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Synthesis and Reactivity of Manganese Tricarbonyl Complexes of the Centropolyindanes 10-Methyltribenzotriquinacene and Fenestrindane

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Summary: The cationic manganese tricarbonyl moiety is readily coordinated to an arene ring of the centropolyindanes 10-methyltribenzotriquinacene (MTBT) and fenestrindane (FET) to afford $[(MTBT)Mn(CO)_3]^+$ *(**1**) and* $[(FET)Mn(CO)_3]^+$ *(**2**). An X-ray structure of **1** shows that the metal is coordinated to the convex face of the MTBT ligand. Both **1** and **2** are electrophilically activated and readily undergo regioselective and stereoselective addition reactions with mild nucleophiles.*

Introduction

Centropolyindanes are polycyclic organic compounds consisting of indane units fused in three dimensions.[1] 10-Methyltribenzotriquinacene (MTBT)[2] and fenestrindane (FET)[3] are two examples of this fascinating class of molecules. The chromium tricarbonyl moiety has been coordinated to the arene rings in several centropolyindanes.[4] In the case of MTBT, complexes containing one, two, and three $Cr(CO)_3$ units were isolated.[4a] Perhaps the primary motivation for coordinating a metal to a centropolyindane is to alter the system's chemical reactivity. In a general sense, coordination of a metal to an arene is a well-established method to induce electrophilic activation and provide for subsequent functionalization of the carbocyclic ring. While $Cr(CO)_3$ has found useful applications in this regard in organic chemistry,[5] it is known[6] that the $Mn(CO)_3^+$ moiety is far more activating and allows the addition of relatively mild nucleophiles to the coordinated arene ring. Functionalization of MTBT at the arene positions offers an interesting potential for the construction of novel convex−concave polycondensed hydrocarbon frameworks, and related reactions with fenestrindanes such as FET may provide a route to saddle-type congeners.[7] Accordingly, we decided to examine the $Mn(CO)_3^+$ complexes of MTBT and FET with respect to synthesis, structure, and electrophilic reactivity. It is demonstrated herein that the tetrafluoroborate salts of $[(MTBT)Mn(CO)_3]^+$ and $[(FET)Mn(CO)_3]^+$ are readily prepared in high yield and that both react stereoselectively with nucleophiles to afford stable cyclohexadienyl complexes.

Results and Discussion

The synthesis of $[(MTBT)Mn(CO)_3]BF_4$ (**1**) and $[(FET)Mn(CO)_3]BF_4$ (**2**) was easily accomplished by a recently developed method that is based on the acenaphthene

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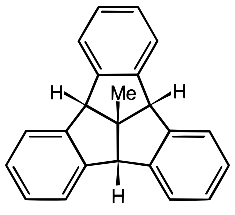
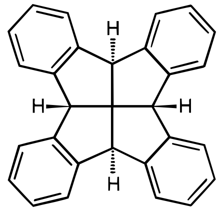


(MTBT)



(FET)

substitution reactions in Scheme 1.[8] The key to this synthetic route is the ease with which the acenaphthene ligand (or any naphthalene type ligand) can slip from η^6 to η^4 bonding as the incoming arene binds to the metal, affording a pathway for subsequent loss of the acenaphthene and η^6-bonding to the metal to give, in the cases under consideration, the centropolyindane complexes **1** and **2**.

An X-ray diffraction study showed that [**1**]BF_4 crystallizes with three molecules in the asymmetric unit. One of the three is illustrated in Figure 1. All three molecules of [**1**]BF_4 have the $Mn(CO)_3^+$ moiety coordinated to the convex face of the MTBT ligand, as was found for the most stable isomer of [(MTBT)$Cr(CO)_3$].[4a] The only chemically interesting difference among the three structures resides in the orientation of the carbonyl groups; the structure shown in Figure 1 has the Mn−C−O vectors roughly bisecting the arene ring C(6)−C(7), C(8)−C(9), and C(10)−C(11) bonds. The other two independent molecules have the Mn−C−O vectors eclipsing C(6), C(8), C(10) and C(7), C(9), C(11), respectively. The existence of these three isomers in equal proportions suggests that the associated rotational barrier is very small and that there is very little energy difference among the isomers.

As expected, the reaction of **1** with the nucleophiles Bu_4NBH_4 and $LiCH_2C(O)CMe_3$ gave cyclohexadienyl complexes in good yields. Analysis of the ^1H NMR data showed that hydride addition to **1** from BH_4^- occurred at positions *ortho* and *meta* to bridgehead indane carbons with a regioselectivity of 5:1 in favor of the *ortho* position to afford the inseparable isomers **3a** and **4a**. With the larger nucleophile lithium pinacolonate, $LiCH_2C(O)CMe_3$, addition occurred from the *anti* side relative to the metal (*exo* addition) with an *ortho:meta* ratio of only 1:1 to give products **3b** and **4b**. It is presumed that the decreased *ortho:meta* ratio is due to steric constraints presented by the pinacolonate nucleophile. The conclusion from these results is that the manganese-mediated functionalization of an arene ring in MTBT is a viable synthetic procedure. Simple methods exist for the removal of the $Mn(CO)_3$ moiety with concomitant loss of the *endo* hydride and rearomatization.[9]

The hydride donor Bu_4NBH_4 was found to add cleanly to the fenestrindane complex [**2**]BF_4 at the coordinated arene ring. Unlike the case with [**1**]BF_4, the addition occurred with high selectivity (>90%) in favor of the *ortho* position to give **5**, with only traces of other addition products. The structure of complex **5** was verified by an X-ray diffraction study and is shown in Figure 2. In this study, and as is generally the case with cyclohexadienyl complexes, a Mn−C−O linkage eclipses the saturated carbon, C(4). The bond distances in **5** are fairly typical and are given in the caption to Figure 2.

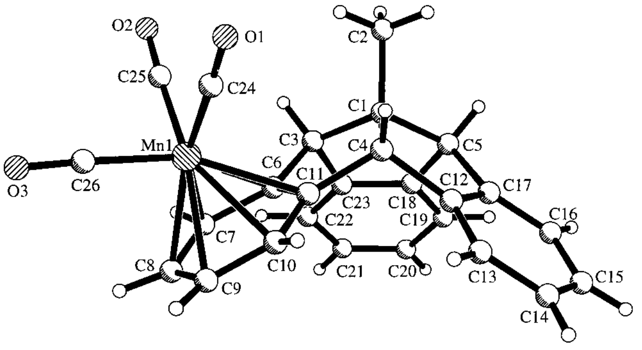
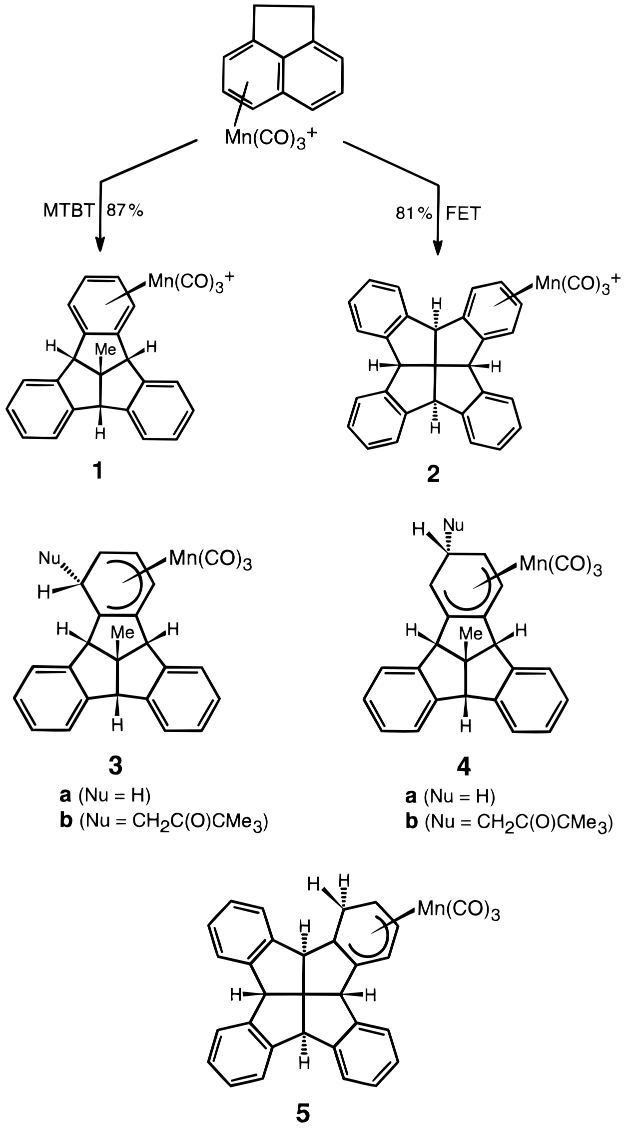


Figure 1. X-ray structure of the cation in [(η^6-MTBT)$Mn(CO)_3$]BF_4 (**1**). Selected bond lengths [Å]: C(4)−C(11) 1.496(10), C(4)−C(12) 1.499(10), C(6)−C(7) 1.422(10), C(7)−C(8) 1.398(11), C(8)−C(9) 1.391(12), C(9)−C(10) 1.384(11), C(10)−C(11) 1.423(10), C(11)−C(6) 1.389(10), Mn−C(6) 2.240(7), Mn−C(7) 2.189(8), Mn−C(8) 2.177(10), Mn−C(9) 2.182(10), Mn−C(10) 2.209(9), Mn−C(11) 2.231(8).

Scheme 1



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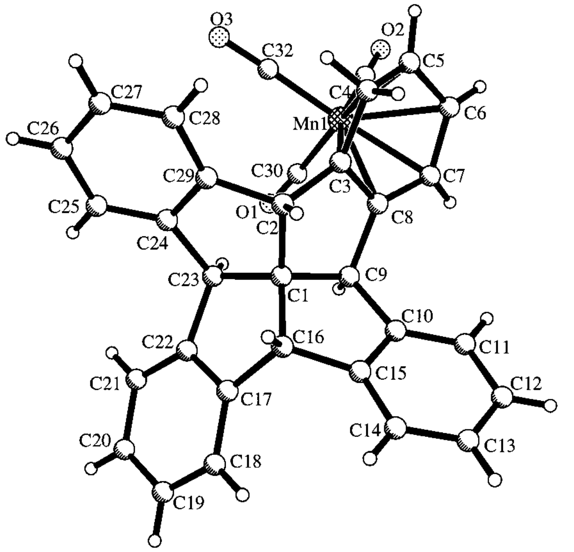

Figure 2. X-ray structure of [(η^5-FET·H)Mn(CO)$_3$] (**5**). Selected bond lengths [Å]: C(3)−C(4) 1.466(8), C(4)−C(5) 1.451(10), C(5)−C(6) 1.411(10), C(6)−C(7) 1.394(9), C(7)−C(8) 1.412(8), C(3)−C(8) 1.382(8), Mn−C(3), 2.247(6), Mn−C(5) 2.206(8), Mn−C(6) 2.226(8), Mn−C(7) 2.132(7), Mn−C(8) 2.165(6).

The pentadienyl carbons in **5** are quite planar and form a fold angle of 26.2° with the C(3)−C(4)−C(5) plane. As with the MTBT system discussed above, it is apparent that FET can also be easily functionalized by precoordination of Mn(CO)$_3^+$ to one of the arene rings.

As in other [(arene)Mn(CO)$_3$]$^+$ complexes,[6] nucleophilic attack on **1** and **2** occurs with high stereoselectivity from the *exo* side with respect to the metal, which represents the sterically hindered side of the centropolyindane ligands. With centropolyindane ligands, the regioselectivty of nucleophilic attack by hydride exhibits a clear preference for the *ortho* positions of MTBT and FET. As has been shown recently,[7] introduction of substituents by *electrophilic* attack into the "bay" regions of the centropolyindanes is suppressed, while exhaustive substitution of the *meta* positions is feasible, and even the construction of *ortho*-substituted centropolyindanes by using appropriately presubstituted building blocks proved to be hampered by steric interactions.[10] Steric hindrance should be more pronounced in MTBT than in FET for two reasons. (i) The concave diindane surfaces of MTBT are more strongly shielded than those of FET since three indane units are fused in a *syn* orientation in the former hydrocarbon but only pairs of them in the latter. (ii) As compared to the conformationally rigid MTBT, the framework of FET is flexible and exists in two interconverting conformers.[1d,11] In accordance with this, hydride attack was found to be much more regioselective for the *ortho* positions in [**2**]BF$_4$ than in [**1**]BF$_4$. The more severe steric hindrance in the bay region of the MTBT complex is also reflected by the lack of regioselectivity with pinacolonate, which adds to the shielded *ortho* and to the much less shielded *meta* positions at the same rate. These results demonstrate that curved condensed aromatic hydrocarbons can be activated by Mn(CO)$_3^+$ complexation toward nucleophilic attack from the sterically hindered side of the aromatic π-system. This should open access to a number of interesting derivatives of the centropolyindanes bearing *ortho*-functionalities in the sterically hindered bay regions.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques, where applicable. Microanalyses were performed by National Chemical Consulting, Inc., Tenafly, NJ. HPLC grade CH$_2$Cl$_2$ was purchased from Fisher Scientific and was stored under N$_2$ over 4 Å molecular sieves. [(η^6-acephthene)Mn(CO)$_3$]BF$_4$ was prepared as recently reported.[8] Activated neutral alumina (Brockmann I, ca. 150 mesh, 58 Å) was deactivated by adding H$_2$O to form a 10%, w/w mixture. ^{1}H NMR spectra were recorded on instruments operating at 250 or 400 MHz; assignments listed as *exo* or *endo* refer to orientation relative to the metal. Mass spectra were recorded with a Kratos MS-80 specrometer, using nitro octyl phenyl ether as the solvent matrix.

[(η^6-10-Methyltribenzotriquinacene)Mn(CO)$_3$]BF$_4$ ([1]BF$_4$). To a solution of [(η^6-acephthene)Mn(CO)$_3$]BF$_4$ (0.150 g, 0.394 mmol) in CH$_2$Cl$_2$ (ca. 10 mL) under N$_2$ was added 10-methyltribenzotriquinacene (0.140 g, 0.48 mmol). The mixture was sealed in a pressure bottle and heated to 70 °C for 2 h. The reaction mixture was then cooled to room temperature and concentrated. Addition of Et$_2$O (ca. 40 mL) precipitated the product as a pale yellow powder, which was collected by filtration, washed with Et$_2$O, and dried in vacuo. Yield: 87%. IR (CH$_2$Cl$_2$): $\nu_{\rm co}$ [cm^{-1}] 2076 (s), 2018 (s, br). ^{1}H NMR ((CD$_3$)$_2$CO): δ 7.69 (m, 4H, ArH), 7.32 (m, 6H, ArH), 6.87 (m, 2H, ArH), 4.81 (s, 2H, H^b), 4.67 (s, H^b), 1.87 (s, Me). Anal. (%) Calcd for C$_{26}$H$_{18}$O$_3$MnBF$_4$: C 60.04, H 3.49. Found: C 59.89, H 3.70.

A crystal of [**1**]BF$_4$ suitable for X-ray diffraction was grown by slow diffusion of diethyl ether into an acetone solution at −4 °C. The crystal structure was determined using a Siemens P4 diffractometer equipped with an area detector and controlled by SMART version 4 software. Data reduction was carried out by SAINT version 4 software and included profile analysis; this was followed by absorption correction by use of the program SADABS. The structure was determined by direct methods and refined on F^2 using the programs in the SHELXTL PC version 5 package. Few hydrogens atoms appeared in difference maps, so each was introduced in an ideal position, riding on the atom to which it is bonded. Each hydrogen atom was refined with an isotropic temperature factor 20% greater than that of the ridden atom. For [**1**]BF$_4$: data collected at 25 °C using Mo Kα radiation, crystal size 0.34 × 0.26 × 0.04 mm, orthorhombic space group $Pna2_1$, a = 29.9759(3) Å, b = 9.8300(2) Å, c = 23.6351(3) Å, V = 6964.4(2) Å^3, Z = 12, $\rho_{\rm calcd}$ = 1.488 g cm^{-3}, μ = 0.627 mm^{-1}, θ range 1.36−23.49°, 946 variables refined with 8474 independent reflections to R = 0.0773, w$R2$ = 0.1265, GOF = 1.126. Although the small size of the crystal and disorder in the BF$_4^-$ anions led to a less than ideal data set, the structure solved immediately. There are three independent molecules in the asymmetric unit. Each independent cation approximated mirrow symmetry about a plane through manganese, the carbon at the apex of the "basket" or "hat", and the terminal methyl group, although the manganese carbonyl groups deviated somewhat from this symmetry. The different orientations of the carbonyl groups made it evident that the three molecules are really independent. The three independent tetrafluoroborate anions were restrained to be similar and to approximate tetrahedral symmetry.

Crystallographic data (excluding structure factors) for the structures reported in this paper ([**1**]BF$_4$ and **5**) have been

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deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132071 and CCDC-132072.

[(η^6-Fenestrindane)Mn(CO)$_3$]BF$_4$ ([2]BF$_4$). This complex was prepared from fenestrindane (0.166 g, 0.45 mmol) by a procedure completely analogous to that described above for [**1**]BF$_4$. Yield: 81%. IR (CH$_2$Cl$_2$): ν_{co} [cm^{-1}] 2079 (s), 2029 (s, br). ^{1}H NMR ((CD$_3$)$_2$CO): δ 7.85−7.71 (m, 5H, ArH), 7.59 (d, 1H, J = 6 Hz, ArH), 7.46−7.31 (m, 8H, ArH), 7.14 (t, 1H, J = 6 Hz, ArH), 6.72 (t, 1H, J = 6 Hz, ArH), 5.31 (s, H^b), 5.28 (s, H^b), 5.19 (3, H^b), 5.10 (s, H^b). Anal. (%) Calcd for C$_{32}$H$_{20}$O$_3$-MnBF$_4$: C 64.68, H 3.39. Found: C 63.27, H 4.17.

Reaction of [1]BF$_4$ with Tetrahydroborate, [(η^5-MTBT·H)Mn(CO)$_3$] (3a, 4a). To a slurry of [**1**]BF$_4$ (0.052 g, 0.10 mmol) in CH$_2$Cl$_2$ (5 mL) under N$_2$ at 0 °C was added [Bu$_4$N]-BH$_4$ (0.040 g, 0.14 mmol), and the mixture was stirred for 10 min, then warmed to room temperature and stirred for an additional 10 min. The solvent was removed in vacuo and the residue extracted with diethyl ether. The ether-soluble product was eluted through a hexanes packed neutral alumina column with Et$_2$O as eluent to afford an inseparable mixture of **3a** and **4a** in a 5:1 ratio. Yield: 72% (0.031 g). IR (hexanes): ν_{co} [cm^{-1}] 2014 (s), 1942 (s), 1929 (s). ^{1}H NMR (CDCl$_3$) for **3a**: δ = 7.59−7.10 (m, 8H, ArH), 6.13 (d, J = 5.3 Hz, H^4), 4.88 (t, J = 5.3 Hz, H^3), 4.34 (s, H^b), 3.96 (s, H^b), 3.92 (s, H^b), 3.17 (dd, J = 13, 5.6 Hz, H$^{1-\text{endo}}$), 3.01 (m, H^2), 1.98 (d, J = 13 Hz, H$^{1-\text{exo}}$), 1.52 (s, Me). HRMS m/z calcd for C$_{26}$H$_{19}$O$_3$MnNa: 457.0612; found 457.0611. FAB-MS: 457 (M + Na$^+$), 433 (M − H$^-$). Anal. (%) Calcd for C$_{26}$H$_{19}$O$_3$Mn: C 71.89, H 4.41. Found: C 71.78, H 4.14.

Reaction of [1]BF$_4$ with Pinacolonate, [(η^5-MTBT·CH$_2$COCMe$_3$)Mn(CO)$_3$] (3b, 4b). To a stirred suspension of [**1**]BF$_4$ (0.104 g, 0.20 mmol) in Et$_2$O at −78 °C was added dropwise LiCH$_2$COCMe$_3$ (1.5 equiv), prepared by adding LDA to a THF solution of pinacolone at −78 °C, over 2 min. The mixture was stirred for 5 min and allowed to warm to room temperature. The solvent was removed in vacuo and the residue extracted with diethyl ether and subjected to chromatography through neutral alumina with hexanes/Et$_2$O (2:1) as eluent to afford a mixture of **3b** and **4b** in a 1:1 ratio. Yield: 69% (0.073 g). Anal. (%) Calcd for C$_{32}$H$_{29}$O$_4$Mn: C 72.18, H 5.49. Found: C 72.35, H 5.54. HRMS m/z calcd for C$_{32}$H$_{29}$O$_3$-MnNa: 555.1344; found 555.1332. FAB MS: 555 (M + Na$^+$), 531 (M − H$^-$), 433 (M − CH$_2$COCMe$_3$$^-$). IR (hexanes): ν_{co} [cm^{-1}] 2016 (s), 1946 (s), 1929 (s), 1701 (w). ^{1}H NMR (CD$_2$Cl$_2$) for **3b**: δ 7.69−7.13 (m, 8H, ArH), 6.34 (d, J = 5 Hz, H^4), 4.94 (t, J = 6 Hz, H^3), 4.45 (s, H^b), 4.05 (s, H^b), 4.03 (s, H^b), 3.32 (m, J = 13 Hz, H$^{1-\text{endo}}$), 3.28 (m, H^2), 1.53 (s, Me), 1.27−1.19 (m, CH$_2$), 0.57 (s, CMe$_3$). ^{1}H NMR (CD$_2$Cl$_2$) for **4b**: δ 7.69−7.13 (m, 8H, ArH), 5.64 (d, J = 7 Hz, H^4), 4.66 (s, H^b), 4.55 (s, H^b), 4.34 (s, H^b), 3.61 (m, H^1), 3.28 (m, H^3), 2.92 (m, H$^{2-\text{endo}}$), 1.66 (s, Me), 1.10 (m, CH$_2$), 0.38 (s, CMe$_3$).

Reaction of [1]BF$_4$ with Tetrahydroborate, [(η^5-FET·H)Mn(CO)$_3$] (5). This compound was prepared as described above for **3a** and **4a**. The product consisted of **5** along with a trace amount of what is believed to be the isomer formed by *meta* addition of hydride. Yield: 76%. IR (hexanes): ν_{co} [cm^{-1}] 2010 (s), 1937 (s), 1915 (s). ^{1}H NMR (CDCl$_3$) for **5**: δ 7.70−7.20 (m, 12H, ArH), 6.20 (d, J = 5.3 Hz, H^4), 5.00 (t, J = 5.3 Hz, H^3), 4.82 (s, H^b), 4.74 (s, H^b), 4.32 (s, H^b), 3.94 (s, H^b), 3.21 (dd, J = 13, 5.5 Hz, H$^{1-\text{endo}}$), 3.04 (t, J = 7 Hz, H^2), 2.44 (d, J = 13 Hz, H$^{1-\text{exo}}$).

A crystal of **5** suitable for X-ray diffraction was grown from a CH$_2$Cl$_2$/pentane solution at −15 °C. The crystal selected was a slightly cloudy yellow prism, with some natural faces. Data collection and reduction was carried out as described above for [**1**]BF$_4$. At the end of data collection the crystal was cloudier than at the beginning, and it proved to have lost some solvent of crystallization, but not enough to preclude solution and refinement. The loss of solvent and the smallness of the crystal account for the comparatively large R values (vide infra). Twenty of the 23 hydrogen atoms appeared in a difference map, and each was introduced in an ideal position, riding on the atom to which it is bonded. Each hydrogen atom was refined with an isotropic temperature factor 20% greater than that of the ridden atom. In the course of refinement, it became clear that the crystal included a molecule of methylene chloride. The displacement parameters were initally large, which suggested less than complete occupancy of the solvent site; this is consistent with the clouding of the crystal during data collection. Cut-and-try refinement with various fixed values for the site occupancy factor showed that the best fit was obtained at about 90% occupancy. A mild restraint was applied to make the carbon−chlorine bonds of similar length. For **5**: data collected at 25 °C using Mo Kα radiation, crystal size 0.16 × 0.18 × 0.20 mm, triclinic space group $P1$, a = 10.4080(5) Å, b = 10.9907(6) Å, c = 12.2715(6) Å, α = 94.5070(10)°, β = 97.899(2)°, γ = 102.0910(10)°, V = 1351.21(12) Å^3, Z = 2, ρ_{calcd} = 1.458 g cm^{-3}, μ = 0.720 mm^{-1}, θ range 1.69−23.60°, 352 variables refined with 3719 independent reflections to R = 0.0740, w$R2$ = 0.1645, GOF = 1.020.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for [**1**]BF$_4$ and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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