Organometallics 1993, 12, 3326-3332

Photoelectron Spectroscopy of f-Element Organometallic Complexes. 10. Investigation of the Electronic Structure and Geometry of Bis(η^5-pentamethylcyclopentadienyl)phosphathoracyclobutane by Relativistic ab Initio, Multipolar DV–Xα Calculations and Gas-Phase UV Photoelectron Spectroscopy

Santo Di Bella, Antonino Gulino, Giuseppe Lanza, and Ignazio L. Fragalà*

Dipartimento di Scienze Chimiche, Università di Catania, 95125 Catania, Italy

Tobin J. Marks*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received January 28, 1993

The electronic structure of the phosphathoracyclobutane $Cp'_2\overline{Th(CH_2PMeC}H_2)$ complex (Cp' = η^5-Me_5C_5) has been investigated by a combination of ab initio relativistic effective core potential calculations for geometry optimization, DV–Xα calculations, and UV photoelectron spectroscopy. The formation of the four-membered ring involves bonding interactions analogous to those found in cyclobutane. Metal–ligand bonding involves both 5f and 6d metal atomic orbitals with a major role of the latter. The gas-phase UV photoelectron spectrum has been assigned using both comparative arguments and TSIE values obtained from DV–Xα calculations, as well as PE data on the closely related $Cp'_2\overline{Th(CH_2SiMe_2C}H_2)$ complex. The optimized structure is indicative of a slightly puckered four-membered metallacyclic ring having the P–CH_3 vector in an endocyclic axial orientation. The structure shows close analogies with diffraction data for the related $Cp'_2\overline{Th(CH_2SiMe_2C}H_2)$ complex. According with NMR data, a single energy minimum has been found for the conformation with smaller intraligand repulsive interactions involving the P_{3p} lone pair.

Introduction

Metallacyclic compounds[1] play an important role in organometallic chemistry either as useful stoichiometric reagents or as catalysts for a host of unusual transformations.[2,3] An intriguing class of metallacycles is represented by thoracyclobutanes because of their facile ring-opening hydrocarbon C–H activation[4] or olefin insertion reactions[4c] to yield a variety of compounds, some of which are otherwise inaccessible.[4] This chemistry is often strikingly different from that of closely related early transition element metallacycles where metal alkylidenes are involved as either intermediates or ground state species.[1b,2d-g] For example, cyclopentadienyltitanacyclobutane complexes undergo reaction with trialkylphosphines to yield the corresponding metallocene methylidene phosphine complexes,[2b] whereas the homologous thoracyclobutane yields[4c] the metallacycle $Cp'_2\overline{Th(CH_2PMeC}H_2)$ (1), which represents a unique example of a phosphametallacyclobutane. The complex was first synthesized and conformationally characterized by Marks *et al.*[4c] and possesses, in addition, sufficient thermal stability for gas-phase photoelectron spectroscopic (PES) studies.

In this paper we report on the electronic structure of phosphathoracyclobutane 1 through a combination of ab initio relativistic effective core potential (RECP) calculations for geometry optimization, of first-principles local density (DV–Xα) calculations for evaluation of ionization energies (IEs), and finally, of experimental He I/He II PE spectroscopic measurements. It is noteworthy that the present paper represents the first example of an ab initio geometry optimization for a large molecule containing a

---

(1) (a) Ciliberto, E.; Di Bella, S.; Gulino, A.; Fragalà, I.; Petersen, J. L.; Marks, T. J. *Organometallics* **1992**, *11*, 1727–1737 and references therein. (b) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1–74. (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 9, Chapter 54, pp 499–551 (see also references therein). (d) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron Report Number 2: The Preparation and Properties of Metallacyclic Compounds of the Transition Elements*; Pergamon Press: Oxford, U.K., 1982; Vol. 1, pp 739–777 (see also references therein).

(2) (a) Erker, G.; Mena, M.; Hoffmann, U.; Menjòn, B.; Petersen, J. L. *Organometallics* **1991**, *10*, 291–298. (b) Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583–589. (c) Anslyn, E. V.; Santarsiero, B. D.; Grubbs, R. H. *Organometallics* **1988**, *7*, 2137–2145. (d) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880–4890. (e) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721–724. (f) Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640–641. (g) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491–7496. (h) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658–1661.

(3) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158–165. (b) General reference: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 459–520. (c) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733–742. (d) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733–1744.

(4) (a) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979–7985. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56. (c) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425–437. (d) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *250*, 237–246. (e) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357–7360.

0276-7333/93/2312-3326$04.00/0

5f atom, since, to date, only structure optimizations of simple oxides, halides, and trimethyls have been reported.[5,6] Moreover, for thorium, only the energy surfaces of ThO and ThO_2 have been studied.[7]

Experimental Section

$Cp'_2\overline{Th(CH_2PMeC}H_2)$ was synthesized according to the published procedure.[4c] It was purified by sublimation in vacuo. The purity was checked by NMR and IR spectra. High resolution PE spectra were accumulated by an IBM PC AT computer directly interfaced to the PE spectrometer. The spectrometer was equipped with a He I/He II (Helectros Development) source. Resolution measured on the He $1s^{-1}$ line was invariably around 30 meV. The He II spectrum was corrected only for the He IIβ "satellite" contributions (10% on the reference N_2 spectrum). The procedure used for spectral deconvolution has been described elsewhere (R values ≤ 0.023).[8] The spectra were run in the 130–160 °C range without any evidence of thermal decomposition.

Computational Details

ECP ab initio restricted Hartree–Fock (RHF) calculations were used for geometry optimizations. The RECPs and basis set of Wadt[7a] were used for Th. The ECPs and basis set of Hay *et al.*[9] and Stevens *et al.*[10] were used for the Cl, P, and C atoms. Dunning's basis set[11] was adopted for H atoms. Valence Gaussian basis sets were contracted in a double-ζ (DZ) quality. A set of d-type polarization functions was added to phosphorus with a 0.45 exponent. Six components for "d" functions and ten for "f" functions were used. Electron correlation effects were included using second-order Møller–Plesset (MP2) perturbation theory[12] on optimized geometries.

The molecular geometry was fully optimized using the Powell method[13] on a model $Cl_2\overline{Th(CH_2PMeC}H_2)$ (**2**) structure, since there is ample precedent for satisfactorily replacing the computationally intractable Cp′ groups with simpler chloride ligands.[14] Two structures were optimized (Figure 1): (i) a puckered conformation (**2a**) obtained by folding the metallacycle ring (assuming C_s symmetry) and (ii) a fully planar structure (**2b**), related to the transition state for inversion at phosphorus (*vide infra*). The potential energy surface of structure **2a** shows a single energy minimum for the conformation with the P–CH_3 bond in an axial position.

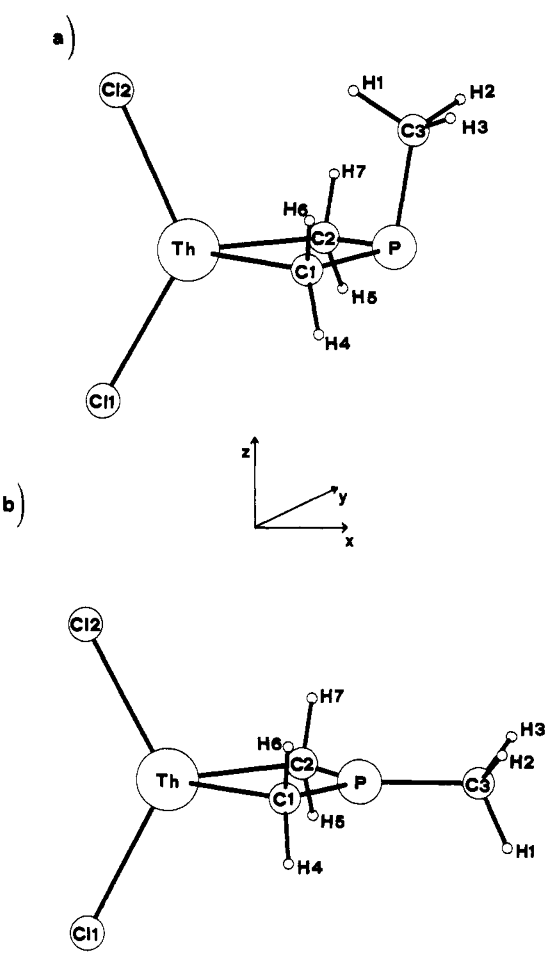


Figure 1. Coordinate system and optimized geometries of the model structure $Cl_2\overline{Th(CH_2PMeC}H_2)$ for the ground state (a) and phosphorus lone pair inversion transition state (b).

Hartree–Fock–Slater DV-Xα calculations[15] were used for ground state (GS) calculations on the model structures **2a** and on $Cp_2\overline{Th(CH_2PMeC}H_2)$ (**3**; Cp = η^5-C_5H_5) where only the ring methyl groups were neglected.[16] Numerical AOs (through 7p on Th, 3d on P, 2p on C, and 1s on H) were used as basis functions.[15,17] A frozen core approximation (1s, ..., 5p on Th; 1s, ..., 2p on P; 1s on C) was used throughout the calculations.[17] The molecular potential was improved by including multipolar fitting functions, which allow a very accurate description of the charge density.[18] Five radial degrees of freedom were allowed in the expansion of the density, in addition to the radial atomic density.[18] Several numerical calculations have been carried out in order to find the best basis set. The integration mesh used 2400 points around the Th atom, 300 points around P, 150 points around the C atoms, and 75 around the H atoms. The IEs were evaluated within the Slater transition state formalism[19] (TSIEs) to account for reorganization effects upon ionization. For a better understanding of the theoretical data, contour plots (CPs) of some selected MOs have also been analyzed. The Cp(centroid)–Th distances and the Cp–Th–Cp angle were

---

(5) (a) Bustern, B. E.; Strittmatter, R. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1069–1085. (b) Pepper, M.; Bustern, B. E. *Chem. Rev.* **1991**, *91*, 719–741. (c) Pyykkö, P. *Inorg. Chim. Acta* **1987**, *139*, 243–245.

(6) Ortiz, J. V.; Hay, P. J.; Martin, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2736–2737.

(7) (a) Wadt, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 6053–6057. (b) Marian, C. M.; Wahlgren, U.; Gropen, O.; Pyykkö, P. *THEOCHEM* **1988**, *169*, 339–354.

(8) Casarin, M.; Ciliberto, E.; Gulino, A.; Fragalá, I. *Organometallics* **1989**, *8*, 900–906.

(9) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284–298.

(10) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026–6033.

(11) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823–2833.

(12) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622.

(13) Powell, M. J. In *Numerical Methods for Nonlinear Algebric Equations*; Gordon and Breach: New York, 1981; p 87.

(14) (a) Hay, P. J.; Ryan, R. R.; Salazar, K. V.; Wrobleski, D. A.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1986**, *108*, 313–315. (b) Upton, T. H.; Rappè, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206–1218.

(15) (a) Averill, F. W.; Ellis, D. E. *J. Chem. Phys.* **1973**, *59*, 6411–6418. (b) Rosen, A.; Ellis, D. E.; Adachi, H.; Averill, F. W. *J. Chem. Phys.* **1976**, *65*, 3629–3634 and references therein. (c) Trogler, W. C.; Ellis, D. E.; Bekowitz, J. *J. Am. Chem. Soc.* **1979**, *101*, 5896–5901. (d) Ellis, D. E. In *Actinides in Perspective*; Edelstein, N. M., Ed.; Pergamon: Oxford, U.K., 1982; pp 123–143.

(16) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839–6846.

(17) (a) Bursten, B. E.; Casarin, M.; Ellis, D. E.; Fragalà, I.; Marks, T. J. *Inorg. Chem.* **1986**, *25*, 1257–1261. (b) Vittadini, A.; Casarin, M.; Ajò, D.; Bertoncello, R.; Ciliberto, E.; Gulino, A.; Fragalà, I. *Inorg. Chim. Acta* **1986**, *121*, L23–L25.

(18) Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949.

(19) Slater, J. C. *Quantum Theory of Molecules and Solids. The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4.

Table I. Selected Optimized Internal Coordinates (Å and deg) for the Ground State of $Cl_2Th(CH_2PMeCH_2)$[a]

Th–Cl1,Cl2	2.705	Cl1–Th–Cl2	126.5
Th–C1,C2	2.435	C1–Th–C2	73.0
P–C1,C2	1.895	Th–C1–C2–P	173.5
P–C3	1.850	C1–P–C3	99.5
		C1–P–C2	99.7

[a] Atom labeling refers to Figure 1a.

Table II. Selected Optimized Internal Coordinates (Å and deg) for the Phosphorus Inversion Transition State in $Cl_2Th(CH_2PMeCH_2)$[a]

Th–Cl1,Cl2	2.705	Cl1–Th–Cl2	125.0
Th–C1,C2	2.480	C1–Th–C2	77.0
P–C1,C2	1.850	Th–C1–C2–P	180.0
P–C3	1.835	C1–P–C3	123.4
		C1–P–C2	113.1

[a] Atom labeling refers to Figure 1b.

Table III. Ab Initio Eigenvalues and Population Analysis for the Highest Lying $Cl_2Th(CH_2PMeCH_2)$ MOs

	eV	Th[a]							dominant
MO	$-\epsilon_i$	7s	p	6d	5f	2Cl	$2CH_2$	PCH_3	character
16a′	8.35	0	0	14	2	1	33	50	$CH_2 + d_y{}^2 + P_{3p}$
8a″	11.08	0	4	17	3	7	59	10	$CH_2 + d_{xy}$
15a′	11.12	0	2	6	1	6	37	48	$P_{3p} + CH_2$
14a′	12.31	0	3	1	2	94	0	0	$\pi\ Cl_{3p}$
7a″	12.34	0	1	1	1	57	25	15	$\pi\ Cl_{3p}$ + P-CH_2
13a′	12.43	0	2	3	1	85	5	4	$\sigma\ Cl_{3p}$
6a″	12.57	0	0	7	1	86	5	1	$\pi\ Cl_{3p}$
5a″	12.67	0	2	5	1	39	42	11	P–CH_2 + $\pi\ Cl_{3p}$
12a′	12.80	0	2	8	1	88	1	0	$\sigma\ Cl_{3p}$
11a′	13.42	0	1	12	1	84	0	2	$\pi\ Cl_{3p}$
10a′	13.94	0	1	6	1	6	42	44	P–CH_2

Overall Charge

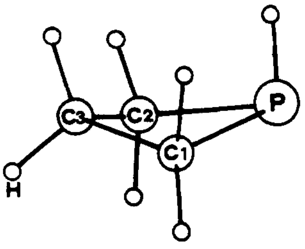
Th[a] = $5f^{0.83}$, $6d^{2.06}$, $7s^{0.01}$, $p^{5.98}$, +1.12
Cl = –0.43
CH_2 = –0.21
PCH_3 = +0.16

[a] 6s electrons are included in the RECP. The "p" population refers to the 6p and 7p contributions.

assumed identical to those of $Cp'_2Th(CH_2SiMe_2CH_2)$ (4).[4e] The geometrical parameters for the $>Th(CH_2PMeCH_2)$ fragment were taken from the optimized geometry of 2. The HONDO-8 code[20] was run on a IBM 9370 minicomputer. DV-Xα calculations were carried out on a Vax 11/750 minicomputer.

Results and Discussion

Geometrical Structure. The optimized ground state structure of the model phosphathoracyclobutane **2a** is shown in Figure 1a. Optimized geometrical data are collected in Table I. The structure consists of a slightly puckered four-membered ring having the P–CH_3 vector along an endocyclic axial orientation, with a pseudotetrahedral environment around the metal. A similar structure has been found using analogous computational techniques for the most stable conformations of both $Cl_2Zr(CH_2PMeCH_2)$[21] and of simpler phosphetane ($(CH_2)_3$-PH, **5**).[22] Furthermore, the calculated structure of **2**



5

exhibits close congruencies with diffraction results for the parent 1-silathoracyclobutane **4**.[4e] The present computationally derived structural parameters associated with the Th atom have typical values (Table I). Thus, the Th–C distance (2.435 Å) and the metallacyclic C–Th–C angle (73.0°) are both comparable to those found in **4**.[4e] The optimized Cl–Th–Cl angle (126.5°) and the Th–Cl distance (2.705 Å) are close to those found in Cp'_2ThCl_2[23] as well as in other thorium(IV) chloride complexes.[24] The geometry about the phosphorus atom is pyramidal with almost identical C–P–C angles (≈100°). The P–C1 distance (1.895 Å) lies in the range of those found in several phosphetanes[25] and close to those reported in the optimized structure of **5**.[22] Moreover, the optimized P–C3 distance (1.850 Å) is almost identical to that reported in the vapor-phase electron diffraction study of the trimethylphosphine (1.846 Å).[26] Note also that the present C1–P–C2 angle and P–C1 distance are comparable to C–Si–C and Si–C geometrical parameters found in **4**.[4e] An obvious consequence is an almost identical folding angle of the thoracycle rings along the C1···C2 vector on passing from **2a** (6.5°) to **4** (5.8°).[4e]

Four-membered ring puckering is known to depend upon two opposing effects: (i) ring strain,[27] which tends to stabilize ring planarity, and (ii) repulsion between neighboring groups, which favors ring puckering.[27] Therefore, while two perfectly symmetric puckered energy minima are found for all-carbon cyclobutane,[28] they are not symmetrical for the parent phosphetane **5**, where the most stable conformation consists of the axial methyl isomer because of electrostatic repulsion involving the P_{3p} lone pair and the H(C3) atom.[22] In phosphathoracyclobutane **2a**, one energy minimum is found at the axial methyl conformation which minimizes the repulsion between the P_{3p} lone pair and Cl1 atom. However, since the Th–C

---

[20] Dupuis, M.; Farazdel, A.; Karna, S. P.; Maluendes, S. A. In *MOTECC-90: Modern Techniques in Computational Chemistry*; Clementi, E., Ed.; ESCOM: Leiden, NL, 1990; Chapter 6, pp 277–342.

[21] The optimized geometrical structure of $Cl_2Zr(CH_2PMeCH_2)$, obtained using a gradient method, is consistent with a puckered four member ring having the P–CH_3 vector in an axial orientation, with a folding angle of 15°; Di Bella, S.; Gulino, A.; Lanza, G.; Fragalà, I. Work in progress.

[22] Bachrach, S. M. *J. Phys. Chem.* **1989**, *93*, 7780–7784.

[23] Marks, T. J.; Day, V. W. Unpublished results.

[24] (a) Marks, T. J.; Day, V. W. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I. L., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1985; pp 115–158. (b) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, W. E., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 21, pp 173–270. (c) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1975; Chapter 9.

[25] Fitzgerald, A.; Campbell, J. A.; Smith, G. D.; Caughlan, C. N.; Cremer, S. E. *J. Org. Chem.* **1978**, *43*, 3513–3517.

[26] Hargittai, M.; Hargittai, I. *The Molecular Geometries of Coordination Compounds in the Vapor Phase*; Elsevier: Amsterdam, NL, 1977; pp 38–64.

[27] (a) Günther, H.; Schrem, G.; Oberhammer, H. *J. Mol. Spectrosc.* **1984**, *104*, 152–164. (b) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311–354.

[28] Boatz, J. A.; Gordon, M. S.; Hilderbrandt, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 352–358.

Table IV. Xα DVM Eigenvalues, Ionization Energies, and Population Analysis for the Highest Lying $Cp_2Th(CH_2PMeCH_2)$ MOs

	−eV	eV		rel int[c]		Th							
MO[a]	GS	TSIE	IE[b]	He I	He II	7s	7p	6d	5f	2Cp	$2CH_2$	PCH_3	dominant character
28a′	4.01					0	0	2	94	4	0	0	f_{xz^2}
27a′	4.72	7.29	6.65 (a)	0.97	0.80	2	2	3	21	6	40	26	$CH_2 + f_{x(x^2-3y^2)} + P_{3p}$
16a″	6.06	8.34	7.10 (b)	0.90	0.88	0	4	7	7	37	44	1	$CH_2 + d_{xy} + f_{y(3x^2-y^2)}$
26a′	6.22	8.51	8.47 (e)	1.03	0.77	0	1	0	0	36	18	45	$P_{3p} + \pi_2 + CH_2$
15a″	6.99	9.26	7.42 (c)	1.77	1.80	0	0	9	4	68	19	0	$\pi_2 + d_{xy}$
25a′	7.00	9.68				0	0	4	3	85	4	2	π_2
24a′	7.21	9.81	7.78 (d)	1.20	1.33	0	0	4	1	74	9	12	π_2
14a″	7.28	9.96	8.08 (d′)	1.16	1.25	0	0	8	1	88	3	0	$\pi_2 + d_{yz}$
13a″	8.25	11.01				0	0	0	0	2	60	38	$P-CH_2$
23a′	8.98	11.34				0	2	0	0	7	39	52	$P-CH_2$

Overall Charge
$Th = 6s^{1.94}, 6p^{5.73}, 5f^{1.05}\ 6d^{1.13}, 7s^{0.04}, 7p^{0.05} = +2.06$
$Cp = -0.625$
$CH_2 = -0.52$
$PCH_3 = +0.23$

[a] 28a′ = LUMO; 27a′ = HOMO. [b] Lettering in parentheses refers to the band labels in Figure 5. Experimental IEs are related to the position of the Gaussian components. [c] Relative intensities are normalized to the total intensity of the a–e envelope assumed as seven arbitrary units. The parameters used for deconvolutions are reported as supplementary material (Table SIII).

distances are substantially greater than the corresponding P–C distances in **5**, repulsive effects between neighboring groups within the ring are correspondingly smaller. The axial methyl isomer of **2a** is the most stable since the energy lowering due to the ring puckering in the equatorial isomer does not balance the greater P_{3p}–Cl1 repulsion. Finally, smaller intraligand nonbonded interactions are responsible for the smaller estimated folding angle in **2a** (6.5°) compared to the simpler phosphetane **5** (24.4°). Note that the folding angle in other structurally characterized IVB group metallacyclobutane complexes varies from 3.25° in $Cp_2Ti(CH_2CMe_2CH_2)$[29] to 4.7 and 7.7° in $Cp_2M(CH_2SiMe_2CH_2)$, M = Zr and Ti, respectively.[30]

The inversion energy barrier about the phosphorus lone pair has been estimated via a transition state structure constrained in a fully planar conformation, **2b** (Figure 1b). Selected optimized geometrical parameters of **2b** are reported in Table II. The evaluated energy barriers are 43.8 and 39.2 kcal/mol at RHF/DZ and MP2/DZ levels, respectively. Both values are comparable to those obtained from calculations on **5**, RHF/DZ (45.8 kcal/mol) and MP2/DZ (42.7 kcal/mol).[22] These results are in excellent agreement with NMR data on **1** which point both to a slightly puckered structure with inversion at the P atom which is slow on the NMR time scale[4c] and to the absence of any interaction between the thorium center and phosphorus lone pair.[4c] Note also that the computationally derived dihedral angles (9 and 109°) defined by the phosphorus lone pair and the methylene C–H bonds in **2a** are in good agreement with values derived from experimental[4c] $^2J_{P-H}$ parameters and straightforward application of Karplus-like relationships for phosphines.[31]

Electronic Structure and Bonding. GS eigenvalues and Mulliken populations of the topmost MOs of the $Cl_2Th(CH_2PMeCH_2)$ model complex (**2a**) are summarized in Table III. The outermost occupied MOs are arranged in an expected[1a,32] energy sequence based on the dominant atomic contributions. Within the context of a simple localized bonding model,[33] the filled 16a′ (HOMO) and the 8a″ orbitals correspond to the symmetry combinations of the two (Th–C) σ bonds. In marked contrast to results obtained for several related Cp_2MMe_2 complexes,[32,34] but in agreement with recent computational and experimental results on $Cp_2Th(CH_2SiMe_2CH_2)$,[1a] the 16a′ in-phase linear combination is less tightly bound than the out-of-phase combination 8a″. This is a straightforward consequence of the greater (17%) metal 6d mixing in the 8a″ than in the 16a′ MO (14%) and of extensive mixing with the more internal 15a′ MO formally representing the P_{3p} lone pair. The 14a′–11a′ orbitals represent the set of Cl_{3p} σ- and π-related[32] orbitals. The remaining orbitals account for the P–C interactions within the metallacyclic ring. The gross atomic population on the Th atom (+1.12 eu) is indicative of an appreciable metal–ligand covalency. Individual atomic contributions ($6d^{2.06}$ and $5f^{0.83}$) indicate a major role of metal 6d AOs in the bonding. These values agree with previous relativistic pseudopotential ab initio,[7] quasi-relativistic HFS,[35] and fully-relativistic DV–Xα[36] calculations on Th compounds.

Upon switching to the bis(cyclopentadienyl) homologue, **3**, comparable results are obtained. Theoretical Xα GS eigenvalues associated with uppermost filled MOs are listed in Table IV. The electronic structure of metallacyclobutane complexes can be better formulated in terms of bridging of the two heterodinuclear units Cp_2Th and PCH_3 by two μ-CH_2 groups. A similar model has already been used successfully to describe the parent 1-silathoracyclobutane homologue, **4**.[1a] The energy sequence, therefore, is that expected on the basis of the earlier results for the aforementioned 1-silathoracyclobutane complex.

---

[29] Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358–7361.

[30] (a) Tikkanen, W. R.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646–1650. (b) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 825–830.

[31] (a) Albrand, J. P.; Gagnaire, D.; Martin, J.; Robert, J. B. *Bull. Soc. Chim. Fr.* **1969**, 40–48. (b) Albrand, J. P.; Gagnaire, D.; Robert, J. B. *J. Chem. Soc., Chem. Commun.* **1968**, 1469–1470.

[32] Ciliberto, E.; Condorelli, G.; Fagan, P. J.; Manriquez, J. M.; Fragalà, I.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 4755–4759.

[33] Evans, S.; Hamnett, A.; Orchard, A. F.; Lloyd, D. R. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 227–250.

[34] (a) Green, J. G.; Jackson, S. E. *J. Chem. Soc., Dalton Trans.* **1976**, 1698–1702. (b) Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 45–145. (c) Creber, D. K.; Bancroft, G. M. *Inorg. Chem.* **1980**, *19*, 643–648.

[35] (a) Höhl, D.; Ellis, D. E.; Rösch, N. *Inorg. Chim. Acta* **1987**, *127*, 195–202. (b) Höhl, D.; Rösch, N. *Inorg. Chem.* **1986**, *25*, 2711–2718. (c) Rösch, N. *Inorg. Chim. Acta* **1984**, *94*, 297–299. (d) Rösch, N.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 7237–7240.

[36] (a) Gulino, A.; Di Bella, S.; Fragalà, I.; Casarin, M.; Seyam, A.; Marks, T. J. *Inorg. Chem.*, in press. (b) Boerrigter, P. M.; Baerends, E. J.; Snijders, J. G. *Chem. Phys.* **1988**, *122*, 357–374.

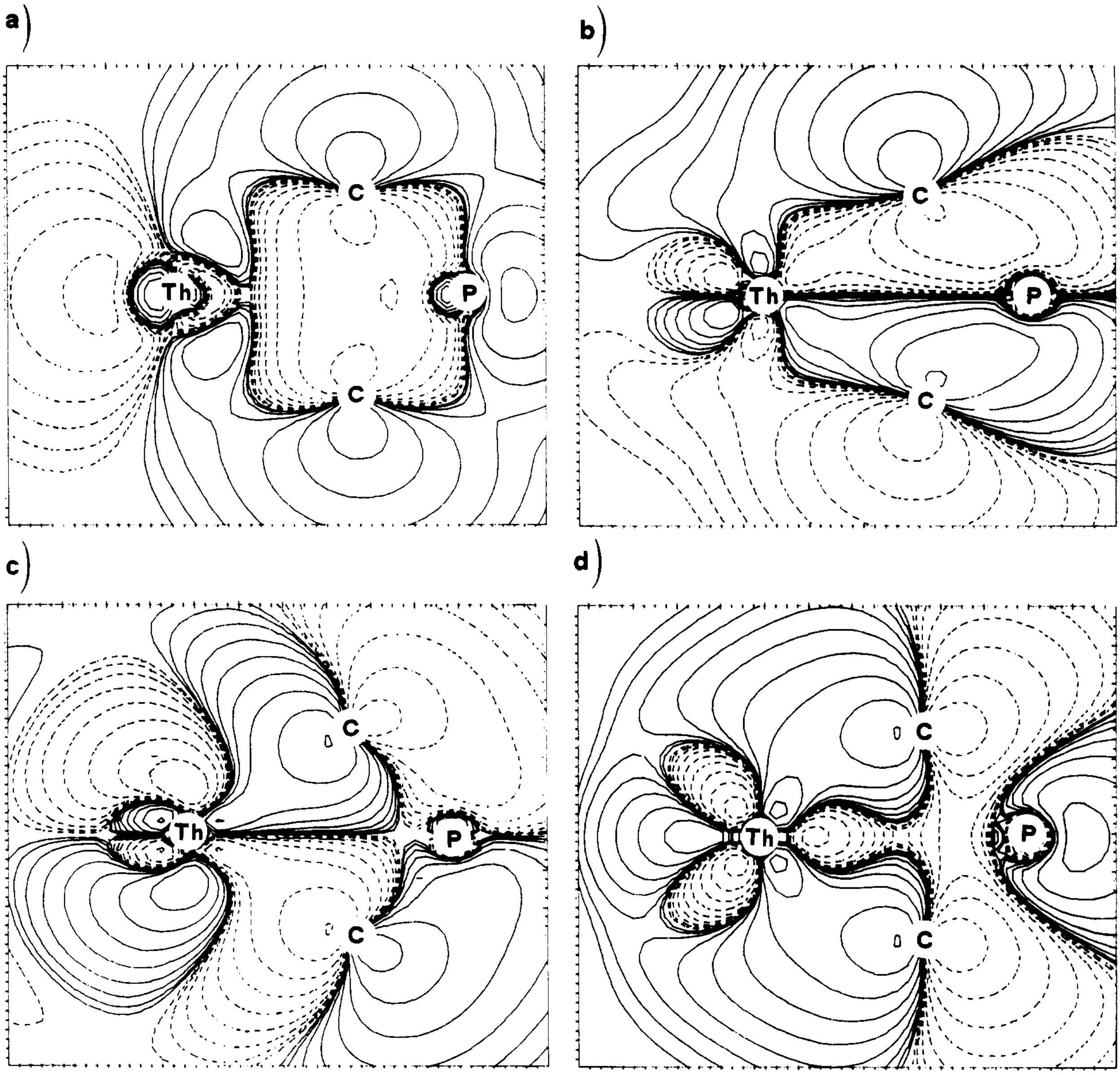


Figure 2. DV-Xα contour plots for the (a) 23a′, (b) 13a″, (c) 16a″, and (d) 27a′ MOs in the xy plane of the complex $Cp_2Th(CH_2PMeCH_2)$. The contour values are ±0.0065, ±0.013, ±0.026, ±0.052, ±0.104, ±0.208, ±0.416, and ±0.832 $e^{1/2}$ Å$^{3/2}$. Dashed lines refer to negative values.

The 27a′, 16a″, 13a″, and 23a′ MOs are associated with the four-membered ring. The corresponding electron density contour plots (Figure 2) are isolobal counterparts of relevant topmost filled MOs of cyclobutane[37] and of the parent 4.[1a] The 26a′–14a″ MOs represent Cp π_2-related MOs,[38] and finally, 26a′ is representative of the P_{3p} lone pair (Figure 3) even though the orbital is comparably admixed with both the Cp π_2- and μ-CH_2-based orbitals. The formation of the heterodinuclear four-membered ring brings about a nearly uniform accumulation of electron density in the internuclear regions of the thoracyclobutane ring, as illustrated by the total and difference charge density contour maps[39] (Figure 4). As generally found with Xα calculations on f-element organometallics, the metal–ligand bonding involves both 5f and 6d metal AOs.[36] In particular, higher energy MOs have dominant 5f contributions while those lying lower have a 6d admixture. Compared to ab initio relativistic results on the parent dichloride **2a** (Tables III and IV), a general and expected[36] underestimation of 6d admixture is also observed.

Photoelectron Spectra. The low IE region of the PE spectrum of 1 consists of six bands labeled a–e (Figure 5a,b). The spectral features have a close counterpart (Figure 5c) in those of the parent 1-sila derivative, 4.[1a] The band envelope of 1, however, possesses a larger width (1.82 vs 1.10 eV) because of the presence of a new higher IE shoulder (e) and of a lower IE shift (0.18 eV) of band a (Figure 5c). The spectra, of course, lack bands assignable to Si–CH_3 ionizations,[40] which are present in the 9–10-eV

---

[37] (a) Hoffmann, R.; Davison, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699–5705. (b) Chu, S.-Y.; Hoffmann, R. *J. Phys. Chem.* **1982**, *86*, 1289–1297.

[38] (a) Evans, S.; Green, M. L. H.; Jewitt, A. F.; Orchard, A. F.; Pygall, C. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1847–1865. (b) Evans, S.; Green, M. L. H.; Jewitt, A. F.; King, G. H.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 356–376.

[39] (a) Kutzler, F. W.; Swepston, P. N.; Berkovitch-Yellin, Z.; Ellis, D. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 2996–3004. (b) Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949–1960. (c) Berkovitch-Yellin, Z.; Ellis, D. E. *J. Am. Chem. Soc.* **1981**, *103*, 6066–6073. (d) Ellis, D. E.; Berkovitch-Yellin, Z. *J. Chem. Phys.* **1981**, *74*, 2427–2435.

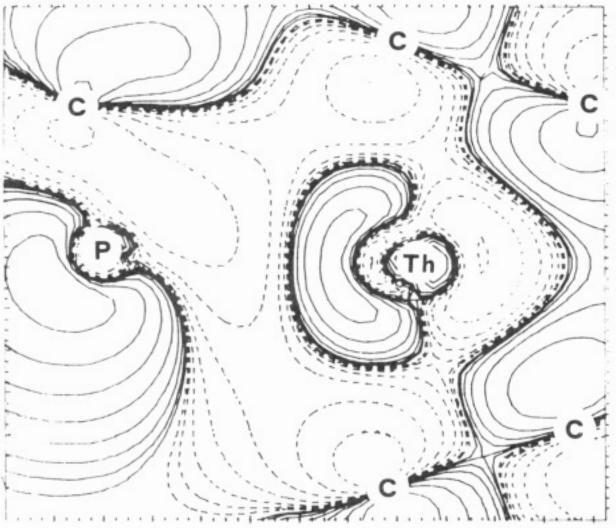


Figure 3. DV–Xα contour plots for the 26a′ MO in the xz plane of the complex $Cp_2Th(CH_2PMeCH_2)$. The contour values are ±0.0065, ±0.013, ±0.026, ±0.052, ±0.104, ±0.208, ±0.416, and ±0.832 $e^{1/2}$ $Å^{3/2}$. Dashed lines refer to negative values.

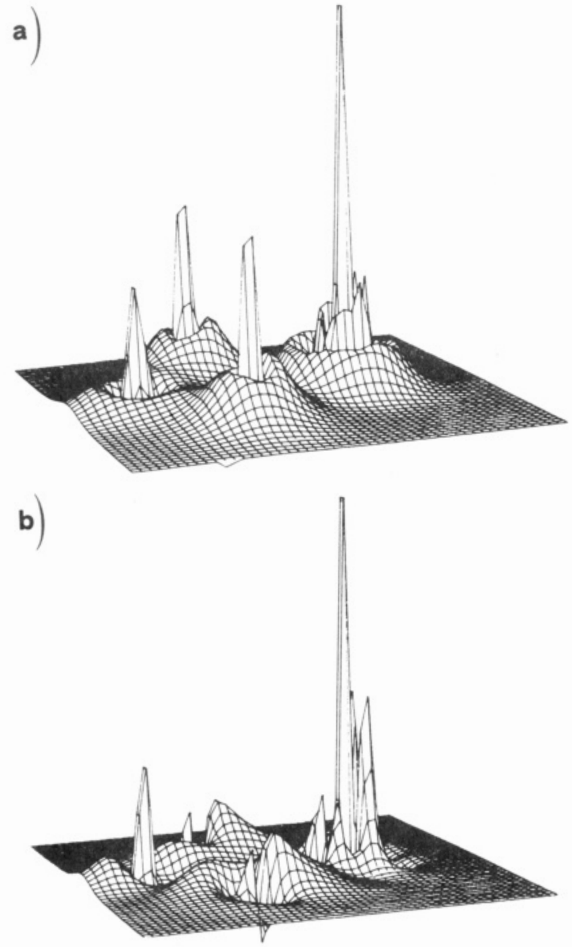


Figure 4. (a) Total charge density and (b) difference charge density pseudo-three-dimensional contour plots for the $Cp_2Th(CH_2PMeCH_2)$ molecule in the xy plane.

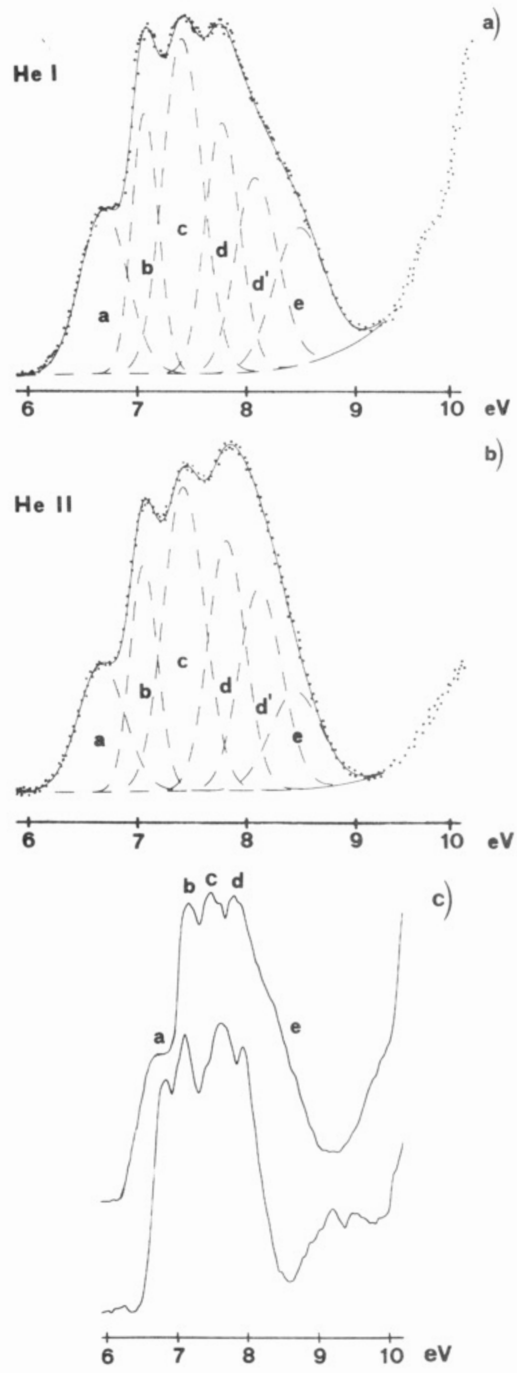


Figure 5. (a) He I and (b) He II PE spectra of $Cp'_2Th(CH_2PMeCH_2)$ in the 5.9–10.2-eV region. Experimental spectra are represented by dotted lines, Gaussian components by dashed lines, and the convolution of Gaussian components by solid lines. (c) He I PE spectra of $Cp'_2Th(CH_2PMeCH_2)$ (top) and $Cp'_2Th(CH_2SiMe_2CH_2)$ (bottom).

region of the PE spectrum of **4** (Figure 5c).[1a] All these observations suggest that the band envelope a–e in the spectra of **1** includes ionization of the P_{3p} lone pair in addition to those of the (Th–C) MOs and the four Cp π_2-related ionizations. Some sizable relative intensity variations are observed on passing to He II radiation (Table IV). In particular, while the intensities of bands b–d′ remain constant (with a few percent), the bands a and e have reduced intensities.

---

(40) (a) Cundy, C. S.; Lappert, M. F.; Pedley, J. B.; Schmidt, W.; Wilkins, B. T. *J. Organomet. Chem.* **1973**, *51*, 99–104. (b) Koenig, T.; McKenna, W. *J. Am. Chem. Soc.* **1981**, *103*, 1212–1213. (c) Dyke, J. M.; Josland, G. D.; Lewis, R. A.; Morris, A. *J. Phys. Chem.* **1982**, *86*, 2913–2916. (d) Evans, S.; Green, J. C.; Joachim, P. J.; Orchard, A. F.; Turner, D. W.; Maier, J. P. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 905–911.

Comparative arguments using both theoretical TSIE values (Table IV) as well as the experimental IE values of parent complex 4[1a] (Figure 5c), suggest that bands a and b represent ionization of 27a′ and 16a″ σ (Th–C) MOs. Bands c, d, and d′ must then be associated with ionization of Cp π_2-related MOs. Finally, the higher IE shoulder, e, is assignable to the P_{3p} lone pair (Table IV). This assignment is also entirely consistent with PE data for related phosphines,[41] as well as with the aforementioned variations of He II relative intensities. On the basis of previous studies, PE bands having significant 5f admixture are expected to have greater intensities relative to those representing either C_{2p}-based or 6d admixed MOs.[42] In addition, there is evidence that P_{3p}-based MOs give PE bands of reduced He II intensity.[41,43] In this context, it becomes understandable that bands a and e decrease in the He II spectrum since corresponding MOs have P_{3p} admixture and, moreover, that the effect is less pronounced in the case of the 27a′ MO since the P_{3p} admixture is partially balanced by the 5f contribution. In addition, the significant (relative to homologue 4[1a]) lower energy shift of band a (6.65 vs 6.83 eV) is in accord with the destabilization of the 27a′ MO caused by admixture with the lower energy P_{3p}-based MO (Table IV). The observed discrepancy with the theoretically derived sequence is likely due to the simplified model adopted for calculations on 1, which lacks cyclopentadienyl ring methyl groups. It is well-known that the effect of ring permethylation is a differential ~1 eV) shift of the ionization associated with Cp π_2-related MOs,[16] and in the present case, this would be expected to invert the $P_{3p} < \pi_2$ sequence.

Conclusions

The relativistic effective core potential formalism has been used for geometry optimization of the model thoracyclobutane $Cl_2Th(CH_2PMeCH_2)$. The calculations predict a slightly puckered four-membered cyclic structure in accordance with NMR data for the known complex $Cp'_2Th(CH_2PMeCH_2)$. These results indicate that this approach can be used to predict the structures of interesting f-element complexes for which diffraction data may not be obtainable, as successfully used for structure predictions of molecules containing main group and early transition elements.[44]

Multipolar DV-Xα calculations together with experimental arguments have provided a convincing rationale for the assignment of the $Cp'_2Th(CH_2PMeCH_2)$ He I and He II PE spectra. The combination of these theoretical and experimental techniques clearly represents an efficient, chemically-oriented tool for describing structure and bonding in f-metal organometallics.

Acknowledgment. We gratefully thank the Ministero della Università e della Ricerca Scientifica e Tecnologica (MURST, Rome, Italy; A.G., G.L., I.L.F.), and the National Science Foundation (Grant CHE 9104112; T.J.M.) for financial support.

Supplementary Material Available: Tables of optimized Cartesian coordinates for the ground state (Table SI) and the phosphorus inversion transition state (Table SII) of $Cl_2Th(CH_2PMeCH_2)$ and PE data for $Cp'_2Th(CH_2PMeCH_2)$ giving integrated intensities and line widths (Table SIII) (3 pages). Ordering information is given on any current masthead page.

OM930050V

---

(41) (a) Puddephatt, R. J.; Bancroft, G. M.; Chan, T. *Inorg. Chim. Acta* **1983**, *73*, 83–89. (b) Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033–7037. (c) Ashe, A. J., III; Burger, F.; El-Sheik, M. Y.; Heilbronner, E.; Maier, J. P.; Muller, J.-F. *Helv. Chim. Acta* **1976**, *59*, 1944–1948.

(42) Brennan, J. G.; Green, J. C.; Redfern, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 2373.

(43) Rabelais, J. W. *Principles of UV Photoelectron Spectroscopy*; Wiley: New York, 1977; p 335.

(44) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986. (b) Schaefer, H. F., III. *Applications of Electronic Structure Theory*; Plenum Press: New York, 1977.