RAPID COMMUNICATION / COMMUNICATION RAPIDE

Synthesis, characterization, and reactivity of the first hafnium alkyl complex stabilized by amidate ligands¹

Robert K. Thomson, Brian O. Patrick, and Laurel L. Schafer

Abstract: A photo and thermally stable bis(amidate)–dibenzyl complex of Hf $([^{DMP}(NO)^{Ph}]_2Hf(CH_2Ph)_2(THF)$ (**2a**) was formed as a monosolvated THF adduct in near quantitative yield from Hf(CH₂Ph)₄ and *N*-2,6-dimethylphenyl(phenyl)amide (**1**). Isomerization between the THF-bound product and the THF-free product can be observed visually by the conversion from a red-orange product at low temperatures to a pale yellow product at high temperatures. Solid-state crystallographic characterization of the orange product confirmed its constitution as a monosolvated species. Kinetic parameters for the exchange of the THF moiety were determined from variable-temperature NMR experiments. The product of the hydrolysis of the Hf dibenzyl species by water was characterized by X-ray crystallography, and was found to be a rare tetrametallic Hf oxo cluster species (**3**).

Key words: hafnium, protonolysis, amidate, coordination chemistry, organometallic chemistry, exchange processes.

Résumé : Un complexe de bis(amidate)–dibenzyle de Hf $([^{DMP}(NO)^{Ph}]_2Hf(CH_2Ph)_2(THF)$ (**2a**) qui est stable à la lumière et à la chaleur a été formé comme adduit monosolvaté de THF avec un rendement presque quantitatif de Hf(CH₂Ph)₄ et *N*-2,6-dimethylphenyl(phenyl)amide (**1**). L'isomérisation entre le produit avec THF et le produit sans THF peut être observée visuellement par la conversion d'un produit rouge-orange aux températures basses en un produit jaune pâle aux températures élevées. La caractérisation cristallographique du produit orange à l'état solide a confirmé sa constitution comme l'espèce monosolvaté. Des paramètres cinétiques pour l'échange du THF ont été déterminés à partir d'expériences de RMN à la température variable. Le produit d'hydrolyse de l'espèce dibenzyle de Hf par l'eau a été caractérisé par cristallographie de rayons X et c'est une espèce rare d'agrégat oxotétramétallique de Hf (**3**).

Mots clés : hafnium, protonolyse, amidate, la chimie de coordination, la chimie organométallique, processus d'échange.

Introduction

Much of the recent research in Group 4 metal chemistry has involved the development of new non-cyclopentadienyl (Cp) ligands and the exploration of their reactivity (1). In recent reports from our research group, we have shown that amidate ligands are versatile ancillary ligands for Group 4 metals (2–4). The amide proligands are highly modifiable and are synthesized in a modular manner, making them attractive alternatives to Cp (Fig. 1). The amide proligands have a p K_a of approximately 15, which makes protonolysis a highly useful method of synthesizing metal complexes. In particular, we have shown that the synthesis of bis(amidate)–bis(amido) complexes of Ti and Zr is facile and high yielding, and can be accomplished via protonolysis of commercially available tetrakisamido metal starting materials (2, 3). Since amidate ligands have been underexplored in early transition metal chemistry, there is a need to discover the general utility of these ligands to support reactive metal centers. To this end, here we report the first examples of stable bis(amidate)–dibenzyl complexes of Hf. The stability and coordination geometry of this new class of complexes has been established by X-ray crystallographic analysis as well as VT NMR spectroscopic investigations.

Received 17 November 2004. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 2 July 2005.

Dedicated to Professor Howard Alper.

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¹This article is part of a Special Issue dedicated to Professor Howard Alper. ²Corresponding author (e-mail: schafer@chem.ubc.ca).





Results and discussion

Easily assembled modular ligand systems are important in expediting the discovery of catalyst systems for various organic transformations (5). Organic amides offer an easily modified scaffold for the study of ligand-based effects in their resultant transition metal complexes. A general synthetic scheme for the preparation of organic amides is shown in eq. [1]. Elimination of HCl upon reaction of an acid chloride and a primary amine results in the formation of the desired amide product in high yields (75%–95% yield). Purification of these proligands for use in metal chemistry can be accomplished by vacuum sublimation or recrystallization from an appropriate solvent. Proligand 1 (N-2,6-dimethylphenyl(phenyl)amide) was synthesized in excellent yield. Purification via recrystallization from CHCl₃ at –20 °C and



subsequent drying while heating under vacuum overnight gave pure proligand **1** in 64% yield.

Protonolysis reactions have been utilized successfully in the synthesis of amidinate (6) and guanidinate (7) complexes of the Group 4 metals. Given the structural similarity of the amidate ligand motif, protonolysis was anticipated to be an efficient route into analogous amidate complexes. The protonolysis methodology used to form this bis(amidate)– bis(alkyl) Group 4 metal complex (**2a**) was facile and high yielding (eq. [2]). Freshly prepared and recrystallized Hf(CH₂Ph)₄ was combined with 2 equiv. of proligand **1** ([^{DMP}(NO)^{Ph}]H) in a darkened Schlenk flask, which was cooled to -78 °C before introduction of THF via cannula transfer. Warming to room temperature resulted in the for-



mation of a bright red-orange solution, which was concentrated in vacuo to give a bright orange powder in 98% crude yield. Low temperatures utilized during this process were necessary to control the rate of reaction, as reaction at room temperature results in the formation of the desired product contaminated with a homoleptic side-product. In addition, the starting material (Hf(CH₂Ph)₄) is well-known to exhibit a high sensitivity towards ambient visible light, and the





protonolysis of the Hf—C bonds proceeds very rapidly and exothermically because of the low pK_a of the organic amide proligands.

Purification of this complex in moderate yield can be achieved by recrystallization from a concentrated solution of **2a** in hexanes, giving orange single crystals. X-ray crystallographic analysis of this complex revealed that the bis(amidate)–dibenzyl species is monosolvated by THF in the solid state, as shown in Fig. 2. Selected bond lengths and angles are found in Table 1 and crystallographic details are located in Table 2.

The solid-state structure of **2a** exhibits pseudo- $C_{2\nu}$ symmetry in a slightly distorted pentagonal bipyramidal geometry. This coordination geometry has been previously observed for seven-coordinate salen complexes of Hf (8), acetylacetonato complexes of Zr (9), and structurally related monothiocarbamate and dithiocarbamate complexes of Ti (10, 11). Both amidate ligands in 2a are found in the equatorial plane, with the O atoms nearly trans to each other at 156°. A bound THF molecule occupies the final equatorial coordination site. The plane containing Hf and the N and O donor atoms is nearly perfectly planar, with the sum of the bond angles about the Hf center being 360.2°. In the axial positions, the two benzyl groups are located 169.8° apart. As expected, the Hf1-O3 bond length of the coordinated THF (2.236 Å) is significantly longer than the Hf1-O1 and Hf1—O2 bond lengths (2.161 and 2.174 Å, respectively). Bond lengths between the amidate N atoms and the Hf center are somewhat longer than the corresponding Hf amidate O bond lengths (Hf1-N1 = 2.265 Å, Hf1-N2 = 2.258 Å), indicating that the amidate ligands are bound in an alkoxy-imine fashion (2). Unexpected elongation of the C-N bond in the ligand backbone is also observed; however, the steric bulk at the N of the amidate ligands precludes the formation of the anticipated shorter C-N bond. This ligand binding motif has been seen previously by our group for bis(amidate)-bis(amido) complexes of Ti and Zr (2, 4). There are some variations from expected bond lengths, which may be due to the unique π -stacking interactions present between the coplanar N-aryl rings of the amidate ligands, whose centroids are separated by approximately 3.6 Å. Intramolecular

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°	
Bond distances (Å)	
Hf(1) - O(1)	2.161(4)
Hf(1)—O(2)	2.174(4)
Hf(1)—O(3)	2.236(4)
Hf(1) - N(1)	2.258(5)
Hf(1) - N(2)	2.265(5)
Hf(1)—C(31)	2.326(6)
Hf(1)—C(38)	2.328(5)
N(1)—C(1)	1.308(7)
N(2)—C(16)	1.325(7)
O(1)—C(1)	1.303(7)
O(2)—C(16)	1.282(7)
Bond angles (°)	
O(1)-Hf(1)-N(1)	59.53(15)
O(2)-Hf(1)-N(2)	59.45(16)
N(1)-Hf(1)-N(2)	84.81(17)
O(1)-Hf(1)-O(3)	77.61(15)
O(2)-Hf(1)-O(3)	78.76(15)
C(31)-Hf(1)-C(38)	169.8(2)
N(1)-C(1)-O(1)	114.7(5)
N(2)-C(16)-O(2)	114.9(5)

Table 1. Selected bond distances (Å) and angles (°) for $[^{DMP}(NO)^{Ph}]_2Hf(CH_2Ph)_2(THF)$ (**2a**).

Table 2. Crystallographic data and refinement details for $[^{DMP}(NO)^{Ph}]_2Hf(CH_2Ph)_2(THF)$ (2a).

Empirical formula	$C_{48}H_{50}HfN_2O_3$
Formula weight	881.39
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a, b, c</i> (Å)	11.605(2), 12.207(2), 16.353(2)
α, β, γ (°)	103.027(2), 102.455(2), 106.651(3)
V (Å ³)	2 062.6(5)
Ζ	2
$D_{\text{calcd}} \text{ (g cm}^{-3})$	1.419
μ (Mo K α) (cm ⁻¹)	34.60
<i>T</i> (K)	173
2θ range (°)	55.7
Total reflections	18 282
Unique reflections	8 417
Parameters	491
R_1^a	0.0624
$R_w^{\ a}$	0.1169
Goodness-of-fit	1.153

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|; R_{w} = \Sigma (|F_{o}^{2}| - |F_{c}^{2}|)^{2} / (\Sigma w |F_{o}^{2}|^{2})^{1/2}.$

monometallic π -stacking interactions of this type are rare, but the phenyl ring separation of 3.6 Å is consistent with a previously reported π -stacking interaction in a Ti – late metal bimetallic species, in which the interactions ranged between 3.51 and 3.77 Å (12). In our case, the bulky 2,6dimethylphenyl rings orient themselves in a cis fashion in the crystal structure and are stabilized by the π interaction between them. Furthermore, the difference between the two ligand C—O, C—N bond asymmetries may be due to the slight canting of the rings to one side, resulting in more steric crowding of the C16—N2 bond than the C1—N1 bond. These observations could also be due to crystal packing effects.

¹H and ¹³C NMR spectra of the recrystallized orange product indicate that the solid state $C_{2\nu}$ symmetry of this species is maintained in solution at room temperature. A single resonance is seen for the aryl methyl protons at δ 2.34 ppm, and the requisite singlet for the benzylic methylene protons is present at δ 2.55 ppm. Bound THF peaks are also present at δ 1.64 and 3.83 ppm. The ¹³C NMR spectrum showed a broadened signal at δ 81.64 ppm, which was correlated to the broadened THF OCH₂CH₂ proton signal at δ 3.83 ppm in the ¹H NMR spectrum by ¹H¹³C HMQC. Dissolution of the orange crystals of 2a in C_6D_6 at room temperature immediately resulted in a light orange solution. Warming of the tube resulted in a color change to pale yellow, and cooling of the tube to temperatures at or below 0 °C was accompanied by a color change to a deep orange. Given these preliminary observations, we suspected that the THF solvated complex 2a is stable in the solid state, but undergoes exchange to the unsolvated species 2b in solution (eq. [3]).

Variable-temperature NMR experiments were performed on the orange product **2a** to verify the THF exchange process and to determine the activation energy (ΔG^{\ddagger}) and the rate of exchange (k_{solv}). The two bound THF peaks are observed to broaden in response to decreased temperature. The peak at δ 3.59 ppm is observed to broaden and split into two peaks at δ 4.12 and 3.50 ppm that sharpen at -50 °C. The co-



alescence temperature for these two peaks, corresponding to bound and free THF, respectively, occurs at (-25 ± 5) °C. The rate constant for the THF exchange process was calculated to be (560 ± 110) s⁻¹, and the activation energy for this process was likewise found to be (47 ± 1.5) kJ mol^{-1.3} To verify that the yellow product observed at higher temperatures was desolvated, this compound was isolated as a powder by removing all solvent at elevated temperatures. The ¹H NMR spectrum of this compound does not show the presence of any THF. Independent synthesis of the yellow product in toluene yielded material that gave identical NMR spectroscopic data as seen in the aforementioned preparation of **2b**. Ongoing investigations are focused on complete structural characterization of this complex.

Although complexes 2a and 2b are stable to ambient light and heat (prolonged heating at 80 °C resulted in slow decomposition), they are highly sensitive to moisture and can be hydrolyzed by the presence of trace amounts of H₂O. Slow hydrolysis of 2a by reaction with adventitious water resulted in the formation of the novel tetrametallic-bridged oxo species shown in Fig. 3. Complex **3** exhibits C_2 symme-

³Determined by NMR methods as described in ref. 13.



Fig. 3. ORTEP representation of the solid-state molecular structure of $\{[^{DMP}(NO)^{Ph}]_2Hf(\mu-O)\}_4$ (3) (the aryl rings have been omitted for clarity).

try in the solid state, with two pairs of different bridging oxo ligands, depicted in Fig. 3. Selected bond lengths and angles are given in Table 3, and crystallographic data is located in Table 4. The C_2 axis is located along the vector joining O9 and O11. It can also be seen that half of the amidate ligands are bound η^2 to a single Hf center analogous to complex 2, and the other half are bridging between two adjacent Hf atoms. This is the first example of these bulky amidate ligands adopting a bridging mode for Group 4 metals. Independent synthesis of the hydrolyzed product resulted in the formation of an insoluble white powder that has resisted recrystallization. EI-MS data of this species did not give a parent ion, however, monomeric fragments ($[^{DMP}(NO)^{Ph}]_2HfO$) and higher order fragments ($[^{DMP}(NO)^{Ph}]_3HfO$, $[^{DMP}(NO)^{Ph}]_3Hf_2O_3$), were observed, which supports the formation of a complex oligomeric structure. Due to the low solubility of this complex, full spectroscopic characterization was not possible: however, the formation of toluene was observed and interestingly, there was no evidence of free ligand in the soluble fraction. The lack of complete hydrolysis of the amidate ligands implies that the amidate-Hf bonding interactions are strong and can act as robust ancillary ligands during reactions at the metal center. We are currently taking advantage of this observed stability and are investigating a wide range of reactivity of complexes 2a and 2b.

Conclusion

The first amidate-stabilized Hf alkyl complex was synthesized and structurally and spectroscopically characterized. The bis(amidate)–dibenzyl Hf species (2a) is pentagonal bipyramidal in the solid state, with an interesting intramolecular π -stacking interaction stabilizing the complex. Monosolvation of 2a was observed in the solid state, with

Table 3. Selected bond distances (Å) and angles (°) for $\{[^{DMP}(NO)^{Ph}]_2Hf(\mu-O)\}_4$ (3).

Bond distances (Å)	
Hf(1) - O(1)	2.182(3)
Hf(1)—O(8)	2.230(3)
Hf(1)—O(10)	2.000(3)
Hf(1) - O(11)	1.978(3)
Hf(1) - N(1)	2.327(4)
Hf(1) - N(2)	2.474(4)
Hf(1)— $Hf(4)$	3.2423(5)
Hf(2)— $O(2)$	2.088(3)
Hf(2)—O(3)	2.177(3)
Hf(2)—O(8)	2.259(3)
Hf(2)—O(9)	2.117(3)
Hf(2) - O(12)	1.944(3)
Hf(2) - N(3)	2.272(4)
Hf(2)— $N(8)$	2.341(4)
O(1) - C(1)	1.299(5)
N(1) - C(1)	1.276(5)
O(2)—C(16)	1.305(4)
N(2)—C(16)	1.300(5)
O(8)—C(106)	1.318(5)
N(8)—C(106)	1.293(6)
Bond angles (°)	
Hf(1)-O(8)-Hf(2)	103.56(11)
Hf(1)-O(10)-Hf(4)	110.40(14)
Hf(1)-O(11)-Hf(3)	113.06(15)
Hf(4)-Hf(1)-O(10)	34.27(9)
N(1)-C(1)-O(1)	115.2(4)
N(2)-C(16)-O(2)	120.9(3)
N(8)-C(106)-O(8)	112.4(4)
O(1)-Hf(1)-N(1)	57.58(13)
O(11)-Hf(1)-Hf(4)	91.31(9)

Table 4. Crystallographic data and refinement details for $\{[^{DMP}(NO)^{Ph}]_2Hf(\mu-O)\}_4$ (3).

Empirical formula	$C_{120}H_{112}Hf_4N_8O_{12}\cdot 3C_7H_8$
Formula weight	2 848.54
Crystal system	Triclinic
Space group	<i>P</i> -1 (No. 2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.7220(8), 20.1280(9), 22.2090(9)
α, β, γ (°)	92.02(1), 99.12(1), 109.55(1)
V (Å ³)	6 095.6(5)
Ζ	2
$D_{\text{calcd}} \text{ (g cm}^{-3})$	1.552
μ (Mo Kα) (cm ⁻¹)	34.60
T (K)	173
2θ range (°)	55.8
Total reflections	57 074
Unique reflections	24 854
Parameters	1 472
R_1^a	0.036
R_w^a	0.079
Goodness-of-fit	1.13

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; R_{w} = \Sigma (|F_{o}^{2}| - |F_{c}^{2}|)^{2} / (\Sigma w |F_{o}^{2}|^{2})^{1/2}.$

the bound THF being coordinatively labile. The rate constant for THF exchange (k_{solv}) is $(560 \pm 110) \text{ s}^{-1}$, and the activation energy (ΔG^{\ddagger}) for this process is $(47 \pm 1.5) \text{ kJ mol}^{-1}$, as determined by variable-temperature NMR spectroscopic experiments. Hydrolysis of **2a** resulted in the formation of a unique tetrametallic Hf oxo cluster species, which was also crystallographically characterized. The amidate ligands in this complex survived the hydrolysis and remained bound to Hf in either a bidentate chelating mode or as a bridge between two Hf centers.

Experimental

General information

Unless otherwise stated, all reactions were carried out using standard Schlenk line and glovebox techniques, under an atmosphere of nitrogen. Tetrahydrofuran and hexanes were purified by passage through a column of activated alumina and degassed with nitrogen. C₆D₆ was degassed and dried over molecular sieves prior to use. d^8 -Toluene was purified by distillation from Na, followed by degassing and storing over molecular sieves. 2,6-Dimethylaniline, benzoyl chloride, and benzylmagnesium chloride (1 mol/L in Et₂O) were purchased from Aldrich and used without further purification. HfCl₄ was purchased from Strem and used as received. Hf(CH₂Ph)₄ was synthesized according to literature procedures and purified by recrystallization at -30 °C in the dark prior to use (14). ¹H, ¹³C, and HMQC NMR spectra were recorded on Bruker 300 MHz or 400 MHz Avance spectrometers at ambient temperature, and chemical shifts are given relative to residual solvent. Variable-temperature ¹H NMR experiments were performed on Bruker 300 MHz or 400 MHz Avance spectrometers equipped with cryoprobes. Mass spectra were recorded on a Kratos MS-50 spectrometer using an electron impact (70 eV) source. Elemental analysis and single crystal X-ray structure determinations were performed at the Department of Chemistry, University of British Columbia.4

[^{DMP}(NO)^{Ph}]H (1)

Ligand preparation was performed on the benchtop with no further precautions. A solution of 11.5 mL (11.3 g, 92.8 mmol) of 2,6-dimethylaniline in 75 mL of CH_2Cl_2 was stirred at room temperature. To this solution was added 12.9 mL (9.40 g, 92.8 mmol) of NEt₃ via pipette over a period of 5 min. The resulting solution was allowed to stir for 1 h before cooling to -78 °C in a dry ice – isopropanol bath. Using an addition funnel, a solution of 8.25 mL (10.0 g, 71.4 mmol) of benzoyl chloride dissolved in 50 mL of CH_2Cl_2 was added dropwise to the amine solution. The resulting colorless solution was allowed to warm to room temperature over a period of 4 h. The product was washed with 1 mol/L HCl (3 × 20 mL), 1 mol/L NaOH (20 mL), and brine (20 mL). The organic fraction was dried over anhydr. MgSO₄, filtered, and the solvent was removed in vacuo, giving 14.6 g of the crude product as a white microcrystalline solid (91% yield). Recrystallization from CHCl₃ gave 10.3 g of the purified product (64% overall yield). The final product was dried by heating under vacuum overnight at 70 °C. ¹H NMR (CDCl₃, 25 °C, 400 MHz) δ : 2.31 (s, 6H, Ar-CH₃), 7.18–7.30 (m, 3H, Ar-H), 7.55 (m, 2H, Ar-H), 7.63–7.75 (m, 2H, Ar-H and N-H), 7.98 (d, 2H, Ar-H). ¹³C NMR (CDCl₃, 25 °C, 100 MHz) δ : 18.35, 127.21, 127.25, 128.13, 128.58, 131.60, 133.98, 134.38, 135.57, 165.90. EI-MS *m/z* (%): 225 ([M⁺], [^{DMP}(NO)^{Ph}]H, 40). Anal. calcd. for C₁₅H₁₅NO (%): C 79.97, H 6.71, N 6.22; found: C 80.24, H 6.72, N 6.20.

$[^{\text{DMP}}(\text{NO})^{\text{Ph}}]_2\text{Hf}(\text{CH}_2\text{Ph})_2(\text{THF})$ (2a)

In a foil-wrapped Schlenk flask, 3.50 g (6.45 mmol) of $Hf(CH_2Ph)_4$ and 2.90 g (12.90 mmol) of $[^{DMP}(NO)^{Ph}]H$ (1) were weighed out together. The mixture of the two solids was cooled to -78 °C in a dry ice - isopropanol bath. To this mixture was added approximately 125 mL of THF via cannula while stirring vigorously. The solution was allowed to warm to room temperature while stirring overnight. Excess THF was removed from the bright red-orange solution in vacuo, resulting in the isolation of 5.60 g of the crude product as a vibrant orange solid (98% yield). The product was dissolved in approximately 150 mL of hexanes at room temperature and filtered through a fritted disk. A small amount of a pale yellow hexanes insoluble product 2b (0.57 g, 11%) yield) was collect on the frit, and the dark orange filtrate was collected and cooled to -30 °C overnight. Microcrystals of a red-orange product **2a** were obtained in 34% yield (1.96 g) in the first batch. Repeated concentration and crystallization of the mother liquor resulted in a combined yield of approximately 65% for **2a**. ¹H NMR (C_6D_6 , 25 °C, 300 MHz) δ : 1.64 (m, 4H, O-(CH₂CH₂)₂), 2.34 (s, 12H, Ar-CH₃), 2.55 (s, 4H, Hf-CH₂Ph), 3.83 (t, 4H, O-(CH₂CH₂)₂), 7.05–7.15 (m, 12H total, Ar-H), 7.35-7.46 (m, 10H total, Ar-H), 7.85 (d, 4H, Ar-H). 13 C NMR (C₆D₆, 25 °C, 75 MHz) δ : 18.69, 25.75, 68.03, 81.64, 122.13, 126.03, 128.55, 128.68, 128.86, 129.08, 131.99, 132.33, 133.07, 142.07, 144.73, 179.56. EI-MS m/z (%): 719 (M⁺ – THF – CH₂Ph, 100). Anal. calcd. for C48H50N2O3Hf (%): C 65.41, H 5.72, N 3.18; found: C 65.15, H 6.00, N 3.54.⁵

Acknowledgments

Funding for this research was provided by the University of British Columbia (UBC) and by the Natural Sciences and Engineering Research Council of Canada (NSERC) in the

⁴Crystallographic data for compounds **2a** and **3** appear in Tables 2 and 4, respectively. All measurements were made on Rigaku/ADSC or Rigaku AFC7 CCD area detectors with graphite-monochromated Mo K α radiation. The data were processed (15) and corrected for Lorentz and polarization effects. The structures were solved by direct methods (16) and expanded by using Fourier (17) techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography (18, 19). Structures are visualized as ORTEP-3 depictions (20).

⁵ Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3665. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 256046 and 256047 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

form of a Discovery Grant to L.L.S. and a postgraduate scholarship to R.K.T.

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