 60 °C. Repeated extraction of the purple material with THF gave a 20% yield of the desired dibenzouranocene. The remaining 80% of the uranium remained incorporated in a purple-insoluble mass that analyzed as UCl_3 plus about 5% of organic material. Clearly, extensive reduction had taken place.

Dibenzouranocene, 4, exhibits some other unusual properties. Unlike the usual four-band cascade at about 620 nm typical of uranocenes, the spectrum of 4 shows only a broad absorption at 624 nm with a single shoulder at 650 nm. The compound is much less soluble than most substituted uranocenes and is more like uranocene itself. Moreover, the compound has a low-temperature coefficient of solubility that makes recrystallization difficult. Nevertheless, crystals suitable for X-ray analysis were obtained by slow crystallization.[21] An important feature of the resulting structure is the location of the uranium centered between the [8]annulene rings despite the almost eclipsed structure of the benzo substituents. In an ion triplet model

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(1) National Science Foundation Postdoctoral fellow, 1980.

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Table I. ^{1}H NMR Spectra (δ)

positn	3[a]	5	4[b,c]	6[d-f]	7[e,g]	11[d,h]
1	6.610	6.738	−48.87	−30.37	−30.83	−48.00
2	6.258	6.283	−19.38	−33.17	−32.71	−16.81
3	5.892	5.984	−24.80	−39.11	−38.82	−23.27
7	7.692	7.756	−10.57	−20.99 (endo) 14.73 (exo)	−22.52 (endo) −3.31 (exo)	−11.56
8	6.067	7.016	−12.69	−8.49	−16.68 (endo) +6.18 (exo)	−13.67

[a] Reference 19. [b] 30 °C. [c] Assignment of 1, 2, and 3 based on spin decoupling; assignment of 7 and 8 based on analysis of contact and pseudocontact components (see text). [d] At 27 °C. [e] The [8]annulene resonances are not assigned to specific positions. [f] $J(7, 7) = 17.09$ Hz. [g] At 29 °C. [h] COT ring, δ −37.51. Other assignments are by analogy to 4.

with U^{4+} between two rings of **3**, the uranium would be expected to lie about 0.3–0.4 Å away from the axis joining the midpoints of the two octagonal rings toward the benzenes. Thus, the observed results provide some structural evidence for significant ring–metal covalency in **4**. This argument is based on the assumption that the cation in an ionic structure would occupy the electrostatic minimum. The observed central location is also preferred sterically.

In a similar manner bis(benzo[8]annulene)thorium(IV), **5**, was also prepared in a poor yield of 20%. The product was obtained by extraction as large thin orange plates.

Reduction of the Diels–Alder adduct **2** also gave a dianion which on reaction with UCl_4 formed the uranocene derivative **6** in a normal fashion. Attempted dehydrogenation to **4** by oxidation yielded only uranium salts and recovered neutral ligand. Hydrogenation of **6**, however, did proceed normally to yield bis(tetrahydrobenzo[8]-annulene)uranium, **7**, in 60% yield. Use of deuterium gave the corresponding deuterium compound which by NMR analysis showed the deuterium to be incorporated 70% exo and 30% endo. This constitutes the first stereoselective reaction on a uranocene. The low selectivity shows that the other ring provides only a minor steric barrier to reaction, perhaps because of conformational twisting of the alicyclic ring.

Authentic **7** was prepared by the route used previously to prepare dicyclopentenouranocene.[22] Reaction of the dilithium adduct of COT with 1,4-dibromobutane in liquid ammonia gave 28% of *cis*-bicyclo[6.4.0]dodeca-2,4,6-triene, **8**. This compound was deprotonated with KNH_2/NH_3, and the resulting dianion **9** was treated with UCl_4 to yield **7**.

The reactions are summarized in Scheme I.

Scheme I

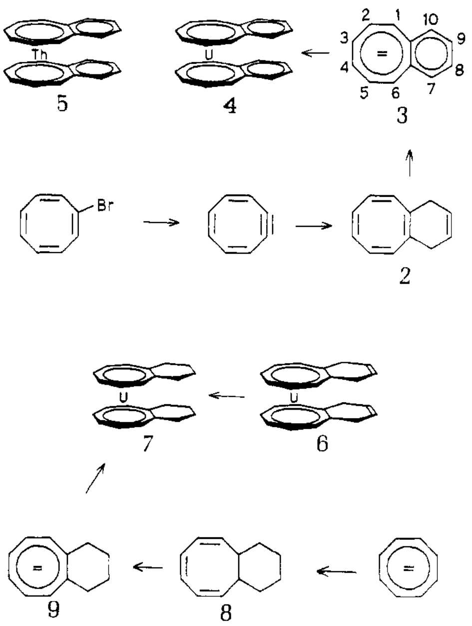

Table II. Coupling Constants in ^{1}H NMR Spectra

J_{ij}, Hz	3	5
1, 2	11.86	13.6
1, 3	0.11	0.1
1, 4	−0.35	−0.4
1, 5	0.10	0.1
1, 6		0.0
2, 3	11.21	13.2
2, 4	0.66	0.7
2, 5	−0.20	−0.2
3, 4	10.22	11.0
7, 8	8.51	8.2
7, 9	1.55	1.3
7, 10	0.47	0.5
8, 9	5.80	5.5

NMR Spectra. Analysis of the ^{1}H NMR spectrum of the thorium compound **5**, as summarized in Tables I and II, yields the essential features of that previously reported[19,20] for the dipotassium salt of the dianion **3** with two notable differences. The chemical shift of the β-protons (H8 and H9) of the benzene ring in **5** is about 1 ppm downfield from that of the dianion **3** and suggests removal of electron density from this periphery of the ring system. Other chemical shift changes are relatively small, but the vicinal coupling constants in the [8]annulene ring, $J(1,2)$, $J(2,3)$, and $J(3,4)$ (Table II), are all significantly higher for the thorium compound. These changes also suggest an increase in the electron population of the 8-membered ring. These results are consistent with the thorium compound **5** being isostructural with the uranium system **4**. Even in a covalent model the rings and the central metal are highly charged; thus, the high positive charge of the centrally located thorium pulls electrons from the periphery of the benzene portion into the [8]annulene ring. We note also that the vicinal couplings in the benzene ring are still consistent with aromatic character for the [8]annulene ring according to Gunther's criterion.[23]

The uranium compound **4** is paramagnetic, and the ^{1}H NMR spectrum shows the large contact and pseudocontact shifts typical of uranocenes.[6] NMR absorption peaks of uranocenes are usually so broad that couplings are obscured; however, in the case of **4** some such couplings were observed that permitted assignments of chemical shifts by decoupling experiments. For the 8-membered ring, irradiation at each resonance gave distinct narrowing of bands

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Table III. Analysis of NMR Spectrum of 4 (30 °C)

positn	δ	isotropic shift[a]	$10^2 G_i$, cm^{-1}	pseudocontact shift[c]	contact shift	α[d]
1	−47.88	−54.6	−2.34	−8.3	−46	0.183
2	−18.94	−25.2	−2.34	−8.3	−17	0.082
3	−24.28	−30.3	−2.34	−8.3	−22	0
7	−10.57	−18.3	−5.05	−17.9	0	0.019
8	−12.69	−19.7	−3.68	−13.1	−7	0.082

[a] Based on NMR of 5 as the diamagnetic reference. [b] Geometric factor = $(3 \cos^2 \theta - 1)/R^3$ using structure 4.[21] [c] Calculated from G_i.[6] [d] Hfsc from ESR spectrum of radical anion of 1.[9]

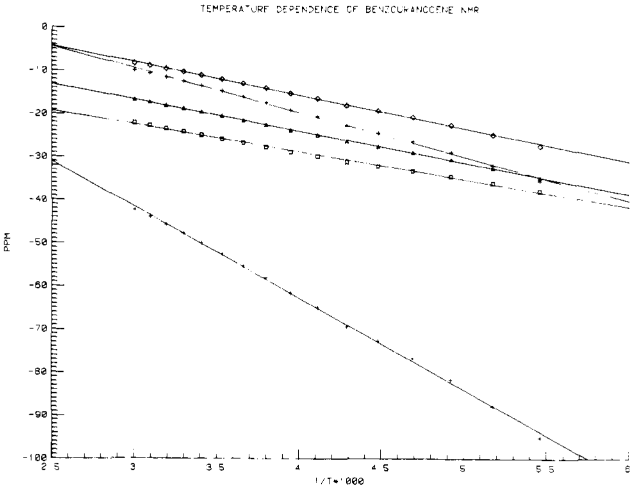


Figure 1. Linear dependence of chemical shifts of 4 with $\delta = a/T + b$. Values of a and b for positions assigned in Tables I and III are, respectively: 1, −2118, 22.06; 2, −7295, 5.13; 3, −6364, −3.32; 7, −7657, 14.72; 8, −10 250, 21.19.

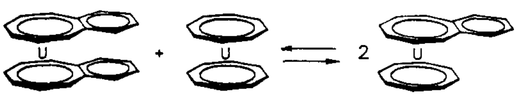
for the adjacent hydrogens. The changes in the benzo ring, however, were at the threshold of detection, and the hydrogens were assigned by the following argument.

The pseudocontact shift for uranocene has been estimated to be about −8 ppm on the basis of calculated geometric factor ($G_i = [3 \cos^2 \theta - 1]/R^3$) = -2.34×10^{21} cm^{-3} and $\mu_{\parallel}{}^2 - \mu_{\perp}{}^2 = 12.5\ \mu_B{}^2$.[5] The geometry about the [8]annulene ring in 4 is essentially the same as in uranocene, and the same value of the pseudocontact shift should apply to all three positions, 1, 2, and 3 of 4. Consequently, the large differences in chemical shifts among these positions reflect the variations in contact shift resulting from the spin density distribution. If the electronic structure of 4 can be regarded as one in which electron density is donated from ligand dianion 3 to a central U^{4+}, the resulting spin polarization should give a spin density distribution in the ligand resembling that of the radical anion of benzocyclooctatetraene. The same picture emerges from an electronic structure derived from interaction of the u and g combinations of the HOMOs of two molecules of 3 and suitable f and d orbitals of U^{4+}. Accordingly, we expect a correlation between the contact shifts and the hyperfine splitting constant (hfsc) of the radical anion. The comparisons in Table III show an excellent parallelism between the two sets of numbers. The G_i value for the 8-proton (benzo β-position) has substantially lower magnitude than for the 7-proton (benzo α-position) reflecting its greater distance from uranium, yet the assigned hfsc is much greater for 8 than for 7. Best agreement is found for assigning the NMR values as given in Tables I and III; this assignment produces a small contact shift for the 7-proton and a substantially larger one for the 8-proton. From the ESR comparison, the spin density and the contact shift should be the same for postions 8 and 2. The smaller value found for 8 could indicate the same kind of electron depletion from the periphery deduced from the thorium compound 5 (vide supra).

The proton NMR spectra of 4 show the linear 1/*T* dependence of chemical shifts typical of uranocenes[6] (Figure 1).

The ^{1}H NMR spectrum of 6 shows three broad singlets typical of 1,2-disubstituted uranocenes. All of the protons in the alicyclic ring could be assigned by analogy with other uranocenes[6] and by considerations of the geometric factors (Table I). For example, the two doublets at −20.99 and 14.73 ppm are clearly the methylene protons and can be assigned as endo and exo, respectively, by analogy with dicyclobutenouranocene.[24] The large Δσ is dominated by the pseudocontact shift and the magic angle passes between these methylene protons. All of the resonances are linear in 1/T. The ^{1}H NMR spectrum of 7 (Table I) is not as straightforward to assign because of the various possible conformations of the six-membered ring and their different geometric factors. However, the deuterogenation experiment (vide supra) marks the β-hydrogens, and for both the α- and β-positions the endo hydrogens are expected to be upfield of the exo hydrogens by considerations of geometric factors and by analogy with other related uranocenes. For this compound, however, some of the resonances are slightly nonlinear in *1/T*, perhaps because of conformational changes with temperature.[25]

Equilibrium of 4 with Uranocenes. We reported previously that uranocenes undergo rapid ligand exchange with cyclooctatetraene dianions.[26] This observation implies that two uranocenes will equilibrate their ligands in the presence of some dianion and led to the following experiment: a crystal of K_2COT was added to an NMR sample of 4 in 50:50 THF-d_8–toluene-d_8. The resulting mixture showed the NMR bands of 4 and uranocene **10** plus a series of bands ascribed to the mixed ring system **11**. The spectrum remained unchanged over several hours. Absolute concentrations could only be estimated (10^{-3} M) but only relative concentrations are required to evaluate the unitless equilibrium constant $K = [11]^2/[4][10]$ for the equilibrium:



4 10 11

The experimental value, *K* = 7.1, is significantly larger than the simple statistical value of *K* = 4. This result means that any attraction between the benzene rings in 4 is more than offset by steric effects. Consequently, the almost eclipsed structure[21] of crystalline 4 is clearly a resultant of crystal packing forces.

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This determination of the equilibrium constant is made possible by the large chemical shift range of uranocenes such that the NMR spectra of mixed-ring uranocenes are generally distinctly different from those of the homoring analogues. The determination of additional such equilibrium constants will undoubtedly provide valuable quantitative data concerning ring–ring interactions in metallocenes.

Experimental Section

Melting points and boiling points are uncorrected. Visible and UV spectra were obtained on a Cary 118 spectrophotometer; ^{1}H NMR spectra were obtained on JEOL FX90Q (90 MHz) and the Berkeley 180- and 250-MHz FT-NMR instruments; ^{13}C NMR spectra were also recorded on a Brucker WH-90/Nicolet FT (25.14-MHz) instrument. Mass spectra were obtained on a CEC-103 spectrometer at 70 eV. Analyses were performed by the Analytical Services Laboratory, University of California, Berkeley, CA. Tetrahydrofuran (THF) was dried by distilling from $LiAlH_4$ or sodium benzophenone ketyl. Cyclooctatetraene was obtained from BASF and used without further purification. All reactions requiring air-free conditions were conducted under an Ar atmosphere or in a Vacuum Atmospheres recirculating glovebox with solvents degassed prior to use.

Bicyclo[6.4.0]dodeca-1(8),2,4,6,10-pentaene, 2. To 300 mL of anhydrous THF saturated with about 60 g of 1,3-butadiene (Matheson) was added under nitrogen 6.0 g (33 mmol) of bromocyclooctatetraene[27] and 4.0 g (0.1 mol) of sodamide. The flask was tightly stoppered, and the mixture was stirred vigorously for 4 days. Because of the pressure involved, the apparatus was kept behind a shield. The reaction mixture was carefully quenched with 200 mL of water and 250 mL of ether. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. The residue was chromatographed on 100 g of silica gel; elution with hexane gave 2.5 g (50%) of 2 as an oil:[12,17] NMR ($DCCl_3$) δ 2.59 (s, 4 H), 5.72 (s, 2 H), 5.75 (s, 4 H), 5.86 (s, 2 H).[17]

Benzocyclooctatetraene, 1. A mixture of 50 mL benzene, 2.5 g of 2, and 4.0 g of dichlorodicyanobenzoquinone (DDQ, Aldrich) was stirred vigorously under reflux for 1 h. The cooled and filtered mixture was diluted with 100 mL of pentane and warmed with 0.1 g of activated charcoal. The cooled mixture was gravity filtered, and the solvent was evaporated to give 2.1 g (85%) of 1, mp 50–51 °C (lit. mp 50–51 °C,[10] 49.5–50 °C[17]).

Dibenzouranocene, 4. To a solution of 1.0 g (6.5 mmol) of benzocyclooctatetraene in 50 mL of dry THF was added 0.51 g (13 mmol) of potassium under argon. The mixture was stirred for 48 h to produce a homogeneous red-orange solution which was cannulated into a solution of 1.2 g of UCl_4 in 50 mL of dry THF contained in a uranocene reactor[28] attached to a vacuum line. The mixture was refluxed for 2 days, and the solvent was removed under vacuum. The reactor was transferred to a glovebox where the solid residue was washed with hexane (to remove neutral ligand) and extracted with THF.

The extract provided 0.35 g (20%) of extremely air-sensitive green powder; mp ~325 °C dec; λ_{max} 624 nm. The air sensitivity precluded combustion analysis, but the product was characterized by the ^{1}H NMR spectrum (Tables I and III) and an X-ray crystal structure.[21] An attempt was made to obtain a ^{13}C NMR spectrum, but the resonances could not be discerned: mass spectrum, base peak *m/e* 154 (1), parent peak *m/e* 546 (40.89% of base).

Dibenzothorocene, 5, was prepared in a similar manner from the benzocyclooctatetraene dianion prepared as above and cannulated into a solution of 1.2 g of $ThCl_4$ in 50 mL of THF. The mixture was refluxed for 2 days, and the solvent was removed. The product is sparingly soluble in THF and toluene. Crystallization of the crude product in the manner used for dibenzouranocene[21] gave 0.33 g (19%) of red-orange crystals after 1 week. This material is exceedingly air sensitive and showed a tendency to decompose in a glovebox if not rigorously oxygen free: ^{1}H NMR, Table I; ^{13}C NMR 136.2, 119.13, 108.21, 104.92, 102.52 ppm; mass spectrum base peak, *m/e* 154 (1), parent peak *m/e* 540 (48.02% of base). The air sensitivity makes combustion analysis difficult as shown by the example. Anal. Calcd. for $C_{24}H_{20}Th$: C, 53.3; H, 3.7. Found: C, 49.7; H, 3.7.

Bis(dihydrobenzo)uranocene, 6. Admixture of THF solutions of 2 equiv of dianion from 2 and 1 equiv of UCl_4 in the glovebox gave an immediate dark green color. The mixture was filtered to remove KCl, and the solvent was evaporated. The residue was washed with a small amount of hexane to give a product characterized and shown to be substantially pure by the ^{1}H NMR spectrum (Table I). The linear regressions for $\delta = a/T + b$ are given, respectively, as δ (27 °C), *a*, and *b*: −39.11, −14847, 9.978; −33.17, −10964, 3.058; −30.37, −10414, 4.047; −20.99, −12434, 20.158; −8.49, −6504, 13.000; 14.73, 979.2, 11.520. Mass spectrum: base peak, *m/e* 156 (ligand), parent peak, *m/e* 550 (78.05% of base peak; normal *n* + 1).

This compound was hydrogenated by stirring 0.1 g with 20 mg of platinum in benzene under 1 atm of H_2 (or D_2) for 24 h. The mixture was filtered, evaporated, and dried under vacuum to give 60 mg (60%) of product whose ^{1}H NMR spectrum was exclusively that of 7. The deuteration marked the 8- and 9-positions by a reduction in area of the δ −16.68 (endo) and +6.18 (exo) resonances. The area ratios showed the incoming deuterium to be 70% exo and 30% endo.

***cis*-Bicyclo[6.4.0]dodeca-2,4,6-triene, 8.** The following procedure is based on the method of Cotton and Deganello that was given without experimental details.[29]

To a suspension of lithium cyclooctatriendiide in liquid ammonia prepared from 10.4 g (0.1 mL of COT and 1.39 g (0.2 mol) of lithium (1% sodium) was added dropwise a solution of 21.6 g (0.1 mol) of 1,4-dibromobutane (Baker) in ether. The resulting solution was stirred for 3 h at −40 °C followed by overnight evaporation of the ammonia. The residue was added to saturated aqueous ammonium chloride and extracted with ether. The washed and dried extract was distilled (46–47 °C (0.65 torr)) to give 4.55 g (28%) of 8: mass spectrum, *m/e* 160; ^{1}H NMR ($CDCl_3$) δ 5.78, 5.67 (br s, 4.2 H, vinyl), 2.65 (br m, 2 H, bridgehead), 1.53 (br s, 6 H, CH_2). Anal. ($C_{12}H_{16}$) C, H.

Bis(tetrahydrobenzo[8]annulene)uranium (IV), 7. Under Ar, to 300 mL of ammonia distilled from a lithium ammonia solution into a flask containing several milligrams of anhydrous $FeCl_3$ was added 2.14 g (0.055 mol) of potassium at −40 °C. After the mixture was stirred for several minutes, the blue color disappeared and 4.5 g (0.028 mole) of 8 was added. The resulting solution was stirred for 1.5 h at −35 °C. It was then allowed to warm slowly to room temperature with the ammonia being swept out with an Ar purge to yield 5.56 g of the crude dianion 9. To a solution of 3.0 g (13.5 mmol) of this dianion salt in 100 mL of THF in a uranocene reactor[28] in the glovebox was added a solution of 2.56 g (68 mmol) of UCl_4 in 25 mL of THF. The resulting green solution was stirred for 18 h, the solvent was removed, and the green solid was purified by Soxhlet extraction[28] with hexane to give 0.57 g (16%) of 7; ^{13}C NMR (dioxane-d_8) δ 308, 297, 270 (C_8 ring), 13.4 (C_β), −32.5 (C_α). The proton NMR (Table I) showed the presence of a slight paramagnetic impurity that could not be removed by sublimation or recrystallization. Magnetic susceptibility measurements were made with a Princeton Applied Research vibrating-sample magnetometer described previously.[30] From 15 to 98 K the magnetic susceptibility shows Curie–Weiss behavior with $\mu_{eff} = +2.65 \pm 0.2$, $\theta = 23.0$ K, and $C = 0.8810$ emu K/mol. NMR spectrum:[31] the linear regressions for $\delta = a/T + b$ are given, respectively, as δ (29 °C), *a*, and *b*: −38.82, −14376, 8.781; −32.72, −10026, 0.497; −30.83, −10304, 3.300; −22.52, −13016, 20.57; −16.68, −6887, 6.103; −3.31, −1609, 2.032; +6.18, −2740, 15.19 (this last line is slightly but distinctly curved).

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76SF00098. Structures were done by Michael Waldyke using a program written by Michael Miller for the Tektronix 4050 series.

Registry No. 1, 265-49-6; 2, 23709-78-6; 4, 87532-97-6; 5, 87532-98-7; 6, 87532-99-8; 7, 87533-00-4; 8, 87532-96-5; 9, 87555-25-7; 11, 87533-01-5; DDQ, 84-58-2; UCl_4, 10026-10-5; $ThCl_4$, 10026-08-1; COT, 629-20-9; K_2COT, 29590-71-4; bromocyclooctatetraene, 7567-22-8; 1,4-dibromobutane, 110-52-1; 1,3-butadiene, 106-99-0.

A Facile Synthesis of 1,2-Bis(phosphino)benzene and Related Alkylated Species

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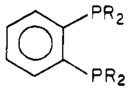
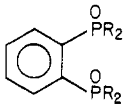
Photolysis of 1,2-dichlorobenzene in trimethyl phosphite at 60 °C for 5 days gives 1,2-bis(dimethoxyphosphoryl)benzene (3) in 50% yield. The reaction can be carried out on a multimolar scale. Species 3 is reduced to 1,2-bis(phosphino)benzene (4) in 83% yield following distillation, utilizing a reagent derived from trimethylsilyl chloride and lithium aluminum hydride in THF. Diphosphine 3 may be transformed in high yields into 1,2-bis(methylphosphino)-, 1,2-bis(dimethylphosphino)-, and 1,2-bis(2-propylphosphino)benzene using deprotonation/alkylation techniques.

Introduction

Reactions that create carbon-phosphorus bonds, especially those which produce two such bonds in the same molecule, have been of considerable interest to coordination and organometallic chemists for years. Particularly attractive are reactions that give 1,2-disubstituted benzenes 1 since these species are "preorganized" entropically for chelation of transition metals. A number of routes have been described to obtain 1 directly from aromatic precursors, all of which suffer from difficulty of manipulation, separation of complex mixtures, and low yields.[1] In particular, an efficient, relatively inexpensive synthesis that yields 1 (R = Me) in high purity has remained a challenge for two decades.[1a–c,f,g] Several routes have been developed to the dioxygenated species 2. One type of reaction involves the substitution of phosphoryl moieties for halogen by using a photocatalyzed reaction of dialkyl phosphite anions[2] or a photocatalyzed[3] or Ni(II)-catalyzed[4] reaction of trialkyl phosphites with 1,2-dihalogenated benzenes. An alternative route to 2 involves a Diels–Alder reaction of a diphosphorylalkyne with a cyclic diene, followed by expulsion of a small molecule concomitant with aromatization.[5]



1, R = H, alkyl, aryl

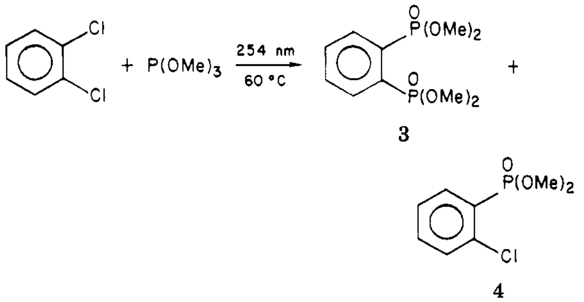


2

Although compounds 2 appear to be somewhat more easily accessible than a direct route to 1, there remains the nontrivial problem of reduction of 2 to 1. This report describes the relatively inexpensive and facile synthesis of 3 and thence to 5–7.

Results and Discussion

The photochemical reaction of 1-iodo-2-bromobenzene with trimethyl phosphite has been reported to give 3 in 87% yield.[3] The same reaction with 1-iodo-2-chlorobenzene gave 3 in 28% yield, and no reaction was reported with 1,2-dichlorobenzene. Since the 1-iodo-2-halobenzenes are expensive,[6] we reinvestigated the reaction with 1,2-dichlorobenzene. When the photolysis is carried out at 60 °C for 5 days, 3 is formed in about 50% yield, along with 4 (20%, eq 1). After removal of the reactants under vacuum, 3 and 4 are separated by recrystallization. The reaction may be carried out routinely on a 3.5-mol scale of the limiting reagent ($Cl_2C_6H_4$) to give about 500-g quantities of purified 3 per run.



(1)

The reduction of 3 to 5 proved to be considerably more challenging than might have been expected from a persual of the pertinent literature.[7] Reaction of 3 with $LiAlH_4$

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(6) E.g.: 1-bromo-2-iodobenzene is available from Aldrich Chemical Co. at 5 g/$19.25.

0276-7333/83/2302-1877$01.50/0