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Synthesis, Characterization, and Reactivity of a Rhenium Complex with a Corannulene-Based Ligand

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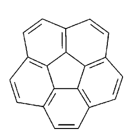
*Summary: A new rhenium carbonyl complex, exo-(η^5-$C_{20}H_{17}$)Re($CO)_3$ (**3**), containing a corannulene-derived ligand has been synthesized in 12% yield. The X-ray structure determination of **3** shows that the rhenium center is bound to the exo face of the bowl-shaped ligand. The reaction of **3** with PPh_3 in benzene at 70 °C produces trans,mer-Re(H)($PPh_3)_2$(CO$)_3$ and $C_{20}H_{16}$ (**4**), a bowl-shaped dibenzofulvene type molecule. The reaction of **3** with PPh_3 proceeds via an η^5-η^3-η^1 ring slip followed by a β-hydride elimination.*

Introduction

Due to recent improvements in the synthesis of corannulene, $C_{20}H_{10}$ (**1**),[1−5] the transition metal chemistry of corannulene has received a great deal of attention in recent years.



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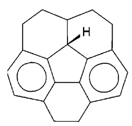
Examples of corannulene transition metal complexes include [(Cp*)Ru(η^6-$C_{20}H_{10}$)]O_3SCF_3,[6] [Cp*Ir (η^6-$C_{20}H_{10}$)]($BF_4)_2$,[7] and [($Rh_2(O_2CCF_3)_4)_m$·($C_{20}H_{10})_n$] (m:n = 1:1 and 3:2).[8]

We are interested in using the inner five-membered ring of the corannulene core as a cyclopentadienyl mimic. To do this, corannulene has to be partially hydrogenated to have a removable proton to generate the anionic center. Recent work by Rabideau and coworkers provided the starting point for our studies.[9] Reaction of corannulene in a Na/THF/NH_3 mixture at −33 °C, followed by an inverse ammonium chloride quench, yields the partially hydrogenated corannulene, hexahydrocorannulene. We recently reported the hydrogenation of hexahydrocorannulene to give $C_{20}H_{18}$ (**2**), which is electronically similar to a 1,4,5,8,9-pentaalkylated fluorene.[10]



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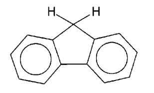
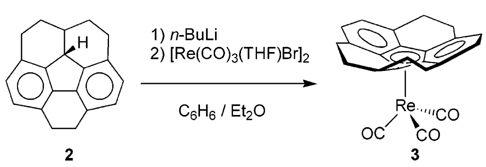


fluorene

Deprotonation of **2** with n-BuLi yields the analogous fluorenyl anion, which can then bind to $CpZrCl_2$ to form *exo*-(η^5-$C_{20}H_{17}$)(η^5-C_5H_5)$ZrCl_2$. Herein we report the use of **2** in synthesizing a new rhenium tricarbonyl complex.

Results and Discussion

Deprotonation of **2** with n-BuLi in Et_2O/C_6H_6 followed by addition of [Re(CO$)_3$(THF)Br$]_2$ afforded *exo*-(η^5-$C_{20}H_{17}$)Re(CO$)_3$, **3**, in 12% yield as a bright yellow powder (eq 1).



(1)

The synthesis of **3** requires a fairly nonpolar solvent medium, as attempted syntheses in THF and ether yielded only uncharacterizable products in the corresponding ^1H NMR spectra. The ^1H and ^{13}C NMR spectral data of **3** are consistent with the predicted C_s symmetry. The CO stretching frequencies for **3** are at lower energy (ν_{CO} = 2009, 1896 cm^{-1}) than (η^5-$C_{13}H_9$)-Re(CO$)_3$ (ν_{CO} = 2027, 1935 cm^{-1}),[11] which is consistent with **2** being a better electron donor than the unsubstituted fluorenyl ligand. An X-ray structure study was undertaken in order to determine which face of the bowl-shaped ligand the rhenium was attached to, the *exo* (convex) or *endo* (concave) face. The study revealed that the rhenium metal center was on the *exo* side of the bowl, which is the same side for the previously reported *exo*-(η^5-$C_{20}H_{17}$)(η^5-C_5H_5)$ZrCl_2$ (Figure 1).

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10.1021/om034111t CCC: $25.00

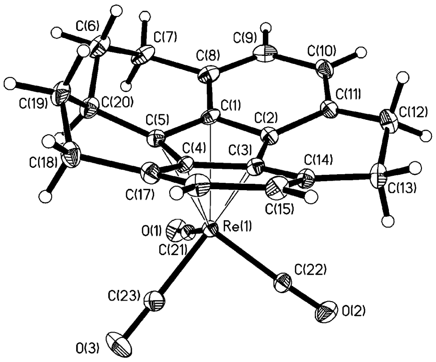


Figure 1. ORTEP plot of **3** (30% probability level).

Table 1. Selected List of Bond Lengths (Å) and Angles (deg) for 3

Re(1)−C(21)	1.881(9)	C(21)−O(1)	1.167(10)
Re(1)−C(23)	1.911(4)	C(22)−O(1)	1.147(11)
Re(1)−C(22)	1.928(8)	C(23)−O(1)	1.148(5)
Re(1)−C(5)	2.290(5)	C(1)−C(2)	1.401(8)
Re(1)−C(2)	2.337(6)	C(2)−C(3)	1.420(7)
Re(1)−C(3)	2.346(5)	C(3)−C(4)	1.388(6)
Re(1)−C(1)	2.352(5)	C(4)−C(5)	1.434(6)
Re(1)−C(4)	2.374(4)	C(1)−C(5)	1.431(8)
C(21)−Re(1)−C(23)	89.7(4)	C(4)−C(3)−C(14)	124.2(4)
C(21)−Re(1)−C(22)	91.01(17)	C(4)−C(3)−C(2)	108.0(5)
C(23)−Re(1)−C(22)	92.8(4)	C(14)−C(3)−C(2)	124.8(5)
C(2)−C(1)−C(8)	121.9(5)	C(3)−C(4)−C(17)	121.9(4)
C(2)−C(1)−C(5)	109.8(6)	C(3)−C(4)−C(5)	109.9(4)
C(8)−C(1)−C(5)	127.2(5)	C(17)−C(4)−C(5)	126.5(4)
C(1)−C(2)−C(11)	123.6(5)	C(4)−C(5)−C(1)	104.3(5)
C(1)−C(2)−C(3)	107.2(5)	C(4)−C(5)−C(20)	124.4(4)
C(11)−C(2)−C(3)	125.1(5)	C(1)−C(5)−C(20)	123.0(5)

Selected bond lengths and angles of **3** are given in Table 1.

The η^5 binding is confirmed by the Re−C bond lengths (2.29−2.374 Å), which are similar in value to the reported values for (η^5-$C_{13}H_9$)Re(CO)$_3$ (2.288−2.351 Å).[12] Also the average OC−Re−CO bond angle for **3** (91.2°) is similar to that of (η^5-$C_{13}H_9$)Re(CO)$_3$ (90.5°), which suggests that even though **2** is larger than fluorene, the steric footprint of **2** around the rhenium center is roughly the same as that of fluorene. This similar spatial occupancy around the metal center can be attributed to the fact that the bowl-shaped ligand curves away from the metal center.

The curvature of the coordinated ligand was determined using the π-orbital axis vector (POAV1, $\theta_p = \theta_{\sigma\pi} - 90$) method.[13,14] The pyramidalization angles for the inside ring of the modified corannulene ligand are shown in Figure 2. C5 has the largest θ_p angle of 9.6°, while C1 and C4 have the smallest pyramidalization angles of 3.5° and 4.3°, respectively. The average pyramidalization angle of the inner Cp core is 6.0° compared with 5.9° for *exo*-(η^5-$C_{20}H_{17}$)(η^5-C_5H_5)ZrCl$_2$.

Reaction of 3 with PPh$_3$. The CO substitution reactions of indenyl and fluorenyl manganese carbonyl complexes have been reported to proceed via an associative ring slip mechanism by Basolo and co-workers.[15] Therefore, we were interested in determining the steric effect that **2** would have on CO substitution reaction in **3**. We initially predicted that **3** would have a slower rate of substitution than (η^5-$C_{13}H_9$)Re(CO)$_3$ due to the larger size of **2**. However, heating a mixture of **3** and PPh$_3$ (2.5 equiv) in a Teflon-capped NMR tube at 70 °C for 1 h did not yield a CO substitution reaction. The ^1H NMR spectrum of the reaction mixture showed that the corannulene-based ligand had left the metal center to form a dibenzofulvene type molecule, $C_{20}H_{16}$ (**4**), and *trans*,*mer*-Re(H)(PPh$_3$)$_2$(CO)$_3$ (eq 2).

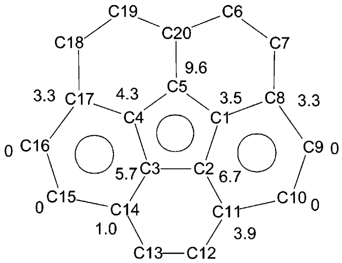
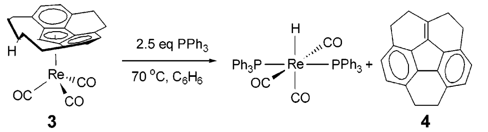


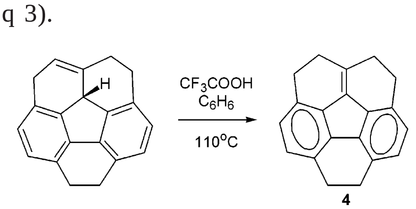
Figure 2. POAV1 angles (deg) of corannulene-based ligand in **3**.



(2)

The ^1H NMR spectrum for *trans*,*mer*-Re(H)(PPh$_3$)$_2$(CO)$_3$ matched the spectral data reported by Jones and Maguire, with the rhenium hydride having a chemical shift of δ −4.51 and $J_{P-H} = 18.2$ Hz.[16]

We have previously synthesized **4** by an acid-catalyzed isomerization of hexahydrocorannulene. Heating a solution of hexahydrocorannulene with trifluoroacetic acid in benzene at 110 °C for 20 h afforded **4** in 50% yield (eq 3).



(3)

The lack of *exo* and *endo* resonances in the ^1H NMR spectrum of **4** at 20 °C indicates that **4** either is undergoing a rapid bowl-to-bowl inversion or is planar. Cooling a CD$_2$Cl$_2$ solution of **4** to −90 °C broadened the methylene resonances, thereby indicating that **4** is undergoing a rapid bowl-to-bowl inversion. However, we were unable to reach the low-temperature limit to resolve the *exo* and *endo* ^1H resonances. Also in the ^1H NMR spectrum of **4**, the aromatic region has only one resonance, a singlet, rather than the expected two doublets for the two nonequivalent hydrogens. We believe this apparent inconsistency is due to the hydrogens being chemical shift equivalent, where $\delta\nu/J = 0$. The ^{13}C NMR spectrum of **4** is consistent with the proposed structure, displaying 11 different ^{13}C resonances.

Our proposed mechanism for the formation of **4** and *trans*,*mer*-Re(H)(PPh$_3$)$_2$(CO)$_3$ in the reaction of **3** with

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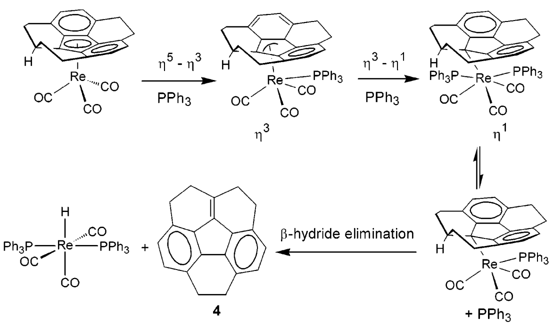
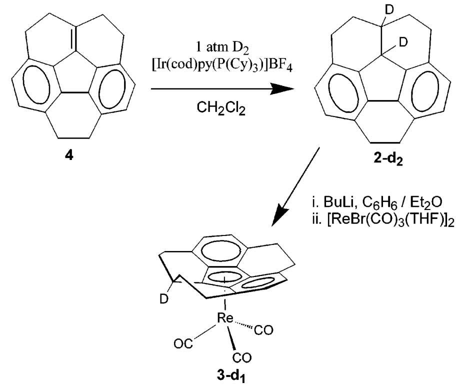
Scheme 1



Scheme 2



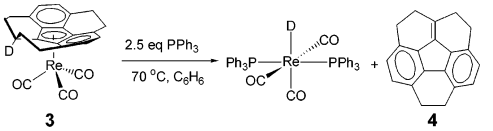
PPh_3 includes an η^5-η^3-η^1 ring slip of the fluorenyl type ligand, followed by a β-hydride elimination of the hydrogen on the β-carbon to the Re metal center (Scheme 1).

η^5-η^1 ring slip of a fluorenyl rhenium complex has been previously reported by Hanks and co-workers in the reaction of (η^5-$C_{13}H_9$)Re(CO)$_3$ with 1 atm of CO to yield (η^1-$C_{13}H_9$)Re(CO)$_5$.[12] Other examples of (η^5-X)Re(CO)$_3$ (X = $C_5H_5^-$, $C_9H_7^-$) complexes undergoing η^5-η^1 ring slip have been reported by Casey and co-workers.[17,18] In those examples, added PMe_3 to the corresponding (η^5-X)Re(CO)$_3$ complexes gave *fac*-Re(η^1-X)(CO)$_3$(PMe_3)$_2$.

To test the proposed β-hydride elimination step, we synthesized (η^5-$C_{20}H_{16}D$)Re(CO)$_3$, **3-*d*₁**, where the deuterium was in the β-position (Scheme 2).

The first step in the synthesis of **3-*d*₁** was achieved by deuteration of the hexahydrocorannulene using Crabtree's catalyst and D_2 to give **2-*d*₂**. The mass spectrum of **2-*d*₂** (*m*/*z* 260) confirmed the presence of the two deuteriums. Dedeuteration of **2-*d*₂** with 1 equiv of *n*-BuLi followed by addition of [Re(CO)$_3$(THF)Br]$_2$ gave **3-*d*₁** in 18% yield. The ^2H NMR spectrum of **3-*d*₁** (δ 3.51, C_6H_6/C_6D_6) confirmed that the deuterium was at the β-carbon when the Re metal center slips to the η^1 configuration.

Reaction of **3-*d*₁** with PPh_3 at 70 °C for 13 min in a 1:1 mixture of C_6H_6/C_6D_6 yielded the corresponding *trans,mer*-Re(D)(PPh_3)$_2$(CO)$_3$ and **4** (eq 4). The presence of the metal deuteride was confirmed by ^2H NMR spectroscopy (δ = −4.45, C_6D_6/C_6H_6), with no noticeable deuterium remaining on **4**.



(4)

Therefore, the results of the labeling study are consistent with **3** undergoing successive ring slips in the presence of PPh_3 followed by a β-hydride elimination.

Conclusion

To summarize, the reaction of $C_{20}H_{18}$ (**2**), a partially hydrogenated corannulene ligand, with *n*-BuLi and [Re(CO)$_3$(THF)Br]$_2$ yields *exo*-(η^5-$C_{20}H_{17}$)Re(CO)$_3$ (**3**), a new rhenium complex with a bowl-shaped ligand. Reaction of **3** with PPh_3 yields *trans,mer*-Re(H)(PPh_3)$_2$(CO)$_3$ and $C_{20}H_{16}$ (**4**), a dibenzofulvene type molecule, rather than the expected CO substitution reaction. A deuterium labeling study is consistent with the proposed mechanism of an η^5-η^3-η^1 ring slip followed by a β-hydride elimination step.

Experimental Section

General Procedures. Reactions that required inert conditions were performed using modified Schlenk techniques or in a MBraun Unilab glovebox under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a GE-QE300 MHz spectrometer running Tecmag Aquarius software. ^1H and ^{13}C NMR chemical shifts are given relative to the residual proton or ^{13}C solvent resonances. Mass spectra were recorded on a Hewlett-Packard 6890-5973 GC−MS.

Solvents and Reagents. Unless otherwise indicated, all chemicals were used as received (reagents from Aldrich, Acros, or Strem Chemical Company). Deuterated solvents and deuterium gas (D, 99.8%) were obtained from Cambridge Isotope Laboratories. Tetrahydrofuran (THF), toluene, and diethyl ether were distilled from dark purple solutions of sodium benzophenone ketyl. Methylene chloride was distilled from CaH_2 before use. Benzene-*d*$_6$ was distilled under vacuum from sodium benzophenone ketyl. $CDCl_3$ and CD_2Cl_2 were distilled under vacuum from CaH_2. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Re(CO)$_5$Br was purchased from Strem Chemical Co. and used as received. Corannulene (**1**), hexahydrocorannulene, and octahydrocorannulene (**2**) were prepared according to literature methods.[4,9,10] Crabtree's catalyst, [Ir(cod)py(PCy_3)]PF_6, was either purchased from Strem Chemical Co. or prepared according to the method described by Stork et al.[19] [ReBr(CO)$_3$(THF)]$_2$ was prepared as described.[20]

Preparation of *exo*-(η^5-$C_{20}H_{17}$)Re(CO)$_3$ (3). **2** (889.0 mg, 3.45 mmol) was dissolved in 25 mL of C_6H_6 and 5 mL of ether. *n*-BuLi (2.5 M in hexane, 1.24 mL) was added to the solution. The color of the solution changed to a dark red. The solution was stirred for 5 min at 20 °C. [ReBr(CO)$_3$(THF)]$_2$ (1.2974 g, l.54 mmol) was then added, and the reaction mixture was stirred for 15 min at 20 °C. The solvent was removed under reduced pressure, and CH_2Cl_2 was added to the resulting residue. The CH_2Cl_2 solution was filtered through a Celite pad, the filtrate collected, and the solvent removed. The crude product was dissolved in C_6H_6 and filtered through a silica gel packed frit. The resulting filtrate was collected and the solvent removed. The crude orange-yellow solid was washed 2 × 1 mL of toluene, yielding a bright yellow powder (262.4 mg, 12% yield). ^1H NMR ($CDCl_3$, 20 °C): δ 6.82 (m, 4H), 3.64 (m, 2H), 3.56 (m, 1H), 3.09 (m, 4H), 2.81 (m, 2H), 2.52 (m,

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2H), 0.96 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 193.55 (CO), 134.61 (quat C), 131.99 (quat C), 125.52 (CH), 121.27 (CH), 116.97 (quat C), 99.58 (quat C), 74.15, 35.19 (CH_2), 29.74 (CH), 28.23 (CH_2), 28.15 (CH_2). IR (KBr) ν (cm^{-1}): 2009, 1896. Anal. Calcd for $C_{23}H_{17}O_3Re$: C, 52.36; H, 3.25 Found: C, 51.97; H, 3.28.

Reaction of 3 with PPh_3. **3** (30 mg, 0.0569 mmol) and PPh_3 (37.3 mg, 0.1423 mmol) were dissolved in ~0.5 mL of C_6D_6 and placed in a Teflon-capped NMR tube. The mixture was heated at 70 °C for 1 h, at which time the ^1H NMR spectrum showed no starting material remaining. A mixture of *trans*,*mer*-Re(H)$(PPh_3)_2(CO)_3$ and **4** was observed in a 1:1 ratio.

Preparation of $C_{20}H_{16}$ (4). In the glovebox, hexahydrocorannulene (298.0 mg, 1.164 mmol) was dissolved in benzene (33 g) and trifluoroacetic acid (679 mg) added to the resulting solution. The mixture was placed into a Teflon-stoppered ampule and heated to 110 °C for 20 h. The solvent was removed under reduced pressure, and the residue was sublimed at 105 °C for 24 h, yielding a white solid (149 mg, 50%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.89 (s, 4H), 3.12 (s, 4H), 3.06 (t, $J = 7.4$ Hz, 4H), 2.41 (t, $J = 7.6$ Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 139.2 (quat C), 138.9 (quat C), 137.5 (quat C), 131.1 (quat C), 130.5 (quat C), 126.8 (CH), 126.5 (CH), 121.8 (quat C), 32.9 (CH_2), 28.1 (CH_2), 27.3 (CH_2). Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29 Found: C, 92.73; H, 6.66. HRMS: calc 256.1252, found 256.1249.

Preparation of 2-d_2. **4** (170.5 mg, 0.666 mmol), Crabtree's catalyst, $[Ir(PCy)_3(cod)py]PF_6$ (80.1 mg, 0.1 mmol), and 5 mL of CH_2Cl_2 were placed in a 25 mL Schlenk flask. A 250 mL round-bottom flask was inverted over the Schlenk flask and the apparatus evacuated and refilled with D_2 gas three times. After 2.5 h at 20 °C, the solvent was removed and the product extracted with 30 mL of C_6H_6 and filtered through a silica gel packed frit. The crude product was sublimed at 100 °C for 2 days and afforded pure **2-d_2** (113.8 mg, 66%). ^2H NMR ($CDCl_3$/$CHCl_3$, 20 °C): 4.01 (br s, 1D), 2.73 (br s, 1D). GC−MS: *m*/*z* 260.

Preparation of 3-d_1. **2-d_2** (199.1 mg, 0.766 mmol) was dissolved in 5.7 mL of C_6H_6 and 1.10 mL of ether. *n*-BuLi (2.5 M in hexane, 0.28 mL) was added to the solution. The color of the solution changed to a dark red. The solution was stirred for 3 min at 20 °C. $[ReBr(CO)_3(THF)]_2$ (290.7 g, 0.344 mmol) was then added and the reaction mixture stirred for 5 min at 20 °C. The solvent was removed under reduced pressure, and CH_2Cl_2 was added to the resulting residue. The CH_2Cl_2 solution was filtered through a Celite pad, the filtrate collected, and the solvent removed. The crude product was dissolved in C_6H_6 and filtered through a silica-packed frit. The resulting filtrate was collected and the solvent removed. The crude orange-yellow solid was recrystallized using 1 mL of toluene at − 40 °C (72.0 mg, 18%). ^2H NMR (C_6H_6/C_6D_6, 20 °C): δ 2.81.

Reaction of 3-d_1 with PPh_3. **3-d_1** (38.2 mg, 0.0722 mmol) and PPh_3 (44.8 mg, 0.171 mmol) were dissolved in ~1.0 mL of a 1:1 mixture of C_6H_6/C_6D_6 and placed in a Teflon-capped NMR tube. The mixture was heated for 13 min at 70 °C. ^2H NMR (C_6H_6/C_6D_6, 20 °C): δ −4.45.

X-ray Structural Determination of 3. A yellow crystal of approximate dimensions 0.12 × 0.2 × 0.4 mm was mounted under Paratone-8277 on a glass fiber and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.5°). The total data collection time was approximately 12 h. Frames were collected and integrated to a maximum 2θ angle of 46.5° with the Siemens SAINT program to yield a total of 5367 reflections, of which 3777 were independent ($R_{int} = 1.29\%$).[21] Laue symmetry revealed a monoclinic crystal system, and the final unit cell parameters (at −80 °C) were determined from the least-squares refinement of three-dimensional centroids of 5367 reflections. Data were corrected for absorption with the SADABS[22] program.

Table 2. Summary of Crystal Data for 3

empirical formula	$C_{23}H_{17}O_3Re$
fw	527.57
temp	193(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*P*2(1)
unit cell dimens	$a = 7.7279(3)$ Å
	$b = 14.1402(6)$ Å
	$c = 8.3068(4)$ Å
	$\alpha = 90°$
	$\beta = 92.1560(10)°$
	$\gamma = 90°$
volume, *Z*	907.08(7) $Å^3$, 2
density (calcd)	1.932 Mg/m^3
abs coeff	6.719 mm^{-1}
F(000)	508
cryst size	0.12 × 0.20 × 0.40 mm
θ range for data collection	2.45 to 28.27°
limiting indices	$-10 \le h \le 10$, $-18 \le k \le 18$, $-3 \le l \le 10$
no. of reflns collected	5367
no. of ind reflns	3777 [*R*(int) = 0.0129]
abs corr	Sadabs
max. and min. transmn	0.928 and 0.625
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	3777/1/246
goodness-of-fit on F^2	1.346
final *R* indices [$I > 2\sigma I$)]	R1 = 0.0198, wR2 = 0.0508
R indices (all data)	R1 = 0.0200, wR2 = 0.0509
abs structure param	0.234(10)
extinction coeff	0.0100(5)
largest diff peak and hole	1.174 and −1.034 e $Å^{-3}$

The space group was assigned as $P2_1$, and the structure was solved by using direct methods and refined employing full-matrix least-squares on F^2 (Siemens, SHELXTL,[23] version 5.04). For a *Z* value of 2, there is one molecule in the asymmetric unit. All of the atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in idealized positions giving a data to parameter ratio of slightly greater than 10:1. The structure refined to a goodness of fit (GOF)[24] of 1.346 and final residuals[25] of $R_1 = 1.98\%$ ($I > 2\sigma(I)$), $wR_2 = 2.92\%$ ($I > 2\sigma(I)$). A summary of crystallographic data for **3** is given in Table 2.

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Supporting Information Available: X-ray structural data (PDF and CIF file) for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$.

(22) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(23) *SHELXTL: Structure Analysis Program, version 5.04*; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(24) GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where *n* and *p* denote the number of data and parameters.

(25) $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\text{Max}; 0,F_o^2) + 2F_c^2]/3$.