

# Zwitterionic, Ring-Borylated Vanadium(III) Complexes from $[\text{Cp}_2\text{VCO}]$ and $\text{B}(\text{C}_6\text{F}_5)_3$

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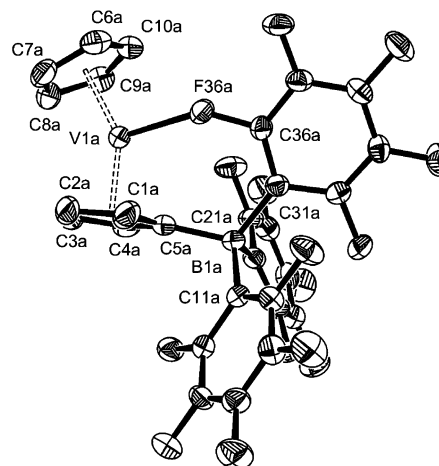
The reaction of the vanadium(II) carbonyl  $[\text{Cp}_2\text{V}(\text{CO})]$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  resulted in formation of zwitterionic, ring-borylated vanadium(III) complexes  $[(\text{Cp})(\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{V}]$  (**3**) and  $[(\text{Cp})(\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{V}(\text{CO})_2]$  (**4**) and of the salt  $[\text{Cp}_2\text{V}(\text{CO})_2][\text{HB}(\text{C}_6\text{F}_5)_3]$  (**5**). All were characterized by crystallography. Formation of a hydride vanadium(IV)  $[(\text{Cp})(\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{VH}(\text{CO})]$  obtained by the electrophilic addition of the borane at the Cp-ring followed by redox and disproportionation reaction is suggested to account for these results.

## Introduction

The reactivity of the borane  $\text{B}(\text{C}_6\text{F}_5)_3$  toward organic and organometallic substrates is of current interest. New organic reactions, new catalytic processes, and new reactivity pathways have been observed for this borane.<sup>1</sup> In our studies of the reactivity of  $\text{B}(\text{C}_6\text{F}_5)_3$  (**1**) with organometallic complexes of the groups 4 and 5 elements,<sup>2,3</sup> in which catalytic application in olefin polymerization is well known, we have explored its reactivity with  $[\text{Cp}_2\text{Ti}(\text{CO})_2]$ . The product of this reaction was the acylborane derivative  $[\text{Cp}_2\text{Ti}(\text{CO})(\eta^2\text{-OCB}(\text{C}_6\text{F}_5)_3)]$ .<sup>3</sup> The preferential attack of borane **1** at the carbon atom of a carbonyl ligand is puzzling if we consider that attack at the more nucleophilic oxygen atom of the carbonyl ligand should be favored.<sup>4</sup> Thus we decided to extend our investigation of the reactivity of **1** toward the readily available  $[\text{Cp}_2\text{VCO}]$  (**2**).

## Results and Discussion

The carbonyl complex  $[\text{Cp}_2\text{VCO}]$  (**2**) reacted with **1** in pentane to give a yellow-brown precipitate that contained a crystalline air-sensitive blue product. The latter, formed in low yield, was isolated by careful separation by hand. This product is a paramagnetic high-spin  $\text{V}^{\text{III}}$  complex ( $\mu_{\text{eff}} = 2.85 \mu_{\text{B}}$ ). Its structure was shown by X-ray crystallography to be that of zwitterionic  $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{V}]$  (**3**) (Figure 1). The borane is linked to one of the cyclopentadienyl rings, and an

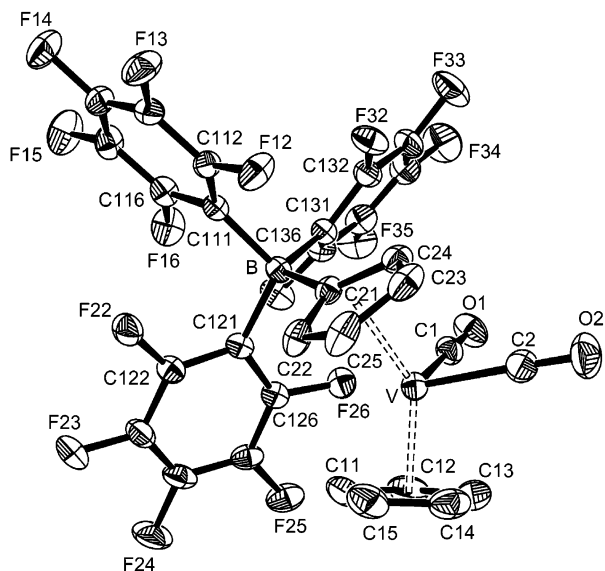


**Figure 1.** Molecular structure of **3**, showing 50% probability thermal ellipsoids and partial atom-labeling schemes. Selected bond distances (Å) and angles (deg):  $\text{V}(1)\cdots\text{F}(36)$  2.1568(14),  $\text{C}(5a)\text{--B}(1)$  1.639(3),  $\text{Cp}\text{--V}(1)$  1.923,  $\text{Cp}^B\text{--V}(1)$  1.913,  $\text{Cp}\text{--V}(1)\text{--Cp}^B$  144.43.  $\text{Cp}^B$  and  $\text{Cp}$  are the centroids of  $\text{C}(1a)\text{--C}(5a)$  and  $\text{C}(6a)\text{--C}(10a)$  rings, respectively.

*ortho*-fluorine atom of one perfluoro phenyl group of the borane is coordinated to the vanadium center with a  $\text{V}\cdots\text{F}$  distance of 2.1568(14) Å, a separation that is in the same range as those reported in the literature<sup>5</sup> for fluorine atoms that bridge neighboring vanadium atoms (2.044–2.173 Å). The paramagnetic vanadium center is  $^{51}\text{V}$  NMR silent, whereas a  $^{11}\text{B}$  NMR resonance at  $-14.8$  ppm confirmed the presence of a tetracoordinated anion (we assume that the boron atom is not affected by the proximity of the paramagnetic vanadium center). Electrophilic substitution of a hydrogen atom of the Cp ring by **1** has been observed previously in group 4.<sup>6</sup> In particular, the interaction of the bis(trimethylsilyl)-acetylene complex of titanocene  $[\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)]$  with **1** gave a zwitterionic complex of titanium(III),

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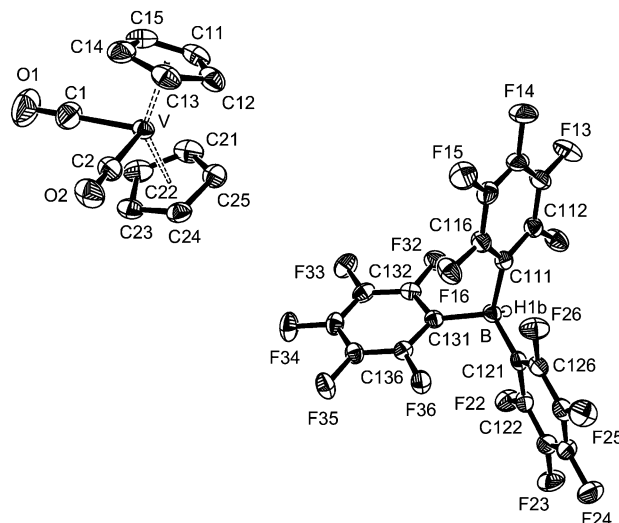
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**Figure 2.** Molecular structure of **4**, showing 50% probability thermal ellipsoids and partial atom-labeling schemes. Selected bond distances (Å) and angles (deg): V(C1) 1.9484(17), V–C(2) 1.9686(17), C(1)–O(1) 1.1369(19), C(2)–O(2) 1.133(2), B–C(21) 1.655(2), C(1)–V–C(2) 85.44(7), (Cp)–V(1) 1.930, (Cp<sup>B</sup>)–V(1) 1.924, (Cp)–V(1)–(Cp<sup>B</sup>) 139.15. (Cp<sup>B</sup>) and (Cp) are the centroids of C(21)–C(25) and C(11)–C(15) rings, respectively.

$[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{Ti}]$ , in which *ortho*-fluorine atoms of two  $\text{C}_6\text{F}_5$  groups are coordinated to the titanium center in a pseudotetrahedral geometry.<sup>6b</sup> The difference in the reactivity between the titanocene and vanadocene units could be the result of a steric effect: the larger atomic radius of Ti versus V may allow two fluorine atoms to coordinate at the Ti center.

Two other products were contained in the yellow-brown crude precipitate as observed by  $^1\text{H}$  NMR spectroscopy (the characteristic cyclopentadienyl signals) as well as by the  $^{51}\text{V}$  and  $^{11}\text{B}$  NMR spectra, in which two resonances were observed, respectively. A magnetic measurement made on the crude product (after careful and tedious separation of **3**) indicated that it consisted of diamagnetic species. We were able to isolate separately each complex by dissolving the crude product in a small amount of toluene or THF followed by pentane diffusion. Formation of crystalline, air-sensitive complexes suitable for an X-ray structure determination were obtained from these selective crystallizations. In the crystals obtained from THF/pentane solution, a dicarbonylvanadium(III) species in which the borane is linked to one of the cyclopentadienyl rings of the vanadocene unit in the zwitterionic  $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{V}(\text{CO})_2]$  (**4**) (Figure 2) was shown to be present. Crystals were obtained from toluene/pentane solution, and the X-ray structure determination established the formation of a salt,  $[\text{Cp}_2\text{V}(\text{CO})_2][\text{HB}(\text{C}_6\text{F}_5)_3]$  (**5**) (Figure 3).<sup>7</sup> The isolated **4** often was contaminated by **5** in low



**Figure 3.** Molecular structure of **5**, showing 50% probability thermal ellipsoids and partial atom-labeling schemes. Selected bond distances (Å) and angles (deg): V(C1) 1.965(3), V–C(2) 1.964(2), C(1)–O(1) 1.132(3), C(2)–O(2) 1.135(3), (Cp)–V (or (Cp')–V) 1.901, (Cp)–V–(Cp') 138.01, B–H(1B) 1.14(2), C(1)–V–C(2) 86.63(11). (Cp) and (Cp') are the centroids of C(11)–C(15) and C(21)–C(25) rings, respectively.

ratio, as judged by  $^1\text{H}$  NMR (0–5%), and isolated **5** often was contaminated by small amounts of **4**. In another procedure, the synthesis carried out in a small amount of toluene as solvent gave **5** as an immediate orange crystalline product in high yield. The filtrate, after 2–3 days at low temperature (–30 °C), afforded blue crystals of **3**. After filtration, the filtrate was layered with pentane to give a brown precipitate, which was analyzed by  $^1\text{H}$  NMR as **4** contaminated with **5**. Both complexes **4** and **5** are diamagnetic (confirmed by Faraday balance experiments and multinuclear NMR). The  $^{11}\text{B}$  NMR shift of **4** (–14.9 ppm) is in the same range as that of **3**, as expected for a tetracoordination of the boron atom. The resonance of the  $^{11}\text{B}$  NMR spectrum of **5** shows a doublet at –25.5 ppm ( $^1J_{\text{B-H}} = 89$  Hz), in agreement with the presence of the  $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$  anion,<sup>8</sup> which is also supported by the  $^1\text{H}$  NMR spectrum, which shows a quadruplet at 3.63 ppm with  $^1J_{\text{BH}} = 91$  Hz. The  $^{51}\text{V}$  NMR spectra of **4** and **5** show very low field peaks at –1652 and 1662 ppm, respectively, due to the high basicity of the cationic  $[\text{V}]^+$  moiety.<sup>9</sup> Both compounds have two infrared C–O stretching vibrations (Nujol mull) at 2050 and 2004  $\text{cm}^{-1}$  and 2038 and 1990  $\text{cm}^{-1}$  for **4** and **5**, respectively (to be compared with the bands at 2050 and 2010  $\text{cm}^{-1}$  reported for the  $[\text{Cp}_2\text{V}(\text{CO})_2]^+$  cation<sup>10</sup>).

From these different results, we can draw a scheme showing the possible formation of **3**, **4**, and **5**. All these compounds seem to arise from the same parent mol-

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**Table 1.** Summary of Crystal Data, Data Collection, and Structure Refinement Parameters for 3–5

	3	4	5
fw	1384.20	748.12	750.14
temperature (K)	180	180	160
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
<i>a</i> (Å)	17.010(5)	10.819(5)	14.594(5)
<i>b</i> (Å)	15.787(5)	13.785(5)	16.127(5)
<i>c</i> (Å)	18.810(5)	18.532(5)	11.890(5)
$\beta$ (deg)	94.282(5)	105.417(5)	97.046(5)
<i>V</i> (Å <sup>3</sup> )	5037(3)	2668.7(17)	2777.3(17)
<i>Z</i> , density (g cm <sup>-3</sup> )	4, 1.825	4, 1.862	4, 1.794
<i>F</i> (000)	2720	1472	1480
abs coeff (mm <sup>-1</sup> )	0.525	0.509	0.489
2 $\theta$ range (deg)	3.3–31.79	2.91–30.51	2.44–28.13
no. of reflns collected/unique	46 805/15892 ( <i>R</i> <sub>int</sub> = 0.0483)	54 611/7749 ( <i>R</i> <sub>int</sub> = 0.0369)	26 433/6555 ( <i>R</i> <sub>int</sub> = 0.0492)
completeness to 2 $\theta$ (%)	63.58 (92.5)	61.02 (95.1)	79.8
no. of data/restraints/params	15 892/0/811	7749/0/442	6555/0/446
GOF on <i>F</i> <sup>2</sup>	0.926	1.099	1.015
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0483, w <i>R</i> 2 = 0.1094	<i>R</i> 1 = 0.0369, w <i>R</i> 2 = 0.0951	<i>R</i> 1 = 0.0369, w <i>R</i> 2 = 0.0799
<i>R</i> indices (total)	<i>R</i> 1 = 0.0936, w <i>R</i> 2 = 0.1269	<i>R</i> 1 = 0.0469, w <i>R</i> 2 = 0.1001	<i>R</i> 1 = 0.0663, w <i>R</i> 2 = 0.0911
largest diff peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	0.370 and –0.456	0.326 and –0.355	0.266 and –0.249

ecule. Electrophilic addition of **1** at the Cp-ring occurred and afforded the suggested intermediate vanadium(IV) hydride  $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{VH}(\text{CO})]$ .<sup>11</sup> The reductive elimination of the hydride leads to simultaneous formation of 0.5 equiv of the monocarbonylvandium(III)  $[(\text{Cp})(\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{V}(\text{CO})]$  **{A}** and 0.5 equiv of the monocarbonyl cationic  $[\text{Cp}_2\text{V}(\text{CO})]^+$  species associated with the anion  $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$  **{B}**. Disproportionation of **{A}** gives the borane-substituted cyclopentadienyl complexes **3** and **4**, whereas **{B}** disproportionates to **5** and a suggested  $[\text{Cp}_2\text{VH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  species that we have not been able to observe due to its probable decomposition (Scheme 1). Gas phase analysis by MS of the gas above the reaction mixture, in a closed vessel, did not show evidence of H<sub>2</sub> evolution during the synthesis of the crude product in pentane.

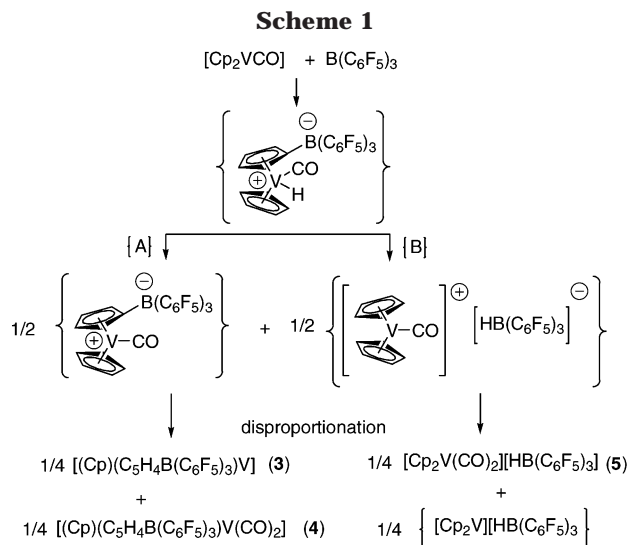
### Conclusion

In summary, combination of **1** with  $[\text{Cp}_2\text{VCO}]$  gives new vanadium complexes. In the same reaction, three vanadium complexes were found showing the complexity of the vanadium chemistry, resulting from the oxidation of the metal center toward the divalent vanadocene **2**. Complexes **3** and **4** represent the first structurally characterized ring-borylated vanadium zwitterionic complexes.

### Experimental Section

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon, collected by distillation,

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and stored in a drybox over activated 4 Å molecular sieves. Deuterated solvents were degassed and dried over activated 4 Å molecular sieves. NMR data were recorded using Bruker AMX-400 and AC-200 spectrometers, referenced internally to residual protio solvent (<sup>1</sup>H) resonances, and are reported relative to tetramethylsilane ( $\delta = 0$  ppm). <sup>19</sup>F NMR (188.298 MHz) spectra were recorded on a Bruker AC-200 spectrometer (reference CF<sub>3</sub>CO<sub>2</sub>H). <sup>51</sup>V NMR (105.24 MHz; reference VOCl<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>, 9:1) and <sup>11</sup>B NMR (128.37 MHz; reference BF<sub>3</sub>·Et<sub>2</sub>O) spectra were recorded on a Bruker AMX-400 spectrometer. Elemental analyses (C, H) were performed at the Laboratoire de Chimie de Coordination (Toulouse, France).  $[\text{Cp}_2\text{VCO}]$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  were prepared according to the literature.<sup>12,13</sup>

**Preparation of  $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{V}]$  (**3**),  $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{V}(\text{CO})_2]$  (**4**), and  $[\text{Cp}_2\text{V}(\text{CO})_2][\text{HB}(\text{C}_6\text{F}_5)_3]$  (**5**).** To a stirred pentane solution (5 mL) of  $[\text{Cp}_2\text{VCO}]$  (**2**) (36 mg, 0.2 mmol) was added in small portions solid  $\text{B}(\text{C}_6\text{F}_5)_3$  (102 mg, 0.2 mmol). The resulting yellow-brown slurry was left one week at room temperature until blue crystals of **3** appeared. After careful hand-separation of **3**, the yellow-brown solid was dissolved in THF (1–2 mL) and layered with pentane to give

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**4** as a crystalline, orange solid suitable for X-ray structure determination. In another experiment (using the same experimental conditions), the crude yellow-brown product was dissolved in toluene (1 mL) and layered with pentane to give **5** as a crystalline, orange-yellow solid suitable for X-ray structure determination. Note that **4** is very often contaminated by some proportion of **5** and similarly **5** by some amount of **4**, as indicated by  $^1\text{H}$  NMR spectroscopy. C, H analytical results are in the same range for **4** ( $\text{C}_{30}\text{H}_9\text{BF}_{15}\text{O}_2\text{V}$ ) as for **5** ( $\text{C}_{30}\text{H}_{11}\text{BF}_{15}\text{O}_2\text{V}$ ) and fall within the experimental error for both compounds, and they are not indicative of the purity of the product. Analysis of **4** and **5** was attempted for characterization and gave reproducible analysis. In another procedure, the crude yellow product can be obtained directly by admission of CO gas in a stoichiometric mixture of  $[\text{VCp}_2]$  and **1** in pentane.

**3**:  $\mu_{\text{eff}} = 2.85 \mu_{\text{B}}$ . Anal. Calcd for  $\text{C}_{28}\text{H}_9\text{BF}_{15}\text{V}$ : C 48.59, H 1.31. Found: C 48.40, H 1.22. Yield: 22 mg (50%). **4**:  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{CN}$ ) 5.19 (5H, Cp), 5.36 (b, 2H,  $\text{C}_5\text{H}_4$ ) 5.49 (t, 2H,  $\text{C}_5\text{H}_4$ );  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ ) -52.9; -86.2; -91.0 (*o*, *p*, *m*-F,  $\text{C}_6\text{F}_5$ );  $^{11}\text{B}$  ( $\text{CD}_3\text{CN}$ ) -14.9;  $^{51}\text{V}$  ( $\text{CD}_3\text{CN}$ ) -1652; IR (Nujol mull)  $\nu_{\text{CO}}$  2050, 2004. Anal. Calcd for  $\text{C}_{30}\text{H}_9\text{BF}_{15}\text{O}_2\text{V}$ : C 48.16, H 1.21. Found: C 48.4, H 1.35. Yield: 21 mg (59%). **5**:  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{CN}$ ) 5.59 (10H, Cp), 3.63 (q ( $^1J_{\text{BH}} = 91$  Hz), *B-H*);  $^{19}\text{F}$  ( $\text{CD}_3\text{CN}$ ) -58.9, -88.8, -92.0 (*o*, *p*, *m*-F,  $\text{C}_6\text{F}_5$ );  $^{11}\text{B}$  ( $\text{CD}_3\text{CN}$ ) -25.5 (d, ( $^1J_{\text{BH}} = 87$  Hz), *B-H*);  $^{51}\text{V}$ : -1661; IR (Nujol mull)  $\nu_{\text{CO}}$  2038, 1990;  $\nu_{\text{BH}}$  3123. Anal. Calcd for  $\text{C}_{30}\text{H}_{11}\text{BF}_{15}\text{O}_2\text{V}$ : C 48.03, H 1.48. Found: 48.38, C 1.30. Yield: 30 mg (83%).

**Crystallographic Data for 3, 4, and 5.** Selected crystals, sensitive to air and moisture, were suspended in oil on a glass slide. Under a microscope, a single block was isolated. For structures **3**, **4**, and **5** (Table 1), data were collected using a Stoe Imaging Plate Diffraction System (IPDS). The final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. No fluctuations of the intensity were observed over the course of the data collection.

A semiempirical correction absorption<sup>14</sup> was applied to the data. The structure was solved by direct methods using SIR92<sup>15</sup> and refined by least-squares procedures on  $F^2$  with the aid of SHELXL97,<sup>16</sup> included in WinGX (version 1.63).<sup>17</sup> The atomic scattering factors were taken from International Tables for X-Ray Crystallography.<sup>18</sup> All hydrogen atoms were located on a difference Fourier map. All the remaining non-hydrogen atoms were anisotropically refined, and in the last refinement cycles a weighting scheme was used where weights were calculated from the following formula:  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . Drawing of the molecules was performed using the program ORTEP32.<sup>19</sup> Criteria for a satisfactory, complete analysis were the ratio of rms shift to standard deviation being less than 0.1 and no significant features in final difference maps.

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**Supporting Information Available:** Crystallographic data for compounds **3**, **4**, and **5** including ORTEP diagrams and tables of crystal data and data collection parameters, atomic coordinates, anisotropic displacement parameters, and all bond lengths and bond angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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