

Synthesis and Structure of a Diphosphonite-Bridged Ruthenium Dication, $\{[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})]_2(\mu\text{-1,2-di}(2'2'\text{-diethyl-1',3'-propanedioxy)-\text{phosphinoethane})\}^{2+}$

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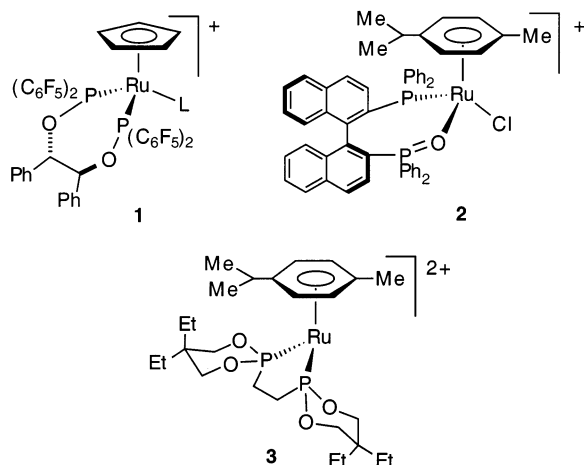
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Summary: Attempted synthesis of $[(p\text{-cymene})\text{Ru}(PP)]^{2+}$ ($PP = 1,2\text{-di}(2'2'\text{-diethyl-1',3'-propanedioxy})\text{phosphinoethane}$) by reaction of $[(p\text{-cymene})\text{RuCl}_2]_2$ with PP followed by chloride abstraction with AgSbF_6 afforded instead the diphosphonite-bridged Ru^{II} dimer, $\{[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})]_2(\mu\text{-PP})\}[\text{SbF}_6]_2$, which was structurally characterized. A neutral intermediate, $[(p\text{-cymene})\text{RuCl}_2]_2(\mu\text{-PP})$, was isolated and was converted to the latter by treatment with AgSbF_6 .

Introduction

Chiral arene or cyclopentadienide ruthenium(II) complexes with a chiral diphosphine or chiral metal center such as **1** and **2** have drawn considerable recent attention because of their applications in asymmetric catalyses.



In complexes with a chiral diphosphine such as **1**, the asymmetric centers normally oriented away from the active metal center. For complexes such as **2**, the mixed donor ligand diphosphine monoxide afforded an additional asymmetric metal center. A potential drawback is that the chiral center may be configurationally unstable because the phosphine oxide is a weaker donor toward ruthenium. We have been interested in transi-

tion metal complexes containing much less explored diphosphonite ligands such as 1,2-di(2'2'-diethyl-1',3'-propanedioxy)phosphinoethane (depicted in **3** and denoted below as PP).³ Aside from different electronic properties compared to diphosphine analogues (e.g., more electron-withdrawing), diphosphonites can easily be made chiral by synthesis from readily available chiral diols. Thus chiral diphosphonite transition metal complexes would position the asymmetric centers on the sides of the active metal center, which should afford catalysts with enhanced chiral induction. In addition, 16e species diphosphonite complexes such as **3** are conceivable and would be highly electrophilic dications with no accessible internal agostic interaction between metal and ligand C–H groups, thus potentially useful in the binding and activation of extremely weak ligands such as alkanes and other σ -bond ligands.^{3,4} Related monocationic Cp^* phosphine complexes of both Fe and Ru are known, and the nature of the phosphine dictates whether an agostic interaction, anion binding, or neither (true 16e species) is present.⁵ For example, the bidentate phosphine system $[\text{Cp}^*\text{Ru}(\text{Pr}_2\text{PC}_2\text{H}_4\text{P}^i\text{Pr}_2)][\text{BAR}_F]$ contains an agostic interaction, while the analogous monodentate phosphine species, $[\text{Cp}^*\text{Ru}(\text{PMe}^i\text{Pr}_2)][\text{BAR}_F]$, does not (BAR_F is the low-coordinating $\text{B}[3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2]_4$ anion).^{5a} Anion coordination can occur since $[\text{Cp}^*\text{Ru}(\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)][\text{CF}_3\text{SO}_3]$ was originally believed⁶ to be a 16e complex but was later shown⁷ to be an 18e complex with coordinated CF_3SO_3 . Remarkably, $[\text{Cp}^*\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)][\text{CF}_3\text{SO}_3]$ is a true 16e complex with no anion or agostic interaction, while the diphosphine congener with one less methylene ($\text{Ph}_2\text{-PCH}_2\text{CH}_2\text{PPh}_2$ with a smaller "bite angle") contains a bound CF_3SO_3 .^{5b} We therefore decided to investigate the feasibility of synthesizing arene half-sandwich diphosphonite systems such as the 16e dication **3** or an 18e adduct with a weakly donating anion or solvento ligand such as CH_2Cl_2 .

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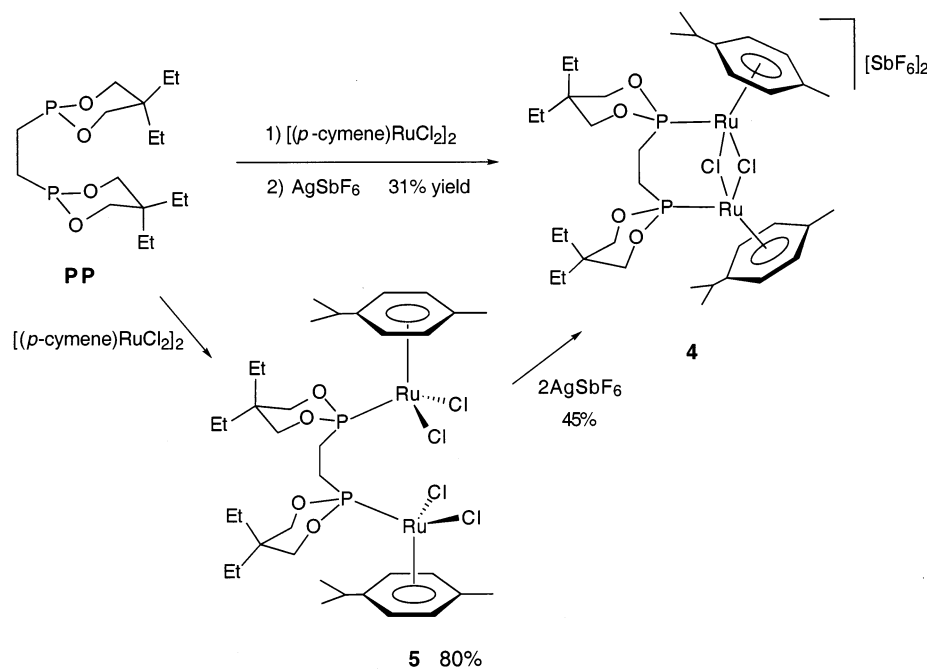
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Scheme 1



Results and Discussion

Attempted synthesis of **3** by reacting PP with $[(p\text{-cymene})\text{RuCl}_2]_2$ followed by chloride abstraction with silver salts afforded instead the dicationic diphosphonite-bridged ruthenium(II) dimer **4** as either SbF_6 or PF_6 salts in 31% yield (Scheme 1). The neutral intermediate **5** apparently initially forms and could be isolated in a separate reaction of $[(p\text{-cymene})\text{RuCl}_2]_2$ with PP. Complex **4** could then be prepared from **5** via treatment with 2 equiv of AgSbF_6 . However, use of excess silver salts in Scheme 1 did not lead to a chloride-free complex such as the desired **3**. To avoid formation of PP-bridged species such as **5**, PP was reacted with the more labile ruthenium(II) precursors $[(\text{arene})\text{RuCl}(\text{NCMe})_2][\text{PF}_6]$ (arene = *p*-cymene⁸ or benzene⁹) in MeCN or CH_2Cl_2 to attempt preparing $[(\text{arene})\text{RuCl}(\text{PP})][\text{PF}_6]$ by direct substitution. The latter might then serve as a precursor to **3** via chloride abstraction. However, only intractable mixtures resulted from which the desired product could not be isolated.

Complexes **4** and **5** were characterized by ^1H , ^{13}C , and ^{31}P NMR spectroscopy and elemental analysis, and **4** appears to be the first diphosphonite-bridged ruthenium dimer reported. The ^1H and ^{13}C NMR chemical shifts of the cymene in both **5** and **4** are shifted to higher fields in relation to those of free cymene, as is generally observed for substituted-metal-bound arenes. For example, the cymene chemical shifts in the SbF_6 salt of complex **4** are δ 6.06–6.10 (CH) and 91.3, 93.2, 99.8, 107.1 (CH). The aromatic protons of the cymene ring for the PF_6 salt of **4** appear as a broad "doublet" at δ 6.10 in CD_2Cl_2 at room temperature, suggesting dynamic behavior on the NMR time scale. The doublet decoalescences at -45 °C and is split into two resonances when the temperature is reduced to -85 °C. The

two resonances, a singlet at δ 6.89 and a doublet at δ 5.32, are also broad in appearance. Considering the solid-state structure of the complex, as defined by the X-ray crystallographic analysis discussed below, the resonance at 5.32 ppm appears to be unusually upfield. This feature, however, seems to be a common characteristic in related cationic $(p\text{-cymene})\text{RuCl}(\text{L}_2)$ systems (where L_2 = chelating bis(phosphine), phosphine-phosphinite, or phosphine-arsine).¹⁰

To confirm the molecular structure of **4** and to understand why the above reaction did not lead to the desired mononuclear ruthenium(II) complex **3**, an X-ray structural analysis was performed on the SbF_6 salt of **4**. However the structural data had a high R1 factor (0.1154, all data) and showed unusual interatomic distances and geometry (e.g., highly asymmetric Cl bridges) that aroused suspicion of their validity.¹¹ Crystals of an analogue of **4** with PF_6 anions, $\{[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})_2(\mu\text{-}1,2\text{-di}(2'2'\text{-diethyl-}1',3'\text{-propanedioxy)phosphinoethane})]\}[\text{PF}_6]_2 \cdot \text{CH}_2\text{Cl}_2$, were therefore grown, and a second structure analysis was carried out. The structure of the cation of the latter is shown in Figure 1, and crystallographic data are listed in Table 1. The structural parameters are now within normal bounds, and apparently the original crystal of **4** had flaws such as twinning, giving rise to an incorrect structure. The molecule has a C2 axis passing through the centers of the diphosphonite backbone carbons and

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(11) The Ru–Cl distances were 2.024(3) and 2.408(3) Å, with the former being shorter than the shortest Ru–Cl distance documented in the Cambridge Crystal Database. The Ru–P(1) distance, 2.773(5) Å, was significantly longer than the normal range of 2.30–2.50 Å found for other Ru–P distances.¹² Last, the cymene rings were asymmetrically bound with Ru–C distances ranging from 1.934(4) to 2.515(6) Å, again a chemically unreasonable situation. The SbF_6 and PF_6 salts had the same space group and C2 axis in the molecule, as well as similar unit cell dimensions. Other than the high R factor and the abnormal metrical parameters, there was no indication (such as obvious disorder or unusual thermal ellipsoids) that the structure of the SbF_6 salt was fallacious and apparently a result of a "bad crystal".

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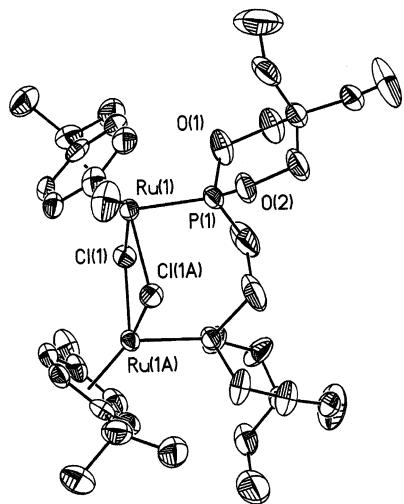


Figure 1. Molecular structure of $\{[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})_2(\mu\text{-}1,2\text{-di}(2',2'\text{-diethyl-}1',3'\text{-propanedioxy)phosphinoethane})\text{Ru}(\mu\text{-Cl})_2\text{CH}_2\text{Cl}_2]_2[\text{PF}_6]_2\}$ (35% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ru(1)–Cl(1), 2.4207(16); Ru(1)–Cl(1A), 2.4252(17); Ru(1A)–Cl(1), 2.4252(17); Ru(1)–P(1), 2.2902(17); Ru–arene carbons, 2.181(6)–2.263(6); P(1)–O(2), 1.565(6); P(1)–O(1), 1.589(7); Ru(1)–Cl(1)–Ru(1A), 96.20(6); Cl(1)–Ru(1)–Cl(1A), 82.87(6); P(1)–Ru(1)–Cl(1), 89.74(7); P(1)–Ru(1)–Cl(1A), 87.04(7); O(2)–P(1)–Ru(1), 111.9(2); O(1)–P(1)–Ru(1), 111.0(2).

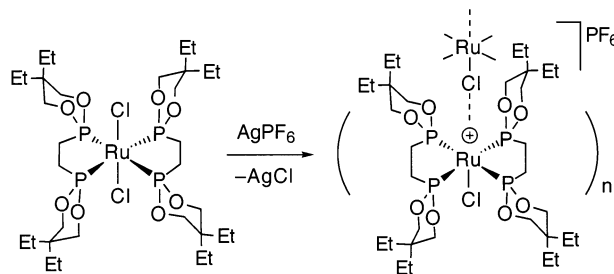
Table 1. Crystal Data and Structure Refinement for $\{[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})_2(\mu\text{-}1,2\text{-di}(2',2'\text{-diethyl-}1',3'\text{-propanedioxy)phosphinoethane})\text{Ru}(\mu\text{-Cl})_2\text{CH}_2\text{Cl}_2]_2[\text{PF}_6]_2\}$

empirical formula	$\text{C}_{37}\text{H}_{62}\text{Cl}_4\text{F}_{12}\text{O}_4\text{P}_4\text{Ru}_2$
temperature	203(2) K
radiation	graphite-monochromatized Mo K α
wavelength	0.71073 Å
cryst syst	orthorhombic
space group	$P2_12_12$
unit cell dimens	$a = 13.842(3)$ Å $b = 16.848(3)$ Å $c = 11.1254(19)$ Å
Z	2
density(calcd)	1.621 Mg/m 3
abs coeff	0.990 mm $^{-1}$
diffractometer	Bruker P4/CCD/PC
cryst size	0.25 × 0.16 × 0.12 mm 3
θ range for data collection	1.83–23.25°
index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 17$, $-12 \leq l \leq 12$
no. of reflns collected	14 303
no. of ind reflns	3728 [$R(\text{int}) = 0.0324$]
max. and min. transmn refinement method	0.89 and 0.79
no. of data/restraints/params	full-matrix least-squares on F^2 3728/1/280
goodness-of-fit on F^2	1.037
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0440$, $wR2 = 0.1219$
R indices (all data)	$R1 = 0.0502$, $wR2 = 0.1256$

Ru(1)–Ru(1A). The cation has no close contact to two PF_6 counteranions or a lattice CH_2Cl_2 . The Ru–Ru distance, 3.6069(9) Å, indicates that there is no significant metal–metal bonding interaction. The chloride bridges are essentially symmetric, and the Ru–Cl distances are within the normal range found for other similar chloride-bridged Ru complexes.¹² An important

lesson here is not to put blind trust in “novel” crystallographic results, especially if the structural parameters are abnormal but tantalizingly close to being believable.

The tightly bridged structure and the electrophilic dicationic nature of **4** may be factors in its reluctance to undergo further chloride abstraction. The chlorides are well protected from attack by the arene and diphosphonite groups. From an electronic standpoint, the diphosphonites are electron-withdrawing ligands, and oligomerization via formation of chloride bridges had been proposed by us to occur in *trans*- $[\text{RuCl}(\text{PP})_2][\text{PF}_6]$.³



In contrast, analogous less-electrophilic complexes such as *trans*- $[\text{RuCl}(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)_2]^+$ ($\text{R} = \text{Cy}$,¹³ Ph ¹⁴) with electron-donating diphosphines are true five-coordinate 16e species with neither intramolecular agostic nor intermolecular interactions at the vacant sixth coordination site. There is thus a fine balance of electronic and steric factors in both octahedral and piano-stool Ru^{II} phosphine complexes that dictate whether 16e (with or without agostic interactions) or 18e complexes (with anion or solvent binding) are stable. The π -donating ability of chloride in stabilizing 16e species,¹⁵ the offsetting electron-withdrawing power of diphosphonite ligands, and possibly even the bite angle of the diphosphonite are important factors for future study of these systems.

Experimental Section

All manipulations were performed either under a helium atmosphere in a Vacuum Atmospheres drybox or under an argon atmosphere using standard Schlenk techniques unless otherwise specified. Hexane, toluene, ether, and THF were purified by passing through columns of activated alumina and activated Cu-0226 S copper catalyst (Engelhard). CH_2Cl_2 was purchased from Aldrich and dried under 4 Å molecular sieves. $[(p\text{-cymene})\text{RuCl}_2]_2$, AgSbF_6 , and AgPF_6 were purchased from Strem Chemicals and used as received. Other reagents were purchased from Aldrich and Acros Chemicals and used as received. ^1H , ^{31}P , and ^{13}C spectra were recorded on a Varian Unity 300 spectrometer with field strengths of 300, 121, and 75 MHz, respectively. ^1H and ^{13}C chemical shifts were referenced to the residual solvent resonance relative to TMS; ^{31}P chemical shifts were referenced to external 85% H_3PO_4 . Elemental analyses were performed in-house on a Perkin-Elmer Series II CHNS/O model 2400 analyzer.

$\{[(p\text{-cymene})\text{Ru}(\mu\text{-Cl})_2(\mu\text{-}1,2\text{-di}(2',2'\text{-diethyl-}1',3'\text{-propanedioxy)phosphinoethane})\text{Ru}(\mu\text{-Cl})_2\text{CH}_2\text{Cl}_2]_2[\text{PF}_6]_2$ (4**).** **Method A.** CH_2Cl_2 (5 mL) was added to a mixture of $[(p\text{-cymene})\text{RuCl}_2]_2$ (0.127 g, 0.21 mmol) and PP (0.160 g, 0.46 mmol). After the mixture was stirred for 5 min at RT, AgSbF_6 (0.144 g, 0.42

(12) See for example: (a) Mauthner, K.; Kalt, D.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **1997**, *128*, 533. (b) Fries, G.; Weberndorfer, B.; Ilg, K.; Werner, H. *Eur. J. Inorg. Chem.* **2000**, 1651.

(13) Mezzetti, A.; Del Zotto, A.; Rigo, P.; Pahor, N. B. *J. Chem. Soc., Dalton Trans.* **1989**, 1045.

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mmol) was added, and the resultant mixture was stirred at RT for 4 h to give an orange suspension. The suspension was filtered through Celite. Hexane was added to the filtrate, and the mixture was cooled to $-30\text{ }^{\circ}\text{C}$ to give an orange solid. On the basis of NMR data, the solid appeared to be a mixture of products. Repeated recrystallization from CH_2Cl_2 /hexane at $-30\text{ }^{\circ}\text{C}$ afforded the product (0.090 g, 31%) as orange crystals. ^1H NMR (CD_2Cl_2): δ 0.86 (t, 6H, $J = 7.6$ Hz), 1.04 (t, 6H, $J = 7.6$ Hz), 1.13 (d, 12H, $J = 7.1$ Hz), 1.35 (q, 4H, $J = 7.6$ Hz), 1.87 (s, 6H), 1.94 (q, 4H, $J = 7.6$ Hz), 2.50 (hept, 2H, $J = 7.1$ Hz), 2.88–2.92 (m, 4H), 4.16 (dd, $J = 19.3, 12.0$ Hz), 4.47 (d, $J = 11.0$ Hz), 6.06–6.10 (br, 8H). ^{31}P NMR (CD_2Cl_2): δ 165.7. ^{13}C NMR (CD_2Cl_2): δ 6.4, 7.4, 15.9 (d, $J = 25.6$ Hz), 21.4, 23.1, 23.7, 30.8, 38.9, 74.0, 91.3, 93.2, 99.8, 107.1. Anal. Calcd for $\text{C}_{36}\text{H}_{60}\text{Cl}_2\text{F}_{12}\text{O}_4\text{P}_2\text{Sb}_2\text{Ru}_2$: C, 31.71; H, 4.40. Found: C, 32.12; H, 4.62. A complex with PF_6 anions was prepared analogously for the single-crystal X-ray study.

Method B. CH_2Cl_2 (6 mL) was added to a mixture of 5 (0.098 g, 0.10 mmol) and AgSbF_6 (0.070 g, 0.20 mmol). The resulting suspension was stirred at RT overnight and filtered. Volatiles were removed, and the residue was washed with hexane to give product (0.061 g, 45%) as an orange solid. NMR data were the same as reported above.

[(*p*-cymene) RuCl_2] $_{\mu-1,2}$ -di(2',2'-diethyl-1',3'-propanedioxy)phosphinoethane] (5). CH_2Cl_2 (6 mL) was added to a mixture of [(*p*-cymene) RuCl_2] (0.230 g, 0.38 mmol) and PP (0.145 g, 0.41 mmol) to give an orange suspension. The suspension was stirred for 2 h at RT and filtered. The solid was washed with hexane and dried to give product (0.288 g, 80%) as an orange solid. ^1H NMR (CD_2Cl_2): δ 0.80 (t, 6H, $J = 7.6$ Hz), 0.99 (t, 6H, $J = 7.6$ Hz), 1.15 (d, 12H, $J = 7.1$ Hz), 1.26 (d, 4H, $J = 7.6$ Hz), 1.90 (d, 4H, $J = 7.6$ Hz), 2.01 (s, 6H), 2.74 (br, 6H, PCH_2 and ArCH), 3.88 (dd, 4H, $J = 18.3, 11.5$ Hz), 4.42 (d, 4H, $J = 11.5$ Hz), 5.46 (d, 4H, $J = 6.3$ Hz), 5.57 (d, 4H, $J = 6.4$ Hz). ^{31}P NMR (CD_2Cl_2): δ 168.0. ^{13}C NMR (CD_2Cl_2): δ 6.8, 7.5, 18.4, 20.7, 21.9, 22.7, 24.1, 30.6, 73.0, 89.4, 90.9. Anal. Calcd for $\text{C}_{36}\text{H}_{60}\text{Cl}_4\text{O}_4\text{P}_2\text{Ru}_2$: C, 44.91; H, 6.24. Found: C, 44.93; H, 6.60.

X-ray Structural Determination of [(*p*-cymene) $\text{Ru}(\mu\text{-Cl})_2(\mu-1,2\text{-di}(2',2'\text{-diethyl-1',3'-propanedioxy)-phosphinoethane)]_2[\text{PF}_6]_2\cdot\text{CH}_2\text{Cl}_2$. An orange crystal of the complex was grown from a CH_2Cl_2 -containing solvent mixture and was attached to a glass fiber using a spot of silicone grease. The crystal was placed on a Bruker P4/CCD/PC diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The data were collected using a sealed, graphite monochromatized $\text{Mo K}\alpha$ X-ray source. A hemisphere of data was

collected using a combination of φ and ω scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART¹⁶ software. Frame integration and final cell parameter calculations were carried out using SAINT¹⁷ software. The data were corrected for absorption using the SADABS¹⁸ program. Decay of reflection intensity was not observed. The structure was solved in space group $P2_12_12$ using direct methods and difference Fourier techniques. The initial solution revealed all non-hydrogen atom positions of the the anion and cation. A dichloromethane lattice molecule was found on the subsequent difference map. Hydrogen atoms positions were idealized: C–H = 0.93 Å (aromatic), 0.96 Å (methyl), 0.97 Å (methylene), 0.98 Å (methyne). The hydrogen atoms were refined using a riding model, with isotropic temperature factors fixed at 1.5 (methyl) or 1.2 (all others) times the equivalent isotropic U of the atom they were bonded to. The final refinement¹⁹ included anisotropic temperature factors on all non-hydrogen atoms and converged with final residuals of $R1(I > 2\sigma) = 0.0870$ and $wR2(I > 2\sigma) = 0.1911$. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXL TL NT.²⁰ Additional details of data collection and structure refinement are listed in Table 1.

Acknowledgment. This work was supported by the Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division. We are most grateful to Ken Caulton for very helpful advice regarding the X-ray structure of **4**, particularly in regard to checking the validity of the structure of the SbF_6 salt that proved to be erroneous.

Supporting Information Available: Detailed X-ray crystallographic data of the structure of compound **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) SMART Version 4.210; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1996.

(17) SAINT Version 4.05; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1996.

(18) Sheldrick, G. *SADABS*, first release; University of Göttingen: Germany, 1996.

(19) $R1 = \sigma|F_o| - |F_c|/|\sigma|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0629P)^2]$.

(20) SHELXL TL NT Version 5.10; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 1997.