

An Unusual Anion– π Interaction in an Irido Organometallic Assembly: Synthesis, First Crystal Structure, and Computational Study

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The organometallic assembly $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2\text{-(CF}_3\text{SO}_3)]$ $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})_3\text{IrCp}^*]$ (**3**) was prepared from $[\text{Cp}^*\text{Ir}(\text{solvent})_3][\text{OTf}]_2$ (**2**) and 1,2,4,5 tetrahydroxybenzene (THB, **1**) in acetone, in the presence of an excess amount of $\text{BF}_3\cdot 2\text{H}_2\text{O}$. Assembly **3** was fully characterized by multinuclear NMR spectroscopy. Remarkably, the X-ray molecular structure of **3** shows that an anion– π interaction occurs between the neutral component $\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2$ of the

assembly and the CF_3SO_3 anion of the cationic species $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})_3\text{IrCp}^*]$. Computational analysis was carried out on **3** to unravel the nature of this noncovalent interaction. Such an example could serve as a model to explain the important role of anions in organometallic chemistry and asymmetric catalysis.

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Introduction

Anion– π interactions have become a highly important topic since first reports by Hiroaka, Schneider and later by Frontera, Deyà, and others.^[1–3] Indeed very recently, several reviews have been devoted to this important subject. Theoretical and later experimental studies showed that such interactions are favorable and occur between anions and electron deficient aromatics (i.e., hexafluorobenzene, s-triazine, and s-tetrazine). There is evidence however that even originally nonelectron deficient aromatics can establish anion– π interactions if the ring is simultaneously interacting with a cation on the opposite face (Figure 1).^[4]

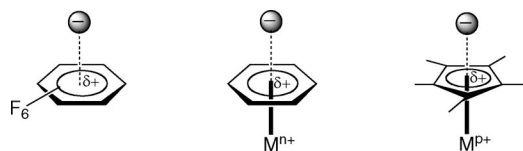


Figure 1. Graphical representation of the anion– π interaction in hexafluorobenzene (left) and in the (arene) M moiety (middle and right; arene = $\eta^6\text{-C}_6\text{H}_6$; $\eta^5\text{-C}_5\text{Me}_5$).

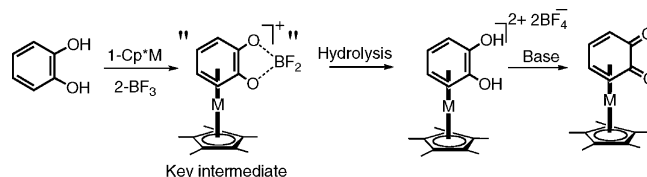
Most of these examples reported so far involve coordination assemblies, where this kind of noncovalent interaction occurs between the electron-deficient aromatic rings of the coordinated ligands and the counteranions of the assemblies.^[5–7] However, we also note the existence of some cationic organometallic compounds that show such anion– π interactions between the organometallic entities (arene) M ; (arene = $\eta^6\text{-C}_6\text{H}_6$; $\eta^5\text{-C}_5\text{Me}_5$, and $\eta^5\text{-C}_5\text{H}_5$) and the counter polyatomic anions, which when reported were not described as such.^[4] We wish to report in this communication an unusual anion– π interaction that occurs between the neutral complex $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2]$ and the triflate anion of another compound $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})_3\text{IrCp}^*][\text{CF}_3\text{SO}_3]$, providing a rare example of an organometallic assembly that can be better described with the chemical formula $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2\text{-(CF}_3\text{SO}_3)]$ $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})_3\text{IrCp}^*]$ (**3**) and illustrating the power of such a noncovalent interaction.

We recently reported a rational method to prepare simple π -bonded *o*-quinone metal complexes of the formulae $[\text{Cp}^*\text{M}(\eta^4\text{-}o\text{-quinone})]$ ($M = \text{Rh, Ir}$).^[8] In these complexes the *o*-quinone moiety is η^4 -bonded to the metal through the arene ring, unlike those examples described previously whether the *o*-quinone is σ -bonded to the metal center

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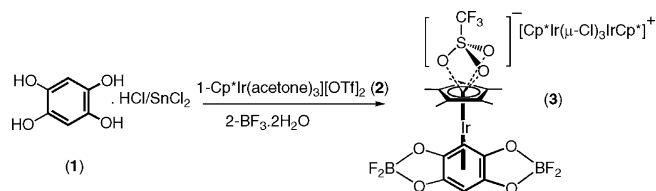


Scheme 1. Synthesis of the organometallic linkers $[\text{Cp}^*\text{M}(\eta^4\text{-}o\text{-quinone})]$ ($M = \text{Rh, Ir}$).

through the oxygen atoms.^[9] Our method seems suitable to selective π complexation of arene rings with Lewis base functionalities that are also available to metal coordination. It involves the use of the Lewis acid BF_3 as an arene activator, whereby it blocks temporarily the oxygen centers of the *o*-quinone and facilitates the metal coordination to the arene ring (Scheme 1).

Results and Discussion

While trying to validate the above mechanism by intercepting the hypothetical key difluoroborate intermediate, we carried out the reaction of $[\text{Cp}^*\text{Ir}(\text{acetone})_3][\text{OTf}]_2$ (**2**), prepared in situ, with 1,2,4,5 tetrahydroxybenzene (THB; **1**) in acetone, in the presence of an excess amount of $\text{BF}_3 \cdot 2\text{H}_2\text{O}$. Precipitation with Et_2O and subsequent recrystallization from acetone/ Et_2O afforded orange crystals of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2(\text{CF}_3\text{SO}_3)][\text{Cp}^*\text{Ir}(\mu\text{-Cl})_3\text{IrCp}^*]$ (**3**) in 41 % yield (Scheme 2). This organometallic assembly was first obtained serendipitously but later reproducibly.^[10]



Scheme 2. Synthesis of the organometallic assembly $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2(\text{CF}_3\text{SO}_3)][\text{Cp}^*\text{Ir}(\mu\text{-Cl})_3\text{IrCp}^*]$ (**3**).

Assembly **3** was characterized by multinuclear NMR spectroscopy (^1H , ^{13}C , ^{19}F , ^{11}B). The ^{19}F NMR spectrum of **3** was very informative (see Supporting Information), as it shows a singlet at $\delta = -79.3$ ppm attributed to the triflate anion. Further, an ABX system ($\text{X} = ^{11}\text{B}$) is also visible for the two BF_2 moieties centered at $\delta F_A = -139.1$ ppm and $\delta F_B = -141.2$ ppm with $^2J_{\text{F,F}} = 67$ Hz and $^1J_{\text{B,F}} = 9$ Hz. We also note the presence of another ABX system, which arises from ^{10}B isotopes (20:80 ratio). The ^{11}B NMR spectrum shows the presence of a broad signal at 6.5 ppm. These data suggest the presence of two BF_2 moieties chelated by the oxygen centers of the π -bonded tetraoxobenzene. This was unambiguously confirmed by X-ray analysis (vide infra).

The organometallic assembly **3** crystallizes in the orthorhombic space group $Pnma$.^[11] A view of the anionic part of the molecule is shown in Figure 2. Interestingly, the presence of the two five-membered cycles fused to the π complexed arene, which can be viewed as definitive proof for the mechanism proposed in Scheme 1, is not the only striking feature of this structure. At first glance one can notice that the CF_3SO_3 anion is perfectly situated on the top of the ring of the Cp^*Ir unit with each of its oxygen atoms oriented over a carbon atom of the electron-poor ring. In

fact, the anion lies on the plane of symmetry that bisects equally the neutral molecule $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2]$ and the CF_3SO_3 anion. The $\text{C}\cdots\text{O}$ distances are 2.94 Å for “C4–O3” and 3.19 Å for the two C6–O4 contacts, which are symmetrically related by the molecule plane of symmetry. These bond lengths are shorter than the sum of their van der Waals radii ($d = 3.22$ Å).^[12] Further, the measured d_{offset} value of 0.13 Å also suggests an anion– π interaction.^[13] This type of anion– π interaction with metallocenes has been recently investigated theoretically by Frontera and Deyà,^[4] however, we are not aware of any precedent experimental work that describes the power of such noncovalent interactions between a neutral species and the counteranion of another organometallic complex and thus providing a rare example of an irido organometallic assembly.

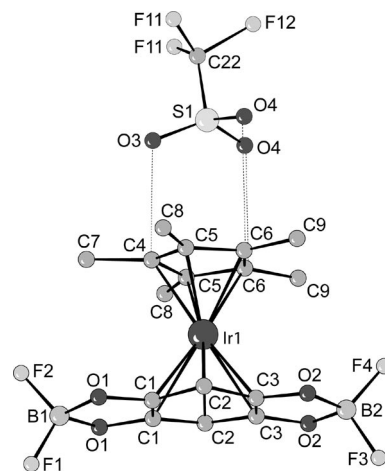


Figure 2. (a) View of the anionic part of organometallic assembly **3** with atom numbering system. (b) The CF_3SO_3 anion is perfectly located on top of the Cp^*Ir moiety and lies on the same plane of symmetry as that of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2]$. (c) $\text{C}\cdots\text{O}$ short contacts are shown by dotted lines.

To the best of our knowledge, this is an unusual type of anion– π interaction occurring between two different organometallic species. To unravel its nature, we have undertaken a computational study performed at the B3P86/LACVP+(d,p) theoretical level.^[14]

The calculations yielded an optimized structure in reasonable agreement with the X-ray analysis (see Supporting Information). Because the anion– π interaction is of polarization but also mostly of electrostatic origin, a map of the electrostatic potential on an isodensity surface of 0.02 e Å^{-3} was created. As expected, the five carbon atoms of the Cp^* ring are areas of low electron concentration. Interestingly, however, the hydrogen atoms of the five methyl groups are the electron-poorer areas of the Cp^* fragment. Therefore, participation of these hydrogen atoms to the coordination of the triflate can be anticipated (Figure 3).

The organometallic fragment remains virtually unchanged after coordination of the triflate above the Cp^* ring, except for the methyl groups that move further away from the ring plane in the direction of the anion to reach a tilt angle of about 5° (vs. 3° without the triflate). The $\text{Cp}^*_{\text{centroid}}\text{S}$ distance matches quite well with that found

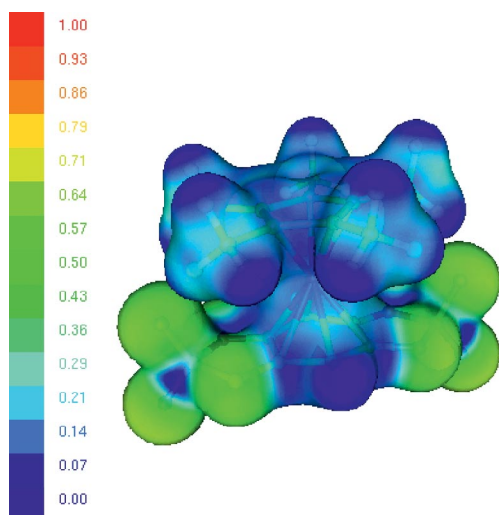


Figure 3. Electrostatic potential on an isodensity surface of 0.02 e Å^{-3} of the neutral complex $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{O}_4)(\text{BF}_3)_2]$ showing low electron concentration for the methyl protons of the Cp^*Ir moiety as illustrated by the deep-blue color.

from the X-ray structure (3.43 vs. 3.47 Å, respectively). So does the $\text{IrCp}^*_{\text{centroid}}\text{S}$ angle of 177.7° (vs. 177.9°), which leads to a d_{offset} value of 0.14 Å (vs. 0.13 Å; vide supra).^[13] However, in the absence of crystal forces, the computed structure slightly deviates from σ_h symmetry. The triflate oxygen atoms are now superimposed with only two carbon atoms of the Cp^* ring and with the center of a C-C bond. Short contacts also appear between the triflate oxygen atoms and the four methyl hydrogen atoms as marked (Figure 4).

The same maximum electron density ($\rho_{\text{max}} = 0.007 \text{ e Å}^{-3}$) between the triflate oxygen atoms and the methyl hydrogen atoms on the one hand and between the triflate oxygen atoms and the ring carbon atoms on the other hand was measured (Figure 5). This value is characteristic of noncovalent bonding interactions.^[3,15] This could be further ascertained by looking at the canonical molecular orbitals [at $0.032 \text{ (e Å}^{-3})^{1/2}$] (see Supporting Information). This inspection revealed no mixing between the Cp^* and the triflate.

Further, the stabilization energy for the triflate- π interaction is estimated $E = -19.42 \text{ kcal mol}^{-1}$ after counterpoise and ZPE corrections. Overall we feel that this unusual non-binding between the neutral organometallic complex and triflate of another organometallic compound to form assembly **3** is the result of a combination of two types of noncovalent interaction mainly hydrogen bonding and anion- π interaction.^[15]

To the best of our knowledge, this is a rare example that describes the power of anion- π interactions in an assembly of two organometallic species; however, we note that chiral anions were used to resolve cationic organometallic compounds through noncovalent interactions.^[16–18] Further, the role of anions in asymmetric catalysis with transition-metal compounds has been widely described; for instance, Togni and co-workers^[19] have shown that fluoride anions increase the enantioselectivity of allylic amination reactions cata-

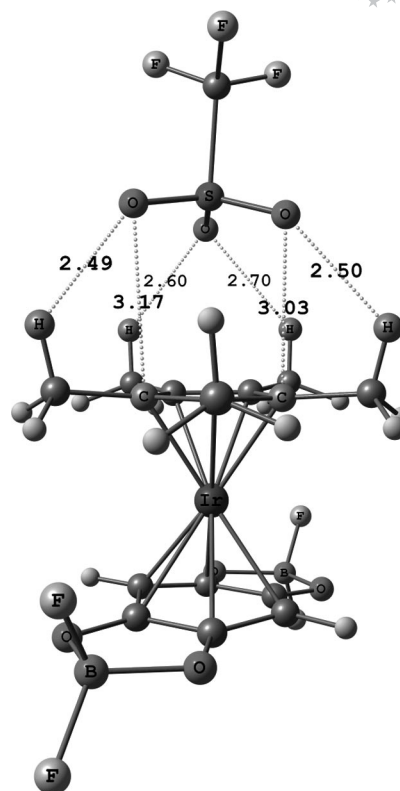


Figure 4. Optimized structures of the anionic part of **3** showing a combination of anion- π interactions and hydrogen bonding from the methyl groups of the Cp^*Ir moiety (selected distances in Å).

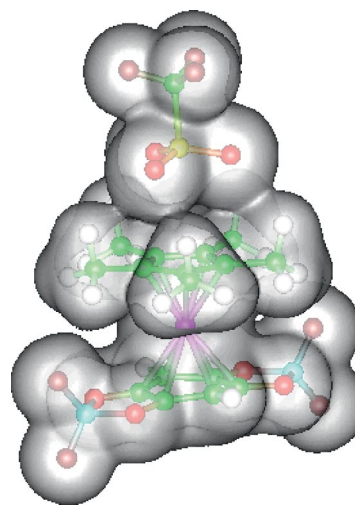


Figure 5. Optimized structure with density surface (0.007 e Å^{-3}).

lyzed by Pd^{II} complexes bearing bidentate N,P ligands. Finally, the use of functionalized BNP (1,1'-binaphthyl-2,2'-diyl phosphate) chiral anions with gold complexes have shown dramatic changes in selectivity of asymmetric hydroalkoxylation reactions.^[20] In a similar way, association of functionalized BNP chiral anions with Cp^*Ir catalysts showed high enantioselectivity in the asymmetric hydrogenation of acyclic imines.^[21]

Conclusions

To close, we have described the synthesis and first crystal structure of a rare example of an organometallic assembly $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2(\text{CF}_3\text{SO}_3)][\text{Cp}^*\text{Ir}(\mu\text{-Cl})_3\text{IrCp}^*]$ (**3**). This assembly results from an unusual anion– π interaction between the neutral organometallic π complex and the triflate anion of another organometallic species. Computational studies show that this noncovalent interaction can be better described as a combination of hydrogen bonding and anion– π interactions. Such an example could serve as a model to explain the role of weakly coordinated anions in organometallic catalysis. Further, the use of BF_3 allowed us to prepare the tetradentate organometallic linker, which could be used in the future to construct chiral coordination assemblies.

Experimental Section

General: All experimental manipulations were carried out under an atmosphere of argon by using Schlenk tube techniques. The ^1H , ^{13}C , ^{19}F , and ^{11}B NMR spectra were recorded in $(\text{CD}_3)_2\text{CO}$ by using a Bruker Avance 400 NMR spectrometer at 400.13, 100.61, 376.45, and 128.4 MHz, respectively. Infrared spectra were recorded with a Bruker Tensor FTIR spectrometer equipped with an ATR Harricks apparatus. 1,2,4,5-Tetrahydroxybenzene was prepared by following a literature procedure, by heating 2,5-dihydroxybenzoquinone in concentrated HCl solution at reflux in the presence of tin for 4 h.^[22]

$[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2(\text{CF}_3\text{SO}_3)][\text{Cp}^*\text{Ir}(\mu\text{-Cl})_3\text{IrCp}^*]$ (3**):** A solution of AgOTf (260 mg, 1 mmol) in acetone (10 mL) was added to $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})\text{Cl}]_2$ (200 mg, 0.25 mmol) in acetone (10 mL) to give rapidly a white precipitate of AgCl . The reaction mixture was stirred for 15 min. The resulting yellow solution of $[\text{Cp}^*\text{Ir}(\text{acetone})_3][\text{OTf}]_2$ (**2**) was then filtered under an atmosphere of argon into a dry Schlenk tube containing 1,2,4,5-tetrahydroxybenzene (145 mg, 1 mmol) and the solvent was removed under vacuum. $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ 98% (1 mL) was added to the brown residue, and the mixture was stirred for 1 h at room temperature and diethyl ether (60 mL) was then added. Compound **3** precipitated as an orange brown microcrystalline powder, which was filtered and washed several times with diethyl ether (20 mL). Recrystallization from acetone/diethyl ether using slow evaporation technique gave orange crystals. Yield: 41% (101 mg, 0.068 mmol). ^1H NMR [400 MHz, $(\text{CD}_3)_2\text{CO}$]: δ = 1.75 (s, 30 H, Cp^*), 2.08 (s, 15 H, Cp^*), 6.94 (s, 2 H, aromatic) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR [100 MHz, $(\text{CD}_3)_2\text{CO}$]: δ = 8.6 (CH_3 , Cp^*), 9.5 (CH_3 , Cp^*), 65.5 (C–H, aromatic), 89.1 (C=C, Cp^*), 99.2 (C=C, Cp^*), 128.6 (C–O, aromatic) ppm. ^{19}F NMR [376 MHz, $(\text{CD}_3)_2\text{CO}$]: δ = –79.3 (s, 3 F, OTf), –139.1 (dd, $^2J_{\text{F,F}} = 67$ Hz, $^1J_{\text{F,B}} = 9$ Hz, 2 F, F_A), –141.2 (dd, $^2J_{\text{F,F}} = 67$ Hz, $^1J_{\text{F,B}} = 9$ Hz, 2 F, F_B) ppm. ^{11}B NMR [128 MHz, $(\text{CD}_3)_2\text{CO}$]: δ = 6.5 (br. s, 2B, $-\text{BF}_2$) ppm. IR (ATR): $\tilde{\nu}$ = 1030 [$\nu(\text{B}-\text{F})$], 243, 292 [$\nu(\text{Ir}-\text{Cl})$] cm^{-1} .

Supporting Information (see footnote on the first page of this article): Additional experimental details; molecular structure of $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2]$; crystal data and structure refinement for $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2]$; ^{19}F NMR spectrum of **3**; calculated coordinates of the species studied; selected bond distances in $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2]$ and $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2(\text{CF}_3\text{SO}_3)]^-$; canonical molecular orbitals.

Acknowledgments

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- [10] We feel that the chloride source in this reaction comes from tiny amount of stannous chloride or HCl left in tetrahydroxybenzene. In fact the neutral complex $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_2\text{O}_4)(\text{BF}_2)_2]$ was prepared in 66% yield and its X-ray molecular structure was also determined when the THB ligand was recrystallized several times from THF to eliminate any chloride source left^[22b,23] (see the Supporting Information).
- [11] Crystal data for **3**. Orange crystals: $\text{C}_{37}\text{H}_{47}\text{B}_2\text{Cl}_3\text{F}_7\text{Ir}_3\text{O}_7\text{S}$, orthorhombic, *Pnma*, $a = 32.512(4)$ Å, $b = 11.2738(16)$ Å, $c = 12.5079(11)$ Å, $V = 4584.5(9)$ Å³, $Z = 4$, $T = 200(2)$ K, $\mu = 8.980$ mm^{–1}, 27046 reflections measured, 5465 independent ($R_{\text{int}} = 0.0470$), 3712 observed [$I = 2\sigma(I)$], 294 parameters, final R indices R_1 [$I = 2\sigma(I)$] = 0.0751 and wR_2 (all data) = 0.1613, GOF on $F^2 = 1.053$, max/min residual electron density = 2.37/–2.39 e Å^{–3}. A single crystal of compound **3** was selected, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Intensity data were collected with a Bruker-Nonius Kappa-CCD with graphite-monochromated Mo- K_α radiation. Unit-cell parameters determination, data collection strategy, and integration were carried out with the Nonius EVAL-14 suite of programs (A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220). Multiscan absorption correction was applied (R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33). The structure was

- solved by direct methods using the SIR92 program (A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, 26, 343) and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 64, 112). The C4, C7, and C8 carbon atoms were restrained so that their Uij approximate isotropic behavior. CCDC-706430 (for **3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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