1628 *Inorg. Chem.* **1992**, *31*, 1628–1633

Contribution from the Nuclear and Radiochemistry Group, INC-11, and Inorganic and Structural Chemistry Group, INC-4,
Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545,
and Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Facile Solution Routes to Hydrocarbon-Soluble Lewis Base Adducts of Thorium Tetrahalides. Synthesis, Characterization, and X-ray Structure of $ThBr_4(THF)_4$

David L. Clark,[*,1a] Tracey M. Frankcom,[1a] Mary M. Miller,[1b] and John G. Watkin[1a]

Received November 7, 1991

The direct combination of thorium metal turnings with 2 equiv of elemental bromine or iodine in THF solution at 0 °C provides white crystalline $ThX_4(THF)_4$ (X = Br, **1**; X = I, **2**; THF = tetrahydrofuran), in 70–80% isolated yield. These new compounds are soluble in hydrocarbon solvents and react readily with oxygen- and nitrogen-donor ligands in toluene solution to give $ThBr_4py_4$ (**3**), ThI_4py_4 (**4**), $ThBr_4(NCMe)_4$, (**5**), and $ThBr_4(DME)_2$ (**6**) in high yield (py = pyridine, DME = 1,2-dimethoxyethane). Compounds **1**–**6** have been characterized by elemental and thermogravimetric analysis, ^1H NMR, infrared, and diffuse-reflectance spectroscopy, and, for **1**, a single-crystal X-ray structure determination. The X-ray diffraction study of **1** revealed a slightly distorted dodecahedral coordination geometry about the central thorium atom with two interpenetrating tetrahedra of bromide and THF ligands. Oxygen atoms of the THF ligands occupy A vertices (Th–O = 2.549 (17) Å, average) and bromide ions occupy B vertices (Th–Br = 2.859 (3) Å, average) of an irregular dodecahedron. **1** is an excellent synthetic precursor to thorium coordination and organometallic complexes and can be prepared on a 100–150-g scale in a single day. Crystal data for **1** (at –40 °C): Rhombohedral space group $R\bar{3}$, with $a = 26.317$ (4) Å, $c = 18.340$ (4) Å, $V = 11000$ Å^3, $d_{calc} = 2.299$ g cm^{-3}, and $Z = 18$.

Introduction

The inorganic and organometallic chemistry of thorium has been an area of considerable recent research, encompassing thermochemical studies of metal–ligand bond strengths,[2,3] catalytic processes,[4–7] C–H bond activation,[8–10] and, most recently, the first authentic examples of molecular Th(III) complexes.[11–13] Almost exclusively, the synthetic starting point in organometallic thorium chemistry has been from thorium tetrahalides, ThX_4 (X = Cl, Br, I). Anhydrous thorium tetrahalides have been prepared by a variety of techniques, the most common of which involve direct combination of thorium metal, hydride, or carbide with elemental halogen or anhydrous hydrogen halide at high temperature (700–900 °C).[14–19] It has been noted that many of these preparations can lead to products which are relatively impure due to insufficient precautions to exclude moisture and oxygen or secondary high-temperature reactions between the thorium tetrahalide product and silica, silicates, graphite, or porcelain during preparation.[19] In addition, when prepared by these traditional high-temperature methods, thorium tetrahalides are polymeric solids.[20] In order to break up the polymer and obtain organic-solvent-soluble, synthetically-useful starting materials, the tetrahalides must first be purified by vacuum sublimation. Similar difficulties have been noted in the inorganic/organometallic chemistry of trivalent uranium, where the anhydrous uranium trihalides are polymeric solids,[21,22] insoluble in common organic solvents and quite unreactive.[23] Sattelberger and co-workers recently demonstrated that uranium metal turnings would react readily with elemental iodine in organic donor solvents to produce Lewis base adducts of uranium triiodide of general formula UI_3L_4 (L = Lewis base).[24] Employing a similar strategy, we have developed a convenient low-temperature solution route to organic-solvent-soluble Lewis base adducts of thorium tetrahalides that are easy to prepare on a large scale and serve as excellent precursors to a variety of inorganic and organometallic complexes of thorium.

Results and Discussion

Synthesis and Reactivity. One-inch strips of thorium metal turnings react readily with 2 equiv of elemental iodine or bromine in THF solution at 0 °C under an argon atmosphere to give complexes of general formula $ThX_4(THF)_4$ (X = Br, I) in 70–80% yield according to eq 1. The dissolution of thorium metal turnings

$$\mathrm{Th} + 2\mathrm{X}_2 \xrightarrow[0\ °\mathrm{C}]{\mathrm{THF}} \mathrm{ThX}_4(\mathrm{THF})_4 \tag{1}$$

is accompanied by the slow discharge of color due to iodine or bromine and, in the case of the bromine reaction, precipitation of an off-white microcrystalline solid. For the iodine dissolution, care must be taken to maintain the reaction temperature at or below ca. 30 °C. At higher temperatures we have experienced considerable acceleration of the reaction, decreased product yield, and large amounts of oily residue.[25] The optimal form of thorium metal for these simple dissolution reactions appears to be metal turnings. Fine metal powders were found to be too reactive and therefore hard to control, while large chips of metal were too

---

(1) (a) Los Alamos National Laboratory. (b) Colorado State University.

(2) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824.

(3) Sonnenberger, D. C.; Morss, L. R.; Marks, T. J. *Organometallics* **1985**, *4*, 352.

(4) He, M.-Y.; Burwell, R. L., Jr.; Marks, T. J. *Organometallics* **1983**, *2*, 566.

(5) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 641.

(6) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 653.

(7) Toscano, P. J.; Marks, T. J. *Langmuir* **1986**, *2*, 820.

(8) Dormond, A.; El Bouadili, A. A.; Moïse, C. *J. Chem. Soc., Chem. Commun.* **1985**, 914.

(9) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728.

(10) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991.

(11) Vallat, A.; Laviron, E.; Dormond, A. *J. Chem. Soc., Dalton Trans.* **1990**, 921.

(12) Blake, P. C.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1148.

(13) Kot, W. K.; Shalimoff, G. V.; Edelstein, N. M.; Edelman, M. A.; Lappert, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 986.

(14) Brown, D. *Halides of the Lanthanides and Actinides*; Wiley-Interscience: London, 1968.

(15) Nilson, L. F. *Ber. Dtsch. Chem. Ges.* **1882**, *9*, 1142; **1882**, *15*, 2537.

(16) Moissan, H.; Étard, A., *C. R. Acad. Sci. Paris* **1896**, *122*, 573.

(17) Moissan, H.; Étard, A. *Ann. Chim. Phys.* **1897**, *7*, 427.

(18) Zalkin, A.; Forrester, J. D.; Templeton, D. H. *Inorg. Chem.* **1964**, *3*, 639.

(19) Guillaumont, R. *Radiochim. Acta* **1983**, *32*, 129.

(20) Hussonnois, M.; Krupa, J. C.; Genet, M.; Brillard, L.; Carlier, R. *J. Cryst. Growth* **1981**, *51*, 11.

(21) Taylor, J. C.; Wilson, P. W. *Acta Crsytallogr.* **1974**, *B30*, 2803.

(22) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *Acta Crystallogr.* **1975**, *B31*, 880.

(23) A 10% yield of $(C_5H_5)_3U$ is obtained on refluxing polymeric UCl_3 with KCp in benzene for *7 days*. See: Kanellakopulos, B.; Fischer, E. O.; Dornberger, E.; Baumgartner, F. *J. Organomet. Chem.* **1970**, *24*, 507.

(24) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. *Inorg. Chem.* **1989**, *28*, 1771.

(25) This may be due to ring-opening of THF during oxidation of thorium metal. See: TerHarr, G. L.; Dubeck, M. *Inorg. Chem.* **1964**, *3*, 1648. McLaren, A. B.; Kanellakopulos, B.; Dornberger, E. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 223.

0020-1669/92/1331-1628$03.00/0

Table I. Summary of Crystallographic Data for $ThBr_4(THF)_4$

empirical formula	$C_{16}H_{32}Br_4O_4Th$
color, habit	white cube coated in Nujol
cryst size, mm	0.20 × 0.15 × 0.20
cryst system	rhombohedral
space group	$R\bar{3}$
unit cell dimens	
a, Å	26.317 (4)
c, Å	18.340 (4)
V, Å^3	11 000 (3)
Z	18
fw	846.1
D_{calc}, g cm^{-3}	2.299
abs coeff, cm^{-1}	128.09
F(000)	7074
diffractometer	Enraf-Nonius CAD-4 (κ geometry)
radiation (λ, Å)	Mo Kα (0.710 73)
temp, °C	−40
monochromator	highly oriented graphite cryst
2θ range, deg	2.0–45.0
no. of measd reflcns	1095
no. of unique reflcns	1095 (R_{int} = 9.10%)
no. of obsd reflcns	1091 ($F > 4.0\sigma(F)$)
abs corr	empirical (XABS)
tot. no. of least-squares params	236
final residuals	
R	0.037
R_w	0.042
goodness-of-fit	1.30
largest and mean Δ/σ	0.581, 0.032
largest diff peak, e Å^{-3}	0.56

Table II. Fractional Coordinates and Equivalent Isotropic Displacement Coefficients[a] for $ThBr_4(THF)_4$

	10^5x	10^5y	10^5z	10^4U(eq), Å^2
Th(1)	86475 (3)	33333 (4)	7175 (4)	219 (5)
Br(1)	74480 (10)	28875 (11)	3289 (15)	436 (13)
Br(2)	82095 (12)	25849 (12)	19748 (13)	461 (15)
Br(3)	96760 (11)	41848 (11)	14377 (14)	447 (14)
Br(4)	93111 (11)	36763 (11)	−6159 (12)	384 (13)
O(1)	86555 (66)	42238 (62)	2103 (70)	314 (71)
O(2)	82914 (62)	23852 (55)	521 (65)	237 (65)
O(3)	82859 (63)	38381 (65)	16206 (77)	339 (71)
O(4)	93156 (60)	28735 (61)	8615 (74)	302 (69)
C(1)	91012 (119)	48344 (96)	3548 (155)	494 (101)
C(2)	89121 (124)	51701 (110)	−929 (133)	547 (105)
C(3)	86754 (131)	48545 (107)	−7633 (144)	596 (106)
C(4)	83766 (110)	42638 (122)	−4601 (116)	453 (100)
C(5)	81175 (117)	22766 (102)	−7301 (134)	482 (99)
C(6)	77781 (112)	16286 (116)	−8334 (137)	599 (105)
C(7)	79871 (125)	14081 (113)	−2205 (120)	552 (105)
C(8)	80710 (98)	18227 (86)	4047 (117)	305 (89)
C(9)	84792 (147)	39926 (151)	23929 (132)	799 (116)
C(10)	80655 (198)	41378 (212)	26224 (239)	1464 (130)
C(11)	77629 (132)	42435 (141)	21416 (152)	716 (112)
C(12)	78644 (125)	40316 (139)	14651 (138)	572 (106)
C(13)	95984 (135)	28630 (132)	15078 (142)	731 (113)
C(14)	99372 (139)	25591 (136)	13585 (122)	639 (108)
C(15)	97382 (97)	23179 (101)	6146 (119)	388 (95)
C(16)	95889 (112)	27311 (119)	2315 (130)	438 (98)

[a] $U(\mathrm{eq}) = {}^1/_3[U_{11} + U_{22} + U_{33}]$.

Table III. Selected Bond Distances (Å) for the $ThBr_4(THF)_4$ Molecule

Th(1)–Br(1)	2.854 (3)	Th(1)–Br(2)	2.873 (3)
Th(1)–Br(3)	2.833 (2)	Th(1)–Br(4)	2.876 (3)
Th(1)–O(1)	2.512 (18)	Th(1)–O(2)	2.501 (13)
Th(1)–O(3)	2.584 (18)	Th(1)–O(4)	2.599 (19)
O(1)–C(1)	1.464 (23)	O(1)–C(4)	1.462 (30)
O(2)–C(5)	1.489 (27)	O(2)–C(8)	1.445 (25)
O(3)–C(9)	1.491 (28)	O(3)–C(12)	1.462 (46)
O(4)–C(13)	1.407 (34)	O(4)–C(16)	1.504 (34)

Table IV. Selected Bond Angles (deg) for the $ThBr_4(THF)_4$ Molecule

Br(1)–Th(1)–Br(2)	86.4 (1)	Br(1)–Th(1)–Br(3)	149.8 (1)
Br(2)–Th(1)–Br(3)	93.7 (1)	Br(1)–Th(1)–Br(4)	106.9 (1)
Br(2)–Th(1)–Br(4)	150.5 (1)	Br(3)–Th(1)–Br(4)	87.6 (1)
Br(1)–Th(1)–O(1)	77.4 (3)	Br(2)–Th(1)–O(1)	138.6 (4)
Br(3)–Th(1)–O(1)	82.9 (3)	Br(4)–Th(1)–O(1)	70.8 (4)
Br(1)–Th(1)–O(2)	71.5 (4)	Br(2)–Th(1)–O(2)	83.4 (3)
Br(3)–Th(1)–O(2)	138.6 (4)	Br(4)–Th(1)–O(2)	76.3 (3)
O(1)–Th(1)–O(2)	125.0 (4)	Br(1)–Th(1)–O(3)	75.9 (3)
Br(2)–Th(1)–O(3)	73.3 (4)	Br(3)–Th(1)–O(3)	75.3 (3)
Br(4)–Th(1)–O(3)	134.9 (3)	O(1)–Th(1)–O(3)	65.9 (5)
O(2)–Th(1)–O(3)	140.8 (4)	Br(1)–Th(1)–O(4)	134.5 (3)
Br(2)–Th(1)–O(4)	74.5 (3)	Br(3)–Th(1)–O(4)	73.7 (3)
Br(4)–Th(1)–O(4)	77.7 (3)	O(1)–Th(1)–O(4)	141.3 (4)
O(2)–Th(1)–O(4)	65.7 (5)	O(3)–Th(1)–O(4)	133.1 (5)
Th(1)–O(1)–C(1)	125.8 (16)	Th(1)–O(1)–C(4)	127.5 (14)
C(1)–O(1)–C(4)	103.2 (18)	Th(1)–O(2)–C(5)	126.0 (14)
Th(1)–O(2)–C(8)	124.2 (11)	C(5)–O(2)–C(8)	107.9 (14)
Th(1)–O(3)–C(9)	125.9 (21)	Th(1)–O(3)–C(12)	126.4 (13)
C(9)–O(3)–C(12)	107.8 (24)	Th(1)–O(4)–C(13)	125.6 (19)
Th(1)–O(4)–C(16)	123.9 (15)	C(13)–O(4)–C(16)	108.6 (23)
O(1)–C(1)–C(2)	103.5 (21)	C(1)–C(2)–C(3)	108.1 (27)
C(2)–C(3)–C(4)	97.9 (21)	O(1)–C(4)–C(3)	112.0 (19)
O(2)–C(5)–C(6)	107.0 (19)	C(5)–C(6)–C(7)	102.9 (20)
C(6)–C(7)–C(8)	103.8 (26)	O(2)–C(8)–C(7)	103.7 (17)
O(3)–C(9)–C(10)	99.0 (31)	C(9)–C(10)–C(11)	120.0 (39)
C(10)–C(11)–C(12)	104.4 (41)	O(3)–C(12)–C(11)	106.7 (25)
O(4)–C(13)–C(14)	108.7 (23)	C(13)–C(14)–C(15)	102.7 (27)

unreactive using our synthetic procedure. Through the use of thorium metal turnings, we have routinely performed these simple dissolution reactions on a 100–150-g scale in a single day. This represents a synthetically useful quantity, and the gentle solution reaction is a dramatic improvement over the high-temperature tube-furnace techniques which yield polymeric ThX_4.

The THF adducts $ThX_4(THF)_4$ (X = Br, I) are soluble in hydrocarbon solvents such as toluene, very soluble in tetrahydrofuran, and exchange readily with other donor solvents in toluene solution to form a series of hydrocarbon-soluble Lewis base adducts of general formula ThX_4L_4, where L = pyridine, acetonitrile, or $^1/_2$ DME (DME = 1,2-dimethoxyethane) according to eq 2. The ThX_4L_4 complexes are also soluble in coordinating

$$ThX_4(THF)_4 + 4L \xrightarrow[25\ ^\circ C]{tol} ThX_4L_4 + 4THF \qquad (2)$$

$$X = Br,\ L = MeCN,\ py,\ ^1\!/_2\ DME;\ X = I,\ L = py$$

solvents, but solvation is generally accompanied by ligand substitution. The solution reaction of thorium metal with elemental halogen is by no means specific to THF solvent, but we have observed that halogen dissolution in THF yields the most soluble and highest-purity products. For example, thorium metal turnings react with elemental iodine in neat pyridine solution at 0 °C to yield an insoluble blue powder. We have been unable to fully characterize this material at the present time, but it is not the simple adduct of formula $ThI_4(py)_4$ (py = pyridine). The latter compound is conveniently prepared by addition of excess pyridine to a toluene solution of $ThI_4(THF)_4$ to yield a yellow, microcrystalline powder (eq 2) that is soluble in hydrocarbon solvents.

Solid-State and Molecular Structure. Single crystals of $ThBr_4(THF)_4$ (**1**) suitable for an X-ray diffraction study were grown directly from a warm reaction mixture by slow cooling to room temperature. $ThBr_4(THF)_4$ crystallizes from THF solutions with half of a molecule of THF per unit cell in the lattice. On standing at room temperature under an inert atmosphere, it was found that the translucent crystals lose solvent, turn opaque, and eventually crumble to an off-white powder. To circumvent this difficulty, a single crystal was removed from a concentrated THF solution, coated in Nujol under an argon stream, mounted on a quartz fiber, and placed in a nitrogen cold stream at −40 °C on the diffractometer. Crystal decay due to solvent loss was observed, and a disordered THF molecule was found in the lattice ($R\bar{3}$) but not refined due to the decay noted above. A summary of data collection and crystallographic parameters is given in Table I, and atomic positional parameters are given in Table II. Selected bond distances and bond angles are given in Tables III and IV, respectively. A view of the molecule giving the atom numbering

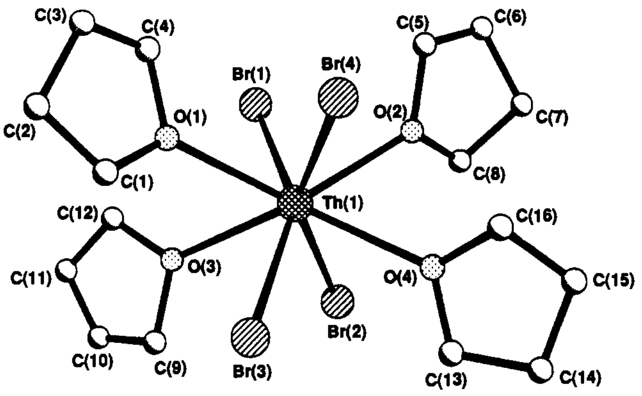


Figure 1. View of the molecular structure of $ThBr_4(THF)_4$ (**1**), showing the atom-numbering scheme for non-hydrogen atoms and emphasizing the distorted dodecahedral coordination geometry about the central thorium atom.

scheme used in the tables is shown in Figure 1.

The central thorium atom in $ThBr_4(THF)_4$ is surrounded by four bromide and four THF ligands located at the corners of an irregular dodecahedron as illustrated in Figure 1. The gross structural features of $ThBr_4(THF)_4$ are very similar to those observed for $ThCl_4(OSPh_2)_4$.[26] A D_{2d} dodecahedron may be viewed as a pair of interpenetrating tetrahedra, one flattened and one elongated such that the eight ligand sites are equally divided into symmetry-equivalent sets of four. These have been referred to as A (flattened) and B (elongated) vertices, respectively.[27] When viewed in this fashion, the four bromine atoms are found to occupy B vertices of the dodecahedron, and the average Th–Br distances of 2.859 (3) Å are similar to that found in the B sites of β-$ThBr_4$, 2.85 (2) Å.[19] The oxygen atoms of the THF ligands occupy A vertices of the dodecahedron, and the average Th–O distances of 2.549 (17) Å are similar to the average Th–O distances observed for coordinated THF in $[(\eta\text{-}Me_5C_5)_2ThMe(THF)_2]^+$ [2.58 (1) Å][28] and $Th(\eta\text{-}C_8H_8)(THF)_2Cl_2$ [2.57 (2) Å].[29]

Spectroscopic Characterization. The primary aim of our spectroscopic studies was to determine the amount of coordinated ligand in bulk samples of $ThX_4(THF)_4$ formed by direct halogen dissolution of thorium metal turnings. On the basis of elemental and thermogravimetric analysis, ^1H NMR integration versus internal standards, and infrared spectroscopy, the stoichiometry has been established as ThX_4L_4 for bulk powdered samples.

As noted previously, *freshly-prepared* crystalline samples correspond to $ThBr_4(THF)_{4.5}$ but tend to powder over a period of hours at room temperature, presumably due to loss of the half-molecule of lattice THF per unit cell, to form $ThBr_4(THF)_4$. Furthermore, analytical studies show that aged powdered samples contain lower THF content than freshly prepared powdered samples. After a period of 3 months of storage in the glovebox, elemental analysis and ^1H NMR integration versus an internal standard revealed a stoichiometry of $ThBr_4(THF)_3$. In the case of the tetraiodide, THF loss is found to be slower such that a sample aged for 14 months analyzed for $ThI_4(THF)_{3.6}$. The more facile loss of THF in the case of the bromide complex, compared with the corresponding iodide, follows a trend also observed for uranium trihalide adducts. Thus, $UCl_3(THF)_x$[30] has been found to lose coordinated THF readily, to form a polymeric material, whereas the iodide complex $UI_3(THF)_4$[24] retains its THF ligands much more tenaciously.

This thermal instability is supported by TGA studies on both single crystals and powdered samples that reveal rapid loss of THF at temperatures slightly above ambient. Thermal gravimetric analysis of a freshly-prepared single crystal of $ThBr_4(THF)_{4.5}$ establishes that 0.5 equiv of THF is removed (loss of 4.1%) at 110 °C and the remaining 4 equiv of THF is expelled between 110 and 210 °C, to produce anhydrous $ThBr_4$ (63% of original mass). Further heating above 210 °C leads to loss of bromine and concomitant formation of $ThOBr_2$ (46.5% of original mass) and, subsequently, ThO_2 (30.1% of original mass) above 650 °C. Similar decomposition stages have been observed previously during thermogravimetric analysis of oxo-ligand adducts of thorium tetrahalides.[31,32] Powdered samples of $ThBr_4(THF)_4$ show a smooth mass loss from 100 to 210 °C, corresponding to loss of four THF ligands and formation of $ThBr_4$. Further heating reveals similar behavior to single crystal samples, namely the formation of $ThOBr_2$ and ThO_2.

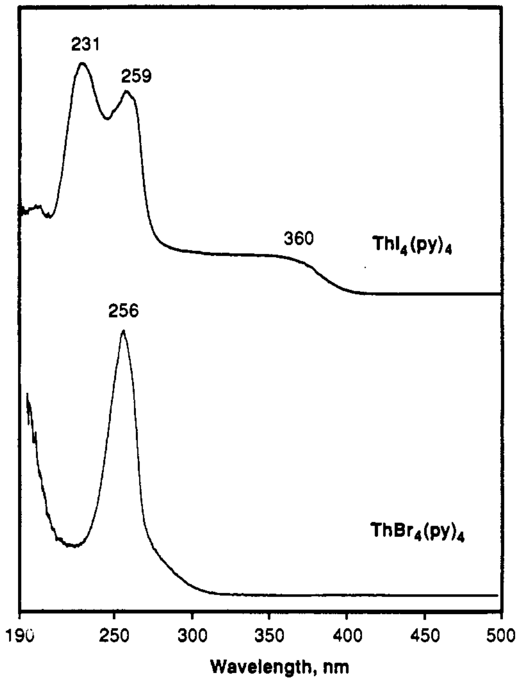


Figure 2. Diffuse-reflectance spectra of ThI_4py_4 (**4**) (top) and $ThBr_4py_4$ (**3**) (bottom).

Infrared spectra (4000–400 cm^{-1}) show only absorption bands characteristic of the coordinated ligands. Upon complex formation, pyridine vibrations in the high-frequency region are not appreciably shifted, whereas the in-plane ring deformation mode is generally shifted from 604 cm^{-1} to higher energy.[33] The observed shift of this vibrational mode to 622 cm^{-1} in ThX_4py_4 complexes is consistent with coordinated pyridine.[33] In a similar fashion, infrared absorption bands at 1000, 921, and 824 cm^{-1} for $ThBr_4(THF)_4$ and 991, 923, and 813 cm^{-1} for $ThI_4(THF)_4$ are indicative of coordinated THF ligands.[34,35] The infrared spectrum of the nitrile adduct $ThBr_4(NCMe)_4$ displays two strong absorption bands in the C≡N stretching region at 2282 and 2274 cm^{-1} consistent with coordinated acetonitrile.

Only one type of THF, DME, or pyridine ligand is observed in the ^1H NMR spectra of ThX_4L_4 complexes at room temperature in benzene-d_6 or toluene-d_8 solvents. Acetonitrile adducts were found to be too insoluble to obtain solution NMR spectra consistent with the observations of others.[36]

---

(26) Rickard, C. E. F.; Woollard, D. C. *Acta Crystallogr. B* **1980**, *B36*, 292.

(27) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235.

(28) Lin, Z.; Le Marechal, J. F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.

(29) Zalkin, A.; Templeton, D. H.; LeVanda, C.; Streitweiser, A., Jr. *Inorg. Chem.* **1980**, *19*, 2560.

(30) Moody, D. C.; Odom, J. D. *J. Inorg. Nucl. Chem.* **1979**, *41*, 533.

(31) Srivastava, A. K.; Agarwal, R. K. *Thermochim. Acta* **1982**, *56*, 247.

(32) Bagnall, K. W.; Brown, D.; Jones, P. J.; du Preez, J. G. H. *J. Chem. Soc. A* **1966**, 737.

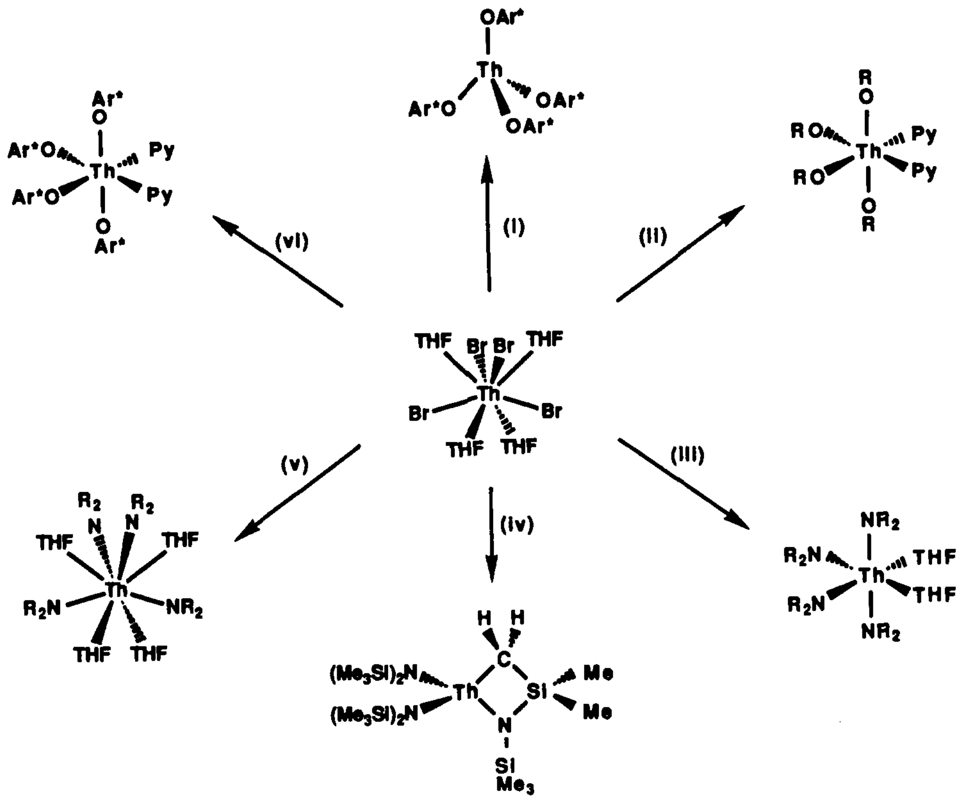
(33) Gill, N. S.; Nutall, R. H.; Scaife, D. E.; Sharp, D. W. A. *J. Inorg. Nucl. Chem.* **1961**, *18*, 79.

(34) Lewis, J.; Miller, J. R.; Richards, R. L.; Thompson, A. *J. Chem. Soc.* **1965**, 5850.

(35) Clark, R. J. H.; Lewis, J.; Machin, D. J.; Nyholm, R. S. *J. Chem. Soc.* **1963**, 379.

(36) Kumar, N.; Tuck, D. *Can. J. Chem.* **1982**, *60*, 2579.

Scheme I[a]



[a] Reagents and conditions: (i) 4 equiv of KOAr* (Ar* = 2,6-$Bu^t_2C_6H_3$), THF; (ii) 4 equiv of KOR (R = Bu^t), THF and then hexane/pyridine; (iii) 4 equiv of KNR_2 (NR_2 = NPh_2), THF; (iv) 4 equiv of $Na[N(SiMe_3)_2]$, toluene, reflux, 6 h; (v) 4 equiv of KNR_2 (NR_2 = NMePh), THF; (vi) 4 equiv of KOAr* (Ar* = 2,6-$Me_2C_6H_3$), THF and then toluene/pyridine.

Diffuse-reflectance spectra were obtained in the UV–vis spectral region (190–800 nm) for powdered samples of ThX_4L_4 complexes. As expected, the bromide complexes show no absorption features in this spectral region with the exception of the pyridine adduct, which displays one intense absorption maximum at 256 nm. The iodide complexes show several absorption maxima in the UV region, and a comparison of diffuse-reflectance spectra of the pyridine adducts ThX_4py_4 (X = I, Br) is shown in Figure 2. With four arene chromophores in the pyridine complexes, the 256- and 259-nm absorption features in $ThBr_4py_4$ and ThI_4py_4, respectively, are tentatively assigned to the arene $\pi \rightarrow \pi^*$ (benzenoid B-band) transition within the pyridine ligand. The presence of absorption features at 360 and 230 nm in the iodide spectrum and their absence in the bromide spectrum are suggestive of charge-transfer transitions originating from the iodide ligands. To gain more insight into the intensity of these transitions, solution electronic absorption spectra were obtained. In THF solution, $ThI_4(THF)_4$ displays four absorption features [λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 370 (45), 242 sh (11400), 224 sh (29500), 209 (54500)] in the same spectral region, and the intensities of the latter three transitions are certainly consistent with LMCT.

Concluding Remarks

We have shown that the gentle dissolution of thorium metal turnings with elemental bromine or iodine represents a convenient and facile preparative route for large (150 g) quantities of ThX_4L_4 complexes (X = Br, I) in high yield. At this point we note that other solution routes to Lewis base adducts of lanthanide and actinide metal halides have been reported. For example, direct electrochemical oxidation of 8- × 1-mm disks of thorium metal into solutions of chlorine or bromine in acetonitrile have been reported to give $ThX_4(NCMe)_4$ compounds,[36] while the analogous dissolution with iodine is reported to yield a remarkable divalent thorium complex of formula $ThI_2(NCMe)_2$.[37] Six hours of electrolysis (15 V, 30 mA) into a solution of iodine resulted in the dissolution of 0.70 g of thorium metal, while 3 h of electrolysis (8 V, 50 mA) into a solution of bromine resulted in the dissolution of 0.60 g of metal. On the basis of our results, it is not clear whether electrolysis is necessary since we find that 50-g quantities of thorium metal turnings dissolve in several hours in a THF solution of bromine. This is probably a result of surface area, since we have found large pieces of thorium metal to be quite unreactive toward bromine on a laboratory time scale. We have also examined redox transmetalation reactions employed by Deacon and co-workers,[38] and find this method to be somewhat unsatisfactory for large-scale preparations since large quantities of thorium/mercury amalgam are produced in the reaction, thereby mandating the use of excess thorium metal. The elegance of the direct halogen dissolution procedure reported here is in its simplicity. For the direct combination of the elements, no special equipment is required.

The $ThX_4(THF)_4$ complexes reported here have proven to be excellent synthetic precursors to a range of inorganic thorium complexes, due in part to their favorable solubility in toluene and THF solutions. Reaction of $ThBr_4(THF)_4$ with alkali-metal salts of the appropriate alkoxide, aryloxide, amide, etc. have been found to provide high-yield routes to many new and known thorium complexes as outlined in Scheme I. In some instances, the large-scale preparation of $ThBr_4(THF)_4$ has allowed for the scale up of known reactions. For example, the preparation of the known metallacycle $[(Me_3Si)_2N]_2\overline{Th[N(SiMe_3)(SiMe_2CH_2)]}$[9,39] is routinely performed in our laboratory on a 30-g scale (Scheme I). The general metathetical procedures for the preparation of thorium amides, alkoxides, and cyclopentadienyls starting from $ThBr_4(THF)_4$ will be presented elsewhere.[40]

Finally, it is worth commenting on the preparation of low oxidation state thorium complexes. Although unstated in the

---

(37) Kumar, N.; Tuck, D. *Inorg. Chem.* **1983**, *22*, 1951.

(38) Deacon, G. B.; Tuong, T. D. *Polyhedron* **1988**, *7*, 249.

(39) Dormond, A.; El Bouadili, A.; Aaliti, A.; Moise, C. *J. Organomet. Chem.* **1985**, *288*, C1.

(40) Clark, D. L.; Huffman, J. C.; Watkin, J. G. Manuscript in preparation.

Introduction, our original investigation into the iodide complexes of thorium focused on the attainability of thorium(III) iodide complexes by iodine dissolution. This procedure has been shown by Sattelberger and co-workers to give trivalent uranium iodides when excess metal is employed.[24] It is not surprising that only thorium(IV) iodides are isolated, even in the presence of excess thorium metal and maintenance of low (0 °C) temperatures during the dissolution process. However, the inability to isolate or even observe Th(III) during our preparations leads us to question earlier reports of a divalent thorium iodide prepared during electrochemical oxidation of thorium metal into acetonitrile solutions of iodine.[37] We find that the simple dissolution of thorium metal with iodine in acetonitrile solution provides an insoluble thorium(IV) product, $ThI_4(NCMe)_4$, which is admittedly only poorly characterized at the time of publication, due in part to its insolubility in common solvents. This material displays a diffuse-reflectance spectrum typical of the ThI_4 moiety with absorption features at 364, 295, and 230 nm. This is notably similar to the absorption spectra of $ThI_2(NCMe)_2$ [λ_{max}, nm (ϵ) 325 (2940), 285 (4200)][37] and is suggestive that the previously reported $ThI_2(NCMe)_2$ complex may actually contain tetravalent thorium. Investigations into the structure and identity of the compound reported as $ThI_2(NCMe)_2$ are clearly worthy of further study.

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmosphere glovebox. Thorium-232 metal (99.99%) was obtained from Los Alamos National Laboratory stock and machined into turnings. ACS grade bromine (Aldrich) and sublimed iodine (Aldrich) were used as received. Solvents, except for acetonitrile and pyridine, were degassed and distilled from Na–K alloy under nitrogen. Pyridine and acetonitrile were distilled from CaH_2 under argon. Benzene-d_6 was degassed, dried over Na–K alloy, and then trap-to-trap distilled before use. Toluene-d_8 was degassed and stored over a potassium mirror. Solvents were taken into a Vacuum Atmospheres glovebox, and a small amount was tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

NMR spectra were recorded at 22 °C on Bruker WM 300 or AM 250 spectrometers in benzene-d_6 or toluene-d_8. All ^1H NMR chemical shifts are reported in ppm relative to the ^1H impurity in benzene-d_6 or toluene-d_8 set at δ 7.15 or 2.09, respectively. Infrared spectra were recorded on a Perkin-Elmer 1500 spectrophotometer interfaced with a 1502 central processor. Thermogravimetric analyses (TGA) were recorded on a Perkin-Elmer 7-Series thermogravimetric analyzer with the furnace under an argon purge. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in aluminum capsules in the glovebox prior to combustion. Solution UV/visible spectra were recorded under argon using a Perkin-Elmer Lambda 9 spectrophotometer. Diffuse-reflectance spectra were recorded on the same instrument employing a 60-mm integrating sphere in diffuse-reflectance mode. Samples were mounted on Al_2O_3-coated TLC plates (no fluorescent indicator) sandwiched between quartz slides and run versus an Al_2O_3 blank.

Syntheses. $ThBr_4(THF)_4$ (1). Th turnings (39 g, 168.1 mmol) were broken into 1-in. strips and placed in a 1-L Schlenk reaction vessel equipped with a 1-in. Teflon-coated magnetic stir bar. The vessel was attached to the vacuum manifold of a conventional Schlenk line and the vessel evacuated and refilled with argon. The evacuate/refill process was repeated two more times, and then 500 mL of THF was added. Using a teat pipet, elemental bromine (50 g, 16.1 mL, 625.7 mmol) was added slowly to the flask in 2–3-mL portions with vigorous shaking. A very exothermic reaction took place as the red color of elemental bromine was discharged. An ice-water bath was used to maintain the reaction temperature between 20 and 30 °C. The dissolution of the Th metal was accompanied by the slow precipitation of an off-white microcrystalline precipitate. After color from the final addition of bromine had been discharged, there was a mixture of off-white microcrystalline precipitate and a gray powder of elemental thorium in a pale orange solution. The reaction vessel was taken into an inert-atmosphere glovebox, and the reaction mixture was transferred to a 1-L Erlenmeyer flask. The reaction mixture was heated to ca. 50 °C until all the white precipitate had redissolved, and the hot mixture was vacuum filtered through Celite on a coarse frit to give a pale yellow filtrate. The Celite pad and glassware were washed with THF (3 × 20 mL) until the washings were colorless. The filtrate volume was reduced to 100 mL, at which time a large amount of white microcrystalline solid had precipitated. A 250-mL volume of hexane was added to the filtrate to precipitate the remainder of the product with stirring. The white crystalline product was allowed to settle, the supernatant liquid decanted, and an additional 200 mL of hexane added to the precipitate with stirring. The solid was again allowed to settle, the supernatant liquid decanted, and the white microcrystalline product dried in vacuo to yield 84 g (70% based on Br_2) of analytically pure $ThBr_4(THF)_4$ (**1**). Large quantities of crystalline material may be obtained from slow cooling of a warm THF solution. IR (Nujol, cm^{-1}): 1345 (m), 1297 (w), 1250 (w), 1222 (w), 1172 (w), 1075 (w), 1038 (m), 1000 (s), 953 (w), 921 (m), 824 (s, br), 665 (m). ^1H NMR (250 MHz, $C_6D_5CD_3$): δ 4.13 (t, α-THF), 1.41 (m, β-THF). TGA: calcd for 34.3% THF, 37.5% weight loss between 60 and 200 °C. Anal. (a) Calcd for $ThBr_4(THF)_4$ (freshly prepared sample): C, 22.88; H, 3.84. Found: C, 23.23; H, 3.96. (b) Calcd for $ThBr_4(THF)_3$ (aged sample): C, 18.77; H, 3.15. Found: C, 18.88, 18.91; H, 2.99, 2.97.

$ThI_4(THF)_4$ (2). A 1-L Schlenk reaction vessel with a Teflon-coated magnetic stir bar was charged with Th turnings (51 g, 219.8 mmol). The vessel was attached to the vacuum manifold of a Schlenk vacuum line and the vessel evacuated and refilled with argon. The evacuate/refill process was repeated two more times, and then 400 mL of THF was added. Elemental I_2 (1.6 equiv, 80% of theoretical value, 90 g, 709 mmol) was slowly added to the Th metal turnings under an argon purge in 12–15-g batches. After addition of each aliquot of I_2, the reaction vessel was shaken vigorously. During this time, the iodine color was slowly discharged and accompanied by the evolution of heat as evidenced by the warmth of the reaction vessel. An ice-water bath was used to maintain the reaction temperature at or below room temperature. After the final aliquot of iodine was added, enough metal turnings had dissolved to allow for magnetic stirring. The solution was allowed to stir at room temperature for 8 h to yield a pale brown solution with excess metal present both in the form of unreacted turnings and as a dark-gray powder. The reaction vessel was taken into an inert-atmosphere glovebox and the solution was vacuum filtered through a 1-in. pad of Celite on a medium frit to give a clear, pale-orange solution. The Celite pad and glassware were washed with THF (3 × 20 mL) until the washings were colorless. The solvent was removed in vacuo to leave a sticky off-white solid. Hexane (400 mL) was added, the sticky solid broken up with a spatula, and the mixture allowed to stand at room temperature. After 12 h, large chunks of an off-white brittle solid remained. These solid chunks were ground up using a mortar and pestle, and the remaining hexane was removed in vacuo. This produced 147 g (80.6% based on I_2) of $ThI_4(THF)_4$ (**2**). IR (Nujol, cm^{-1}): 1344 (m), 1295 (w), 1247 (w), 1222 (2), 1170 (w), 1074 (m), 1039 (m), 991 (s), 953 (w), 923 (m), 813 (s, br), 666 (m). ^1H NMR (250 MHz, C_6D_6): δ 4.35 (t, α-THF), 1.42 (m, β-THF). UV-vis absorption spectra in THF solution [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 370 (45), 242 sh (11 400), 224 sh (29 500), 209 (54 500). Anal. Calcd for $C_{16}H_{32}I_4Th$: C, 18.69; H, 3.14. Found: C, 17.46, 17.43; H, 2.68, 2.64.

$ThBr_4(py)_4$ (3). A 4.00-g (4.76-mmol) sample of $ThBr_4(THF)_4$ was placed in a 50-mL Schlenk vessel together with 25 mL of pyridine. A reflux condenser was fitted to the flask, and the contents were refluxed under argon for 24 h. All volatiles were removed in vacuo to leave an off-white solid. Yield: 3.00 g (73%). IR (Nujol, cm^{-1}): 1624 (w), 1598 (s), 1488 (m), 1438 (s), 1222 (s), 1146 (w), 1068 (m), 1040 (m), 1000 (s), 758 (s), 700 (s), 620 (s). ^1H NMR (300 MHz, C_6D_6): δ 9.10 (d, $^3J_{HH}$ = 5 Hz, 2 H, ortho, C_5H_5N), 6.79 (t, $^3J_{HH}$ = 7 Hz, 1 H, para, C_5H_5N), 6.52 (m, 2 H, meta, C_5H_5N). Diffuse-reflectance spectra: single absorption at 256 nm. Anal. Calcd for $C_{20}H_{20}Br_4N_4Th$: C, 27.67; H, 2.32; N, 6.45. Found: C, 28.29, 28.16; H, 1.64, 1.56; N, 6.19, 6.16.

$ThI_4(py)_4$ (4). A 5.00-g (4.86-mmol) amount of $ThI_4(THF)_4$ was slurried in 50 mL of toluene in a 125-mL Erlenmeyer flask. To the vigorously stirred suspension was added 5 mL of pyridine, at which point the starting material dissolved. Over the next 20 min a pale yellow solid was deposited from the solution. After a further 1 h of stirring the solid was filtered off and pumped dry. Yield: 4.74 g (92%). IR (Nujol, cm^{-1}): 1628 (m), 1600 (s), 1486 (m), 1442 (s), 1220 (s), 1152 (m), 1084 (m), 1066 (m), 1038 (m), 1000 (m), 756 (m), 696 (s), 678 (m), 622 (m) 572 (w). ^1H NMR (300 MHz, $C_6D_5CD_3$): δ 9.14 (d, $^3J_{HH}$ = 4 Hz, 2 H, ortho, C_5H_5N), 6.93 (m, 1 H, para, C_5H_5N), 6.63 (m, 2 H, meta, C_5H_5N). Diffuse-reflectance spectra: absorption maxima at 360, 259, and 231 nm. Anal. Calcd for $C_{20}H_{20}I_4N_4Th$: C, 22.75; H, 1.91; N, 5.31. Found: C, 24.93; H, 1.93, N, 4.75.

$ThBr_4(MeCN)_4$ (5). A 4.00-g (4.76-mmol) sample of $ThBr_4(THF)_4$ was slurried in 20 mL of toluene, and then 5 mL of acetonitrile was added dropwise. The slurry was stirred at room temperature for a further 24 h, before the white solid was collected on a frit and pumped to dryness. Yield: 2.85 g (84%). IR (Nujol, cm^{-1}): 2282 (s), 2274 (s), 1404 (m), 1366 (m), 1026 (w), 936 (m), 790 (w), 722 (w). The complex was found to be too insoluble to obtain solution NMR data. Diffuse-reflectance spectra: no absorption features. Anal. Calcd for $C_8H_{12}Br_4N_4Th$: C, 13.42; H, 1.69; N, 7.83. Found: C, 13.99; H, 1.16; N, 7.51.

$ThBr_4(DME)_2$ (6). A 3.00-g (3.57-mmol) amount of $ThBr_4(THF)_4$ was placed in a 125-mL Erlenmeyer flask and 20 mL of toluene added. To this slurry was then added 5 mL of DME, and the resulting suspension stirred at room temperature for 24 h. The white solid was filtered off onto a frit and pumped dry. Yield: 2.10 g (80%). IR (Nujol, cm^{-1}): 1456 (s), 1288 (w), 1256 (m), 1246 (w), 1188 (m), 1152 (w), 1116 (m), 1084 (s), 1010 (vs), 852 (vs), 844 (s), 830 (m). ^1H NMR (300 MHz, C_6D_6): δ 3.83 (s, 6 H, O*Me*), 3.41 (s, 4 H, CH_2O). Anal. Calcd for $C_8H_{20}Br_4O_4Th$: C, 13.13; H, 2.75. Found: C, 13.61; H, 1.60.

Crystallographic Studies: $ThBr_4(THF)_4$. Crystal data, collection, and processing parameters are given in Table I. Since crystal decomposition occurred at room temperature, presumably due to loss of solvent trapped in the lattice, the data were collected at −40 °C. A crystal measuring 0.20 × 0.15 × 0.20 mm was coated in Nujol and mounted on a glass fiber under an argon purge. The fiber was then placed on the goniometer head of an Enraf-Nonius CAD-4 diffractometer in a −40 °C nitrogen cold stream. Graphite-monochromated Mo Kα radiation was used. Unit cell parameters were determined from the least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 24 accurately-centered reflections. Two reflections were chosen as intensity standards and measured every 150 reflections. Data were collected by ω scans.

Equivalent reflections were merged, and systematically absent reflections were rejected. The structure was solved by routine Patterson and Fourier methods. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 1091 unique observed [$F > 4\sigma(F)$] reflections converged at $R = 0.037$ and $R_w = 0.042$ {where $w = 1/[\sigma^2(F)^2 + 0.0005F^2]$}. All calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instruments Inc., 1990). A correction for absorption was applied.[41]

Acknowledgment. We wish to thank Dr. A. P. Sattelberger, Dr. W. G. Van Der Sluys, and Dr. C. J. Burns for helpful discussions and Dr. R. R. Ryan for the generous use of X-ray diffraction facilities. We acknowledge the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract No. W-7405-eng-36 with the University of California and the Yucca Mountain Site Characterization Project Office as part of the Civilian Radioactive Waste Management Program managed by the U.S. Department of Energy, Nevada Operations Office, for financial support.

Supplementary Material Available: For $ThBr_4(THF)_4$, a table of anisotropic thermal parameters (Table S1) (2 pages); a table of crystallographic structure factors (Table S2) (12 pages). Ordering information is given on any current masthead page.

---

[41] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. Uguzzli, F. *Comput. Chem.* **1987**, *11*, 109. Katayama, C. *Acta Crystallogr.* **1986**, *A42*, 19.

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Reactions of Perfluoromethyl-Substituted Cyclopolyphosphines with Zerovalent Group 10 Metal Complexes. Crystal and Molecular Structure of a Complex with a Coordinated Diphosphene, $[Pd(\eta^2\text{-}CF_3P{=}PCF_3)(PPh_3)_2]$

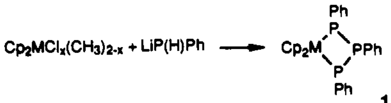
Ian G. Phillips, Richard G. Ball, and Ronald G. Cavell*

Received January 23, 1991

Reactions of trifluoromethyl-substituted cyclopolyphosphines $(CF_3P)_4$ and $(CF_3P)_5$ with zerovalent Pt, Pd, and Ni complexes gave a variety of products under different conditions. The most definitive reactions were those in which $(CF_3P)_4$ reacted with the zerovalent metal complexes under refluxing conditions in benzene to give η^2-CF_3PPCF_3 complexes of the formula $L_2M(CF_3PPCF_3)$. The crystal and molecular structure of $(Ph_3P)_2Pd(\eta^2\text{-}CF_3PPCF_3)$ (monoclinic $P2_1/n$, $Z = 4$, $a = 11.200$ (2) Å, $b = 19.441$ (3) Å, $c = 17.502$ (3) Å, $\beta = 101.71$ (1)°, $R_1 = 0.048$, $R_2 = 0.062$) showed clearly the η^2 adduct in the *E* configuration. The P=P bond length of 2.121 Å is consistent with a coordinated diphosphene as formulated. The CF_3PPCF_3 group can be transferred to different metals (e.g. Pt) by simple metathetical exchange. The various coordinated and ring-opened intermediates formed via initial 1,3-coordination of the cyclic polyphosphines both $(CF_3P)_4$ and $(CF_3P)_5$ and subsequent ring opening were identified by NMR spectroscopy, and some aspects of the mechanism of formation of the intermediates and the final η^2 adduct are discussed.

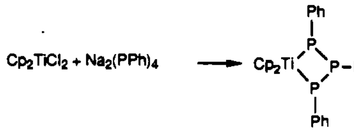
Introduction

Many examples of transition-metal-induced reductive ring-opening reactions of *cyclo*-$[ER]_n$ (E = P, As) to give homoatomic polyorganophosphorus or -arsenic catenates are known.[1a-d] These polyphosphine–transition metal metallacyclic complexes may also be accessed from reaction of lithiated phosphines with organometallic alkyls or chlorides (eq 1)[1e] (M = Zr, Hf; $x = 0, 1, 2$)



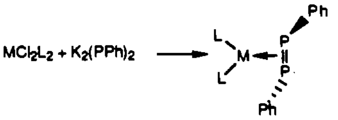
1 (1)

or by reaction of reduced ring fragments with metal chlorides,[1f] such as is shown in eq 2. These reactions are not necessarily



1 c (M=Ti) (2)

stoichiometric. Complexes of η^2-(side-bonded)-diphosphenes (e.g., $L_2Pt(\eta^2\text{-}PhPPPh)$; L = PPh_3 (**2**), dppe (**3**)) are also prepared via a similar route[2] (eq 3). The reactions of $(EC_6F_5)_4$ (E = P, As)



2,3 (3)

with $[Pt(PPh_3)_3]$ (1:1 Pt/"$(C_6F_5P)_2$") in refluxing benzene have been shown to give η^2-diphosphene (or diarsene) compounds $[Pt(\eta^2\text{-}C_6F_5E{=}EC_6F_5)(PPh_3)_2]^3$ (E = P (**4**), As (**5**)). An X-ray

---

[1] (a) Caminade, A.-M.; Majoral, J.-P.; Mathieu, R. *Chem. Revs.* **1991**, *91*, 575. (b) West, B. O. In *Homoatomic Rings, Chains and Macromolecules of the Main Group Elements*; Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; Chapter 18. (c) Rheingold, A. L.; Fountain, M. E. *Organometallics* **1984**, *3*, 1417. (d) Mercando, P.; DiMaio, A.-J.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 244 and references therein. (e) Hey, E.; Bott, S. G.; Atwood, J. L. *Chem. Ber.* **1988**, *121*, 561. (f) Köpf, H.; Voigtländer, R. *Chem. Ber.* **1981**, *114*, 2731.

[2] Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932; *J. Chem. Soc., Dalton Trans.* **1984**, 2237 and references therein.

0020-1669/92/1331-1633$03.00/0