

$C_6H_5)_2Mn_2(NO)_3(C_6H_5)_3$, 59539-19-4; *cis*-(η^5 - C_5H_5) $_2Mn_2(NO)_3$ -(CH_3), 75847-52-8; *cis*-(η^5 - C_5H_5) $_2Mn_2(NO)_3(C_6H_7)$, 75862-70-3; (η^5 - $CH_3C_5H_4$) $_2Mn_2(NO)_3I$, 69120-60-1; (η^5 - $CH_3C_5H_4$) $_2Mn_2(NO)_3Br$, 70616-48-7; (η^5 - $CH_3C_5H_4$) $_2Mn_2(NO)_3Cl$, 70616-27-2; (η^5 - $CH_3C_5H_4$) $_2Mn_2(NO)_3NO_2$, 75847-53-9; (η^5 - $CH_3C_5H_4$) $Fe(CO)[P(C_6H_5)_3]I$, 32054-66-3; (η^5 - $CH_3C_5H_4$) $Mn(CO)_3$, 12108-13-3; (η^5 - $CH_3C_5H_4$) $Mn(CO)_2[P(C_6H_5)_3]$, 12100-95-7; [(η^5 - $CH_3C_5H_4$) $Mn(CO)(NO)[P(C_6H_5)_3]$] PF_6 , 32965-23-4; (η^5 - $CH_3C_5H_4$) $Mn(NO)[P(C_6H_5)_3]I$, 69120-58-7; (η^5 - C_5H_5) $Re(CO)(NO)I$, 75847-54-0; (η^5 - $CH_3C_5H_4$) $Mn(CO)(NO)I$, 69120-56-5; [(η^5 - $CH_3C_5H_4$) $Mn(CO)$ -

(NO) $_2$, 69155-23-3; (η^5 - C_5H_5) $Mn(CO)(NO)I$, 69120-55-4; (η^5 - $CH_3C_5H_4$) $Fe(CO)_2I$, 32628-97-0; [(η^5 - C_5H_5) $Mn(CO)_2(NO)]PF_6$, 31921-90-1; [(η^5 - $CH_3C_5H_4$) $Mn(CO)_2(NO)]PF_6$, 52202-14-9; (η^5 - C_5H_5) $Re(CO)_3$, 12079-73-1; (η^5 - C_5H_5) $Re(CO)(NO)CH_3$, 38814-45-8; *trans*-(η^5 - C_5H_5) $_2Mn_2(NO)_3I$, 69155-17-5; *trans*-(η^5 - C_5H_5) $_2Mn_2(NO)_3(C_6H_5)$, 75880-24-9.

Supplementary Material Available: Tables VII-X, listings of mass spectral data (4 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of Substituted Thorocenes

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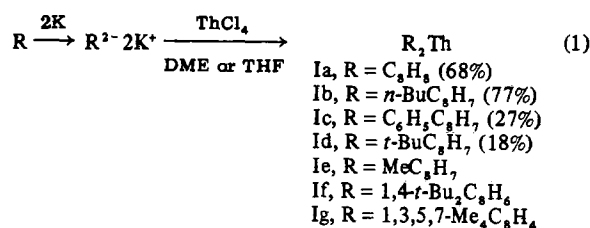
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Disubstituted bis(cyclooctatetraene)thorium(I) (thorocene) complexes have been prepared. Unlike thorocene itself, these derivatives are soluble in organic solvents. Proton and ^{13}C NMR spectra of these air-sensitive diamagnetic compounds show a significant decrease in electron density in the rings relative to dipotassium cyclooctatetraene salts. The chemistry of thorocenes and uranocenes is compared. Like uranocenes, thorocenes do not undergo facile ligand-exchange reactions with cyclooctatetraenes; both, however, do give rapid exchange with cyclooctatetraene dianions.

Thorocene (bis(η^8 -cyclooctatetraene)thorium, $Th(COT)_2$, Ia) was first prepared by Streitwieser and Yoshida¹ shortly after the preparation of uranocene.² Reaction of 2 equiv of dipotassium cyclooctatetraene (K_2COT) with $ThCl_4$ in tetrahydrofuran (THF) yielded yellow crystals of $(COT)_2Th$ upon sublimation. Thorocene has also been produced in the direct reaction of finely divided thorium metal (produced from thorium hydride) with COT at 150 °C.³ The uranium and plutonium analogues have been prepared in a similar manner. These preparations attest to the thermodynamic stability of the bis(cyclooctatetraene)actinide complexes. X-ray crystal structure analysis showed thorocene to be isostructural with uranocene.⁴ Both have a π -sandwich structure with D_{8h} molecular symmetry. The carbon-metal bond distance is slightly longer for the thorium compound, which reflects the generally larger bond radius of $Th(IV)$ vs. $U(IV)$.

The sparing solubility of thorocene in common organic solvents limits investigation of solution properties such as NMR spectra and relative reactivity compared to uranocene. Several physical properties have been determined: mass spectrum;¹ infrared and Raman spectra.⁵ By analogy to uranocenes,⁶ substituted thorocenes were expected to have greater solubility than the parent compound. The synthesis, spectral characterization, and some reaction chemistry of substituted thorocenes are reported in this paper.

Synthesis. A variety of substituted thorocenes was prepared by reaction of the substituted COT^7 dianion with $ThCl_4$ (eq 1). The success of these preparations depends critically on the thorium tetrachloride used. Material from one supplier was essentially insoluble in THF or DME and gave poor yields



or no reaction. Thorium tetrachloride from Alfa was more soluble and gave satisfactory results. Initially, dimethoxyethane (DME) was used as solvent because $ThCl_4$ is reported to decompose upon prolonged exposure to tetrahydrofuran (THF).⁸ Subsequently, THF was shown to be a suitable solvent since reaction 1 proceeds readily at room temperature. Compounds Ia-Id were prepared in moderate to good yield on a 5-10-mmol scale and were purified by hexane extraction. Smaller amounts of Ie-Ig (0.5-1.0 mmol) were prepared for spectroscopic studies and were purified by sublimation with substantial material loss due to concomitant decomposition. Yields for Ie-Ig were not determined; Id was prepared by both procedures. Substituted thorocenes are bright yellow solids, and some have sharp melting points. They show strong parent ions (often the base peak) in the mass spectra.

Thorocenes react rapidly with oxygen in a fashion similar to uranocenes to give cyclooctatetraenes (eq 2).² The inor-



ganic product, by analogy, is undoubtedly ThO_2 . This reaction serves as an additional means of characterization of new thorocenes, since the liberated ligand can be identified by NMR. More importantly, it means that all thorocene chemistry must be performed with the scrupulous exclusion of oxygen. This oxygen sensitivity makes it difficult to obtain satisfactory combustion analyses, but with careful work it was possible to get good analyses; this shows that the crystals are stoichiometric and do not contain solvent of crystallization.

As expected, the substituted thorocenes are more soluble in organic solvents than the parent. Because of the availability of n -butylcyclooctatetraene and the high yields in the reaction

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- Starks, D. F.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 3423-4.
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- Streitwieser, A., Jr.; Harmon, C. A. *Inorg. Chem.* **1973**, *12*, 1102-4.
- The ligands for compounds Id and If were generously donated by M. J. Miller; Miller, M. J.; Lytle, M. H.; Streitwieser, A., Jr., submitted for publication in *J. Org. Chem.*

- Marks, T. J.; Seyam, A. M.; Wachter, W. A. *Inorg. Synth.* **1976**, *16*, 147-51.

Table I. Visible Spectra [λ_{max} , nm (ϵ)] of Organometallic COT Compounds in THF

ligand	Th	U ^a	Np ^b	Pu ^b
C ₈ H ₈	450	615 (1800)	518 (1300)	404 (670)
CH ₃ C ₈ H ₇	453			
<i>n</i> -BuC ₈ H ₇	456 (64)	623	523	407
1,3,5,7-Me ₄ C ₈ H ₄	480	650	546	429 ^c
C ₆ H ₅ C ₈ H ₇	457	625		
1,4- <i>t</i> -Bu ₂ C ₈ H ₆	474	631 ^d		

^a Reference 6. ^b Reference 10. ^c Reference 9. ^d M. J. Miller, unpublished results.

of the dianion with ThCl₄, Ib is especially convenient for studies of this class of compound.

Visible Spectra. Each of the bis(cyclooctatetraene) complexes of the lower actinides has a characteristic visible spectrum.⁹ The spectra for (COT)₂M with M = U,^{2,6} Np,¹⁰ and Pu¹⁰ are complex and highly structured; each shows four or more moderately intense bands in the visible region. The band maxima for the most prominent absorption in each case are listed in Table I. By comparison, the visible spectrum of thorocene is undistinguished. A broad band of low intensity is centered at 450 nm with a shoulder at shorter wavelength. Due to its sparing solubility, the extinction coefficient of (COT)₂Th was not determined but appears to be the same order of magnitude as that for Ib.

Electron-donating substituents have been shown generally to cause a bathochromic shift in the visible spectra of bis(cyclooctatetraene) complexes of U, Np, and Pu.^{6,10} This observation, coupled with the magnitude of the extinction coefficients ($\epsilon \sim 10^3$) led to an assignment of the bands as ligand-to-metal charge-transfer transitions. Thorocenes show similar substituent effects, in both the direction and the magnitude of the shifts. The intensities, however, are at least 1 order of magnitude lower.

NMR Spectra. Uranocene is paramagnetic with two unpaired electrons on uranium. As a result, the ¹H and ¹³C NMR spectra involve a combination of contact and pseudo-contact shifts.¹¹ Since thorocene is too insoluble for determination of the NMR spectrum, the substituted thorocenes provide the first group of diamagnetic bis(cyclooctatetraene)actinide compounds analyzed by NMR.

When COT is reduced by potassium, the ¹H NMR spectrum of the resulting dianion is coincident with that of COT itself. The same phenomenon is observed for the ring protons of substituted COT's (Table II). The increased proton shielding provided by the added electrons is compensated by an opposing ring-current effect in the aromatic dianion.¹² Protons on carbons α to the ring also feel the effect of a ring current and are shifted downfield relative to the neutral species.

In the NMR spectra of substituted thorocenes, the ring protons are shifted significantly downfield from the ionic potassium salts. These shifts apparently reflect the net charge transfer from the dianionic ligand to the central M⁴⁺ ion and provide suggestive evidence for some ring-metal covalency in bis(cyclooctatetraene)actinides.¹³

Table II. Proton NMR Spectra of Cyclooctatetraenes and Thorocenes

ligand		cyclooctatetraene	dipotassium salt	thorocene
CH ₃ C ₈ H ₇	ring H	5.6	5.6	6.5
	CH ₃	1.8	2.8	3.1
(CH ₃) ₃ CC ₈ H ₇	ring H	5.7	5.7	6.5
	CH ₃	1.1	1.5	1.7
1,3,5,7-(CH ₃) ₄ -C ₈ H ₄	ring H	5.4	5.6	6.4
	CH ₃	1.7	2.8	3.0
<i>n</i> -BuC ₈ H ₇	ring H	5.7	5.7	6.5
	Bu	2.1	2.9	3.2
		1.4	1.3	1.6
		1.0	0.9	1.0
C ₆ H ₅ C ₈ H ₇	C ₆ -ring H	6.0, 5.8	6.2, 5.8	6.8, 6.6
	Ph H	7.2	7.6, 7.1	7.7, 7.5
			6.65 (p)	7.3 (p)
1,4-[(CH ₃) ₃ C] ₂ -C ₈ H ₆	C ₆ -ring H	5.6-6.1 ^a	6.0, 5.7	6.6
	CH ₃	1.1 ^a	1.6	1.7

^a Reference 7. ^b δ relative to Me₄Si in THF-*d*₈.

Table III. ¹³C NMR Spectra of Cyclooctatetraenes and Thorocenes

		δ		
ligand		cyclooctatetraene	dipotassium salt	thorocene
CH ₃ C ₈ H ₇	ring C ₁	141	93	120
	ring C ₂₋₅	136-128	92-89	109-106
	CH ₃	24	34	33
<i>n</i> -BuC ₈ H ₇	ring C ₁	145	101	121
	ring C ₂₋₅	134-126	92-89	109-106
	Bu	38, 31, 22, 14	50, 41, 24, 15	49, 38, 23, 14
C ₆ H ₅ C ₈ H ₇	COTC ₁	142	103	121
	COTC ₂₋₅	132	94-91	109-108
	Ph p-H	128	119	126

These effects are still more dramatic in ¹³C NMR. Correlations of ¹³C shifts and electron populations in aromatic systems are fairly well established.¹⁴ The ¹³C shifts from the COT ring carbons in thorocenes (Table III) are found to be about midway between those of the neutral and dianionic ligand species. That is, they correspond roughly to a monoanion. This interpretation is oversimplified for it neglects solvent effects and metal anisotropy effects. A better reference than the potassium dianion would be the diamagnetic (RC₈H₇)₂La⁻ complex, but ¹³C spectra of compounds of this sort have not yet been recorded.

In phenyl-substituted compounds, the shieldings of the aryl carbons are sensitive to electronic effects imparted by polar substituents on the ring. A linear relationship has been established between the ¹³C chemical shift of the para carbon of the phenyl ring and Hammett σ constants from monosubstituted benzenes.¹⁴ Such shifts provide a method for estimating σ constants for COT dianion and (COT)₂Th from the corresponding phenyl-substituted compounds. The dianion, as expected, is strongly electron donating. More surprisingly, the ¹³C shift for the para position in diphenylthorocene is only slightly upfield from that in phenylcyclooctatetraene and demonstrates again that a substantial amount of charge has been transferred from the ligand dianion to the central Th(IV).

Hydrolysis. Compared to ionic COT organometallic complexes such as K₂COT and Ln(COT)₂⁻, uranocene is remarkably stable to water.² Dibutyluranocene, for example, hydrolyzes with $k = 2.2 \times 10^{-6} \text{ s}^{-1}$ in 1 M THF in H₂O.¹⁵

(9) Solar, J. P.; Burghard, H.; Banks, R.; Streitwieser, A., Jr.; Brown, D. *Inorg. Chem.* **1980**, *19*, 2186.

(10) Karraker, D. G. *Inorg. Chem.* **1973**, *12*, 1105-8.

(11) (a) Edelstein, N.; LaMar, G. N.; Mares, F.; Streitwieser, A., Jr. *Chem. Phys. Lett.* **1971**, *8*, 399-402. (b) Streitwieser, A., Jr.; Dempf, D.; LaMar, G. N.; Karraker, D. G.; Edelstein, N. *J. Am. Chem. Soc.* **1971**, *93*, 7343-4. (c) In the dissection of the observed shifts to contact and dipolar components, the shifts of uranocenes were referenced to the dianions. The corresponding thorocenes probably provide a better reference, but the difference is small.

(12) Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3784-5.

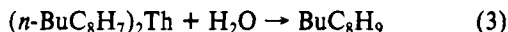
(13) Rösch, N.; Streitwieser, A., Jr. *J. Organomet. Chem.* **1978**, *145*, 195-200.

(14) Nelson, G. L.; Williams, E. A. *Prog. Phys. Org. Chem.* **1976**, *12*, 229-342.

(15) Walker, R. P., unpublished data.

This corresponds to a half-life of about 80 h. Acetolysis proceeds at an even slower rate.²

Dibutylthorocene reacts instantaneously with both water and acetic acid in THF to give butylcyclooctatrienes (eq 3). Since



thorocenes do not otherwise behave as typical salts, we interpret these results on the basis of the general Lewis acid character of Th(IV) compounds. We hypothesize that coordination with water at the central Th requires separation of the rings for steric reasons with consequent weakening of ring-metal bonding (vide infra).

Nitro Reductions. The reaction of uranocenes with nitro compounds has been shown to give azo compounds and cyclooctatetraenes in good yield (eq 4).¹⁶ Nitrenes, hydroxy-



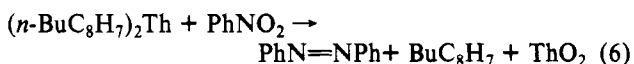
amines, and azoxy compounds have been eliminated from the list of possible intermediates. Nitrosobenzene and the nitrobenzene radical anion, on the other hand, also react rapidly with uranocenes to give azobenzene and are potential intermediates in the reduction of nitrobenzene.

The reaction is exceedingly rapid but may be retarded slightly by electron-donating substituents in the nitro compound (e.g., nitrobenzene reacts faster than 4-nitrotoluene). One mechanism that we considered to account for these observations involves initial electron transfer from the uranocene to the nitro acceptor, forming a nitro radical anion and an organometallic species that is formally U(V) (eq 5). The nitro



radical anion, however, must be complexed to the metal, since reactions known to occur for free radical anions such as loss of iodide from the 2-iodonitrobenzene radical anion were not observed in the reaction of iodo-nitro compounds with uranocenes.¹⁶ This mechanism, however, requires that nitro compounds be stable to thorocenes, since the Th(V) oxidation state is unknown; Th(IV) is a closed-shell system and has no 5f electrons to lose.

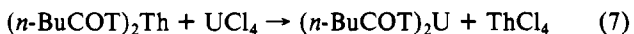
When dibutylthorocene is allowed to react with nitrobenzene in THF, a rapid oxidation occurs at room temperature (eq 6).



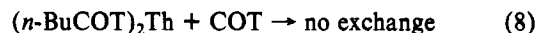
The major nitrogen-containing product is azobenzene. The inorganic product is presumably ThO₂.

This result renders improbable the electron-transfer process of eq 5 as a reaction mechanism. Our presently favored mechanism involves attack by a nitro group oxygen at the metal to liberate one ligand ring as the cyclooctatetraene and form an intermediate monoring organometallic species, (COT)M=O, and nitrosobenzene, which undergo rapid further reaction to products. This mechanism is still consistent with the present thorocene results.

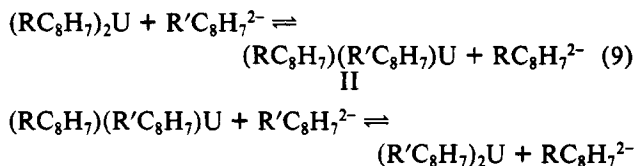
Ligand and Metal Exchange. The lanthanide COT complexes react rapidly with UCl₄ to give uranocene,¹⁷ consistent with their characterization as almost wholly ionic compounds. When dibutylthorocene and UCl₄ are allowed to react, dibutyluranocene is produced but only slowly (eq 7). The



reaction does not proceed by a dissociative mechanism, since dibutylthorocene does not exchange ligands with neutral COT (eq 8).



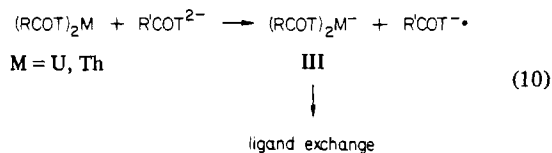
Uranocenes have been shown to undergo rather rapid ligand exchange with COT dianions at room temperature (eq 9).



These reactions were followed by NMR. In all cases, equilibrium was reached before the spectrum could be recorded. Yet the rate of exchange is slow on the NMR time scale, since the peaks for both the uranocene and the dianion were observed and not just an averaged spectrum. The mixed-ligand product (II) was observed by mass spectroscopic analysis of the isolated products for the case of R = Et and R' = *n*-Bu.

Comparable reactions occur with thorocenes; for example, (PhC₈H₇)₂Th reacts rapidly with BuC₈H₇²⁻ to give an unmistakable signal for PhC₈H₇²⁻ in the NMR.

A plausible mechanism for these ligand-exchange reactions involves preliminary reduction to a M(III) complex (eq 10).



By analogy to the Np(III) and Pu(III) complexes isolated by Karraker and Stone¹⁸ and the Ln(COT)₂⁻ complexes,¹⁷ intermediates such as III should be more ionic than the corresponding M(IV) complexes and should have greater ligand mobility. We would expect formation of III to be less feasible for M = Th, but rate data are not yet available for comparison.

Summary

The physical and chemical properties of the thorocenes indicate substantial covalent ligand-metal bonding, but the compounds appear generally to be more ionic and less covalent than the corresponding uranocenes. Thorocenes do not show the Lewis acid behavior of many Th(IV) compounds; they give no evidence of stable complexes with Lewis bases. Water and other hydroxylic compounds do cause rapid decomposition. A reasonable hypothesis is that steric effects involving the ligand rings preclude additional coordination at the central metal. We note that the ring-ring distance in the bis(cyclooctatetraene)actinides (4.01 Å for thorocene⁴) is relatively small for incorporation of additional atoms or groups. For example, intercalation of atoms or molecules within layer planes of graphite results in an increase of the interlayer distance from 3.35 Å to more than 5 Å.¹⁹ We suggest that reaction at the central actinide in the COT compound is accompanied by separation of the rings with consequent reduction of ring-metal bonding and decomposition. If this hypothesis is correct, these sandwich structures will not find use as catalyst or reagent systems that require reversible coordination sites at the metal.

Experimental Section

General Data. All solvents were carefully dried over sodium/benzophenone or LiAlH₄, vacuum transferred, and stored in an argon atmosphere in a Vacuum Atmospheres recirculating glovebox. All reactions were run under an atmosphere of dry argon. Visible spectra were obtained on a Cary 118 spectrophotometer, ¹H NMR spectra were run on a Varian T-60, and ¹³C NMR spectra were run on a Bruker WH-90/Nicolet Fourier Transform spectrometer at 25.144 MHz at a probe temperature of 37 ± 1 °C. Thorium tetrachloride

(16) Grant, C. B.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 2433-9.
(17) Hodgson, K. O.; Mares, F.; Starks, D. F.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8650-8.

(18) Karraker, D. G.; Stone, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 6885-8.
(19) Croft, R. C. *Q. Rev., Chem. Soc.* **1960**, *14*, 1-45.

from Alfa showed some solubility in tetrahydrofuran (THF) and dimethoxyethane (DME) and gave good results in these preparations; that of another supplier was insoluble and gave much poorer yields.

1,1'-Di-*n*-butylthorocene. The following procedure is typical of the preparation of substituted thorocenes and is derived from the general procedure for preparation of thorocenes:^{2c} To a 500-mL reactor was added ThCl₄ (Alfa) (2.57 g, 6.9 mmol) and K₂BuCOT (3.0 g, 12.6 mmol). The reactor was evacuated, and 250 mL of DME was added via vacuum transfer. The mixture was warmed to room temperature and allowed to stir under argon for 1 week. The solvent was removed by vacuum transfer, and the dried solid was scraped into the thimble of an evacuable extractor. Extraction with hexane, following the normal thorocene-type extraction procedure, produced 2.68 g (77%) of di-*n*-butylthorocene (mp 148–150 °C). Anal. Calcd for C₂₄H₃₂Th: C, 52.17; H, 5.84. Found: C, 52.38; H, 5.97.

1,1'-Diphenylthorocene was prepared in a similar manner from phenylcyclooctatetraene but was characterized only by its spectra.

1,1'-Di-*tert*-butylthorocene. The following procedure²⁰ is comparable but uses THF: A suspension of ThCl₄ (0.56 g, 1.5 mmol) in 10 mL of THF was added to a solution prepared from *tert*-butylcyclooctatetraene (0.48 g, 3.0 mmol) and 0.234 g (6 mmol) of potassium in 50 mL of THF. After 40 h the mixture was centrifuged and the yellow solution was evaporated to give 0.7 g of crude product. Soxhlet extraction with hexane gave 0.3 g (18%) of yellow powder, mp 235–237 °C, soluble in THF to about 60 mg/mL; λ_{max} (THF) 454 nm. Anal. Calcd for C₂₄H₃₂Th: C, 52.17; H, 5.84. Found: C, 52.18; H, 5.76.

Thorocene. K₂COT was prepared in the standard manner from COT (1.0 g, 10 mmol) in THF. ThCl₄ (1.86 g, 5.0 mmol) was added, and the reaction mixture was allowed to stir under argon for 3 days. Toluene extraction yielded 1.5 g (68%) of product. Anal. Calcd for C₁₆H₁₆Th: C, 43.6; H, 3.66. Found: C, 41.77; H, 3.61.

Small-Scale Thorocene Preparations. To a solution of 200–300 mg of the potassium salt of a cyclooctatetraene dianion in 20 mL of THF was added a suspension of an equivalent weight of ThCl₄ in 10 mL of THF. The mixture was allowed to stir overnight in the glovebox. The solid was removed by centrifugation and washed with fresh THF until colorless. The THF solution was degassed, and the solvent was removed with stirring. The dried solid was transferred to a tube and sublimed in low yield (with concomitant decomposition) with a yellow flame at 10⁻² mm. In this manner 1,1'-dimethylthorocene, 1,1',3,3',5,5',7,7'-octamethylthorocene, and 1,1',4,4'-tetra-*tert*-butylthorocene were prepared. These compounds were prepared in small quantity primarily for NMR comparisons and were characterized only by mass spectroscopy (molecular ion) and NMR and visible spectra (Tables I–III). 1,1'-Di-*tert*-butylthorocene was also prepared by this procedure.

***tert*-Butylcyclooctatetraene.** This compound was prepared by the modified cuprate technique of Posner et al.²¹ A solution of 16.5 g (0.15 mol) of thiophenol in 60 mL of THF was allowed to react at 0 °C with an equivalent amount of *n*-butyllithium. The mixture was stirred for 0.5 h, allowed to warm to room temperature, and was added dropwise to a mixture of 28.5 g (0.15 mol) of cuprous iodide in 300 mL of THF under nitrogen. The mixture was cooled to –78 °C and 94 mL of 1.6 M *tert*-butyllithium was added dropwise, followed by a precooled (–70 °C) solution of 9.2 g (0.05 mol) of bromocyclooctatetraene in 100 mL of THF. The mixture was stirred for 3 h at –70 °C, quenched with 15 mL of methanol, and allowed to warm to room temperature. The reaction mixture was poured into saturated aqueous ammonium chloride and filtered. Both the filtrate and precipitate were extracted thoroughly with ether. The combined ether

solutions were washed, dried, and distilled. Distillation of the residue at 78–83 °C (10 torr) gave 3.13 g (40%) of product that on redistillation at 47 °C (4 torr) gave product still containing some bromocyclooctatetraene, determined by mass spectroscopy.

Oxidation. A solution of (BuCOT)₂Th in THF-*d*₈ was sealed in an NMR tube, and its spectrum was recorded. The tube was cracked open, and the contents were filtered through glass wool. The NMR spectrum of the resulting solution was identical with that of authentic BuCOT.

Hydrolysis. A solution of (BuCOT)₂Th (1.2 × 10⁻² M) in THF was placed in a cuvette equipped with a two-way stopcock. The initial spectrum was recorded. Water was degassed well by four freeze–pump–thaw cycles, and 0.1 mL was added via syringe. Upon being shaken, the solution immediately turned colorless and a white precipitate formed. No absorptions appeared in the visible spectrum.

So that it could be ensured that no oxidation had occurred during the introduction of H₂O, the experiment was repeated in the following manner: A solution of (BuCOT)₂Th in THF (6.6 × 10⁻³ M) was added to an evacuable cuvette. The solution was degassed, and degassed water was added via vacuum transfer. When the solution was warmed, an immediate reaction occurred to give a colorless solution and a white precipitate.

Acetolysis. Glacial acetic acid was stirred over P₂O₅ for 1 day and then distilled under nitrogen. A middle fraction was collected and degassed by three freeze–pump–thaw cycles. A solution of (BuCOT)₂Th in THF (1.5 × 10⁻² M) was placed in an evacuable cuvette and degassed. Acetic acid (approximately 0.5 mL) was added via vacuum transfer. When the mixture thawed, there was an immediate decoloration of the solution and formation of a white precipitate.

Reaction of Dibutylthorocene with Nitrobenzene. Nitrobenzene was predried with 4A molecular sieves, vacuum distilled (5 mm, 69 °C) from P₂O₅, degassed, and vacuum transferred from P₂O₅. A solution of 400 mg (7.2 × 10⁻⁴ mol) of (BuCOT)₂Th in 15 mL of THF was prepared in a Schlenk tube. Under a stream of argon, nitrobenzene was added dropwise at room temperature. The solution warmed slightly, and there was an immediate reaction to give dark red coloration. Nitrobenzene was added until the yellow thorocene color disappeared (about 0.05 mL). No additional color change occurred upon exposure to air. The dark suspension was transferred to centrifuge tubes and spun down. The solid was washed with THF until colorless. The THF washes were combined, and the solvent was removed by rotary evaporation. BuCOT was removed by Kugelrohr distillation. The remaining red oil was chromatographed on silica gel, and azobenzene was eluted as the first and major band with hexane. Azobenzene was identified by its NMR and mass spectra.

NMR Experiments. NMR samples for ligand-exchange experiments were prepared in the following manner: The solid reactants were added to an NMR tube in the glovebox, and dry THF-*d*₈ was added either by means of syringe or by distillation on a vacuum line. The tubes were degassed and sealed under vacuum.

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(20) Preparation by H.-K. Wang.

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