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Insights into the Molecular Structure and Reactivity of α,ω-Dialkoxy-Substituted Ethyne and Butadiyne

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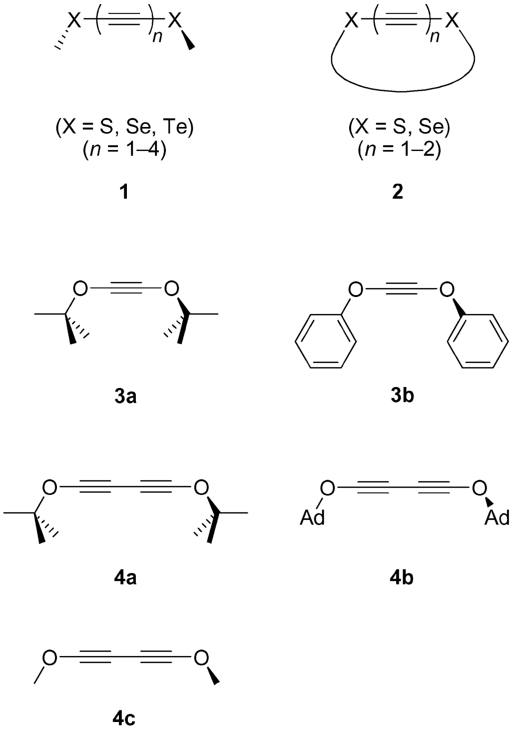
The molecular structure derived by X-ray crystallography and the He(I) photoelectron spectrum of bis(*tert*-butoxy)butadiyne (**4a**) are reported. Bis(*tert*-butoxy)ethyne (**3a**) and **4a** were treated with highly electrophilic [η^2-bis(*tert*-butylsulfonyl)ethyne](carbonyl)(η^5-cyclopentadienyl)cobalt (**10**). In both cases a CpCo-stabilized cyclobutadiene ring resulted substituted by two *tert*-butylsulfonyl groups and either two *tert*-butoxy groups (→**11**) or one *tert*-butoxy group and one *tert*-butoxyethynyl group (→**12**). The structural data of **11** and of (η^4-tetrakis(*tert*-butoxy)cyclopentadienone)(cyclopentadienyl)cobalt (**15**) are reported and compared with related species.

Introduction

Recently we have synthesized linear and cyclic systems containing units with chalcogen–alkyne–chalcogen motives as building blocks (**1**, **2**).[1,2] The studies of such species with sulfur, selenium and tellurium as heteroatoms (X = S, Se, Te) revealed that the molecular structures are highly determined by torsion angles in the range of 60° to 100° between the $CH_2–X\cdots X–CH_2$ bonds. The arrangements of the various molecules in the solid state are strongly influenced by intermolecular chalcogen–chalcogen interactions.[3]

In connection with these studies we were also interested in the properties of the corresponding oxygen congeners, the bis(organooxy)ethynes.[4] So far only four bis(organooxy)alkynes that are stable at room temperature are available (Scheme 1): bis(*tert*-butoxy)ethyne (**3a**),[5] bis(phenoxy)ethyne (**3b**),[6] bis(*tert*-butoxy)butadiyne (**4a**)[7] and bis(1-adamantyloxy)butadiyne (**4b**).[7] Due to difficulties during preparation, especially of **3a**, the chemistry of **3** and **4** was not fully explored.[4,5,8]

We prepared **3a** according to the protocols published in the literature (see Scheme 2). Starting point was *trans*-2,3-dichloro-1,4-dioxane (**5**)[5a,5b], which was converted into *trans*-2,3-bis(*tert*-butoxy)-1,4-dioxane (**6**) and further to (*E*)-1,2-bis(*tert*-butoxy)-1-chloroethene (**8**) via **7**. Dehydrohalogenation with five equivalents of sodium amide in liquid ammonia afforded **3a** in an overall yield of about 40%.



Scheme 1.

Compound **4a** was readily available from *tert*-butoxyethyne (**9**) by oxidative dimerization.[7] Under the usual Hay conditions[9] **4a** was obtained in about 70% yield (Scheme 3).

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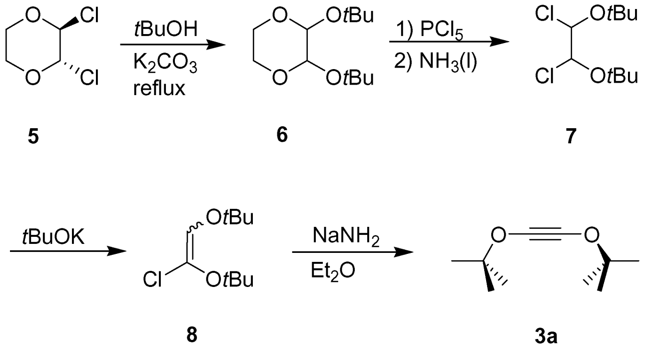
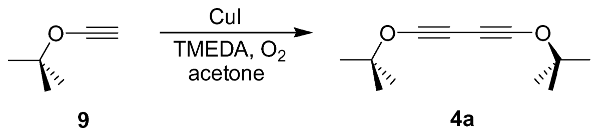


Scheme 2.



Scheme 3.

Results and Discussion

Structural and Spectroscopic Properties of 4a

We were able to grow single crystals of the oxygen-substituted butadiyne **4a** which allowed an X-ray study. In Figure 1 we present the molecular structure of **4a** in the solid state. The most relevant bond lengths of **4a** are given in the caption of Figure 1. A symmetry induced torsion angle between the CH_2–O···O–CH_2 bonds of 180° is encountered.

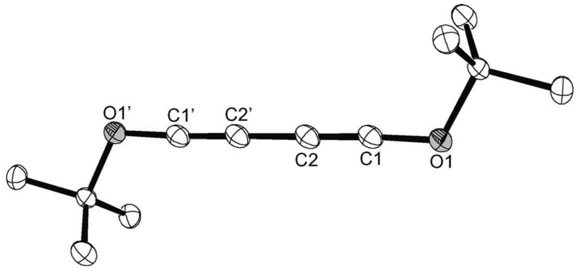


Figure 1. ORTEP plot (50% ellipsoid probability) of the molecular structure of **4a** as derived from X-ray diffraction studies. The hydrogen atoms are omitted for the sake of clarity. Most relevant bond lengths: C1–C2 1.200(1) Å, C2–C2′ 1.378(2) Å, C1–O1 1.303(1) Å.

The He(I) photoelectron (PE) spectrum of **4a** is depicted in Figure 2. It exhibits two broad features at 8.2 eV and 10.6 eV, to which we have assigned two ionization events each. This assignment is based on the assumption of the validity of Koopmans' theorem[10] which assumes that the vertical ionization energies, $I_{v,j}$, are equal to the negative energies, $-\varepsilon_j$, of the occupied canonical molecular orbitals. To derive the molecular orbital energies we have first calculated the geometrical parameters of **4c** by using the density functional theory (DFT)[11] applying the three-parameter hybrid functionals suggested by Becke (B3)[12] and the correlation functionals by Lee, Yang and Parr (LYP).[13] As basis set we used those recommended by Pople et al.[14] as

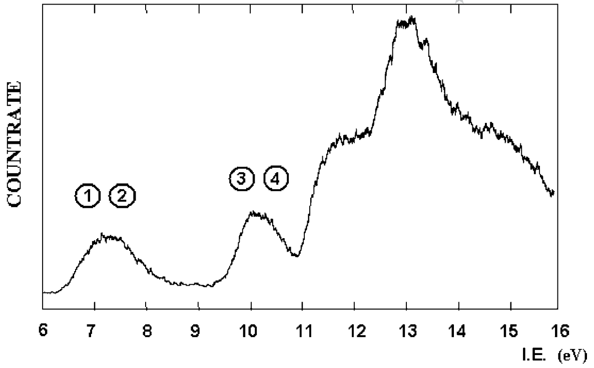


Figure 2. He(I) photoelectron (PE) spectrum of **4a**.

Table 1. Comparison between the recorded vertical ionization energies, $I_{v,j}$, of **4a** and the calculated orbital energies $-\varepsilon_j$ of **4c** (C_2 conformation). The orbital energies were derived by HF/6-311G(d) calculations based on B3LYP/6-311G(d) optimized geometry. The assignments given assume C_2 symmetry as predicted by the calculations. All values are given in eV.

Band	$I_{v,j}$	$-\varepsilon_j$	Assignment
1	8.2	–8.68	14b [n(p), π]
2		–8.72	15a [n(p), π]
3	10.6	–12.13	14a [n(p), π]
4		–12.15	13b [n(p), π]

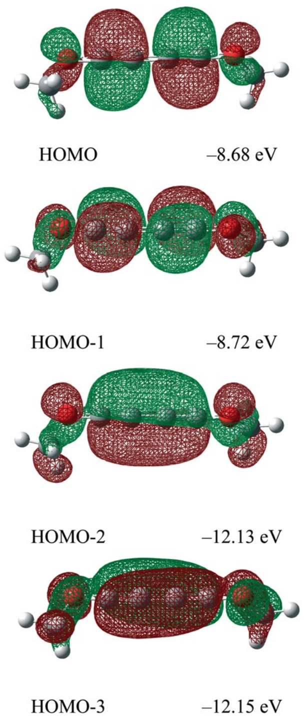


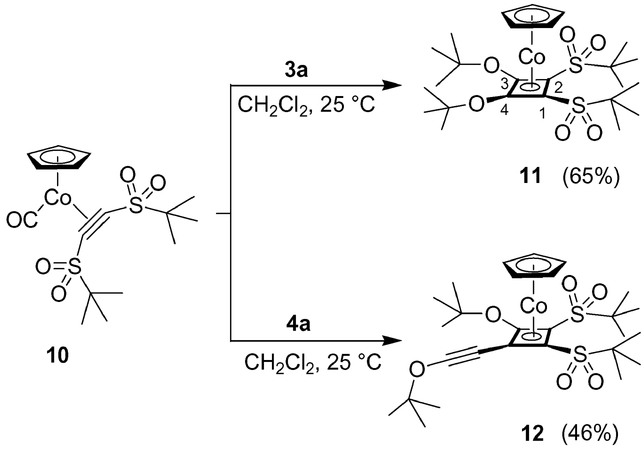
Figure 3. Plot of the four highest occupied molecular orbitals (HOMO to HOMO-3 from top to bottom) of **4c** (C_2 symmetry) as derived by a HF/6-311G(d) calculation. The calculated orbital energies in eV are given below each orbital.

implemented in Gaussian03.[15] The calculations predict C_2 symmetry for **4c** with geometrical parameters close to those derived for **4a**. The orbital energies were derived by HF/6-311G(d) calculations.

A comparison between the results of the calculations and experiment confirms the assignment of two ionization events to each peak (Table 1). The resulting molecular orbitals are drawn in Figure 3 where the anticipated linear combinations of the π orbitals at the 1,3-butadiyne unit and the lone pairs at the oxygen atoms indicating a considerable interaction between the lone pairs and the π system are shown. A further confirmation is given by comparing the PE data of **4a** with those reported for 2,7-dithia- and 2,7-diselenaocta-3,5-diyne.[2e] The PE spectra of these two species revealed two close lying peaks at around 8 and 10 eV which were assigned to ionization events from orbitals of p and π character.[2e] Due to the very low rotational barrier of only 3.3 kJ/mol calculated for **4c**[2e] many conformations are populated and only broad bands are observed in the PE spectrum.

Reactions of 3a and 4a with CpCo(BTSA)CO

[η^2-Bis(*tert*-butylsulfonyl)ethyne](carbonyl)(η^5-cyclopentadienyl)cobalt (CpCo(BTSA)(CO), **10**)[16] exhibits strong electrophilic properties. Therefore, we reacted **10** with the electron-rich alkynes **3a** and **4a** (Scheme 4).



Scheme 4.

When the reaction was carried out at room temperature in dichloromethane we could isolate the cyclobutadiene complexes **11** and **12** in good yields. In the case of **11** we were able to grow single crystals which allowed X-ray diffraction studies. The molecular structure is shown in Figure 4. It was found that diagonal *tert*-butyl groups are directed either towards the Cp ring or away from it. Especially the *tert*-butyl groups which are directed towards the Cp ring cause strain. This causes a bending of the S2 and O6 atom out of the cyclobutadiene plane in **11** by 23° and 16°, respectively. The C–C bond lengths within the cyclobutadiene moiety alternate considerably.

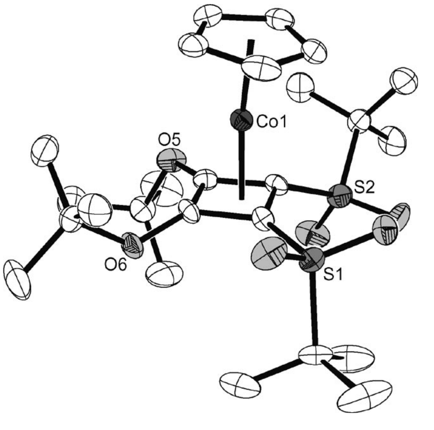


Figure 4. ORTEP plot (50% ellipsoid probability) of the molecular structure of the cobalt complex **11**. The hydrogen atoms are omitted for the sake of clarity.

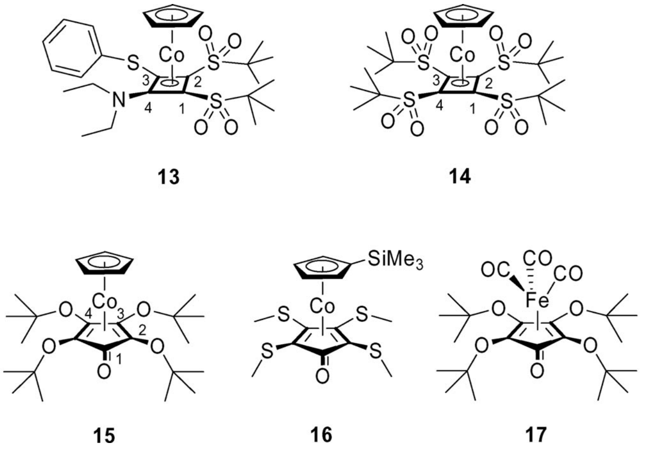
In Table 2 the structural parameters of the cyclobutadiene ring of **11** are compared with those of **13**[17] and **14** (Scheme 5).[18] In the two "push-pull" systems **11** and **13** we find the shortest bond length between C3 and C4 and the longest bond length between C1 and C2. This is remarkable since the *tert*-butyl groups in **11** and the phenyl group in **13** are bent out of the plane of the cyclobutadiene ring which hampers a good conjugation between the p lone pair of the ether oxygen atoms or the sulfide center, respectively, with the cyclobutadiene ring. In Table 2 also the angles between cyclopentadiene and cyclobutadiene rings (Cp/Cbd) of **11**, **13** and **14** are listed. The largest angle is observed for **11** (8.3°), the smallest for **14** (2.5°), indicating strong steric interaction for **11**. Also listed are the distances between the Co center and the centers of the C1–C2 and C3–C4 bonds for **11**, **13** and **14**. The Co atom is shifted strongest in **11** out of the center for steric reasons. In the case of **14** the Co atom is situated in the center of the cyclobutadiene ring.

Furthermore, we prepared (η^5-cyclopentadienyl)(η^5-tetra-*tert*-butoxycyclopentadienone)cobalt (**15**) by irradiation of a solution of **4a** and $CpCo(CO)_2$ in pentane.[8a] The molecular structure of **15** is shown in Figure 5.

A comparison of the C–C bond lengths within the cyclopentadienone rings of **15**, **16**[19] and **17**[8b] reveals for all three species very similar bond lengths in the cyclopentadienone ring. The substituents do not show a strong influence on the bond lengths.

Table 2. Comparison of the relevant bond lengths and angles (with standard deviation) of **11**, **13**[17] and **14**.[18] All distances are given in Å, the angle between the Cp and the Cbd plane is given in °. The numbering refers to that given in Scheme 5.

	C1–C2	C2–C3	C1–C4	C3–C4	Cp–Co	Co–C1/C2	Co–C3/C4	Cp/Cbd
11	1.491(6)	1.467(6)	1.465(6)	1.431(6)	1.689(4)	1.942(3)	2.052(4)	8.3(1)
13	1.494(6)	1.484(7)	1.476(7)	1.459(7)	1.667(6)	1.947(5)	2.022(5)	4.7(1)
14	1.45(1)	1.47(1)	1.45(1)	1.47(1)	1.68(1)	1.977(7)	1.977(7)	2.5(1)



Scheme 5.

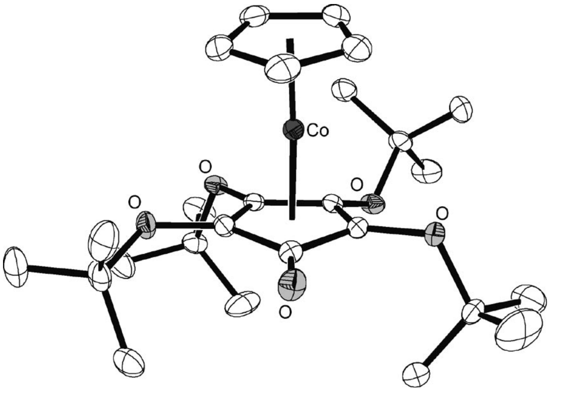


Figure 5. ORTEP plot (50% ellipsoid probability) of the molecular structure of the cobalt complex **15**. The hydrogen atoms are omitted for the sake of clarity. Most relevant bond lengths (mean values): C1–C2 1.479(3) Å, C2–C3 1.429(3) Å, C3–C4 1.431(3) Å, C1–O 1.246(2) Å, Co–C1 2.206(2) Å, Co–C2 2.040(2) Å, Co–C3 2.030(2) Å. The numbering refers to that given in Scheme 5.

Conclusions

Our studies on dialkoxy-substituted ethyne and butadiyne revealed the structural parameters of bis(*tert*-butoxy)butadiyne (**4a**) in the solid state and the first ionization energies in the gas phase. The latter studies evidenced a considerable interaction between the π system and the lone pairs on the *tert*-butoxy groups. The reaction of **3a** and **4a**, respectively, with CpCo(BTSA)CO afforded the anticipated cyclobutadiene complexes **11** and **12**, substituted with two adjacent donor and two acceptor groups. The X-ray crystal structure investigations on **11** showed a strong difference of the bond lengths within the push-pull-substituted cyclobutadiene ring.

Experimental Section

General Methods: The NMR spectra were measured with a Bruker AS 300 spectrometer (^{1}H NMR at 300 MHz and ^{13}C NMR at 75.5 MHz) using the solvent as internal standard. FAB mass spectra refer to data from a JEOL JMS-700 instrument. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der University of Heidelberg. UV/Vis light absorption data were recorded using a Hewlett–Packard 8452A spectrometer. IR spectra were measured with a Bruker Vector 22 apparatus. The alkynes **3a**[5a,5b] and **4a**[7] were prepared according to literature procedures. In the case of **3a** we used the raw material as recommended.[5b] The complex **14** was obtained following the published protocol.[8a] Some additional analytical data for **14** are given below.

General Procedure for the Synthesis of the Cyclobutadiene Complexes: The reactions with Cp(BTSA)(CO)Co and CpCo(CO)$_2$ were carried out under argon atmosphere using dry, oxygen free solvents.

CpCo Complex 11: This compound was prepared from the (C$_5$H$_5$)(BTSA)(CO)Co complex **8** (125 mg, 0.30 mmol) dissolved in 60 mL of dichloromethane and bis(*tert*-butoxy)ethyne (**3a**) (51 mg, 0.30 mmol). The reaction was stirred at 25 °C for 3 d. After removal of the solvent in vacuo the residue was separated by column chromatography on silica gel (petroleum ether/Et$_2$O, 1:1) affording 110 mg (65%) of **11** as yellow crystals. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 1.48 (s, 18 H, OC(CH$_3$)$_3$), 1.53 (s, 18 H, SO$_2$C(CH$_3$)$_3$), 5.28 (s, 5 H, CpH) ppm. ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ = 24.7 (SO$_2$-(*C*H$_3$)$_3$), 29.0 (OC(*C*H$_3$)$_3$), 62.2 (SO$_2$*C*(CH$_3$)$_3$), 78.7 (O*C*(CH$_3$)$_3$), 84.3 (C=*C*O), 85.6 (Cp*C*), 100.3 (C=*C*-SO$_2$) ppm. MS (CI): *m*/*z* = 562 [M$^+$]. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (log ε) = 246 (3.95), 294 (4.35), 336 (3.25), 402 (2.05) nm. IR (KBr): $\tilde{\nu}$ = 3441, 2978, 2934, 1631, 1497 cm^{-1}. C$_{25}$H$_{41}$CoO$_6$S$_2$ (560.7): calcd. C 53.56, H 7.37, S 11.44; found C 53.60, H 7.35, S 11.57.

CpCo Complex 12: A mixture of 209 mg (0.50 mmol) of **10** and 97 mg (0.50 mmol) of **4a** in 80 mL of dichloromethane was stirred at 25 °C for 1 d. After removal of the solvent the crude product was separated by column chromatography on silica gel (petroleum ether/Et$_2$O, 1:1) affording 134 mg (46%) of yellow-brown crystals. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 1.32 (s, 9 H, OC(CH$_3$)$_3$), 1.49 (s, 9 H, OC(CH$_3$)$_3$), 1.50 (s, 9 H, SO$_2$*t*Bu), 1.54 (s, 9 H, SO$_2$*t*Bu), 5.31 (s, 5 H, Cp) ppm. ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ = 24.4 (*C*H$_3$), 24.6 (*C*H$_3$), 27.1 (*C*H$_3$), 27.1 (*C*H$_3$), 28.6 (*C*(sp)), 28.6 (*C*H$_3$), 28.6 (*C*(sp^3)), 60.7 (*C*(sp^3)), 60.9 (*C*(sp^3)), 78.9 (*C*(sp^3)), 78.9 (*C*(sp^3)), 81.8 (*C*(sp^2)), 82.9 (*C*(sp^2)), 85.0 (*C*(Cp)), 85.0 (*C*(sp)), 89.0 (*C*(sp)), 96.7 (*C*(sp^2)) ppm. MS (FAB$^+$): *m*/*z* = 585.4 [M$^+$], 371.1 [M$^+$ – C$_4$H$_8$]. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (log ε) = 246 (4.21), 300 (4.16), 348 (3.54), 416 (3.23) nm. IR (KBr): $\tilde{\nu}$ = 3442, 2980, 2934, 2246, 1632, 1305 cm^{-1}. C$_{27}$H$_{41}$CoO$_6$S$_2$ (584.7): calcd. C 55.46, H 7.07; found C 55.83, H 7.11.

CpCo Complex 15:[8a] ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 1.52 (s, 18 H, CH$_3$), 1.78 (s, 18 H, CH$_3$), 4.79 (s, 5 H, CpH) ppm. ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ = 29.5 (*C*H$_3$), 29.9 (*C*H$_3$), 78.9 (*C*(CH$_3$)$_3$), 81.2 (*C*(CH$_3$)$_3$), 85.7 (Cp*C*), 102.6 (*C*-O*t*Bu), 104.6 (*C*-O*t*Bu), 157.2 (*C*=O) ppm. MS (FAB+): *m*/*z* = 493.5 [M$^+$]. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (log ε) = 252 (3.69), 310 (4.42), 388 (3.22) nm. IR (KBr): $\tilde{\nu}$ = 3432, 2975, 2931, 1587, 1438 cm^{-1}. C$_{26}$H$_{41}$CoO$_5$ (492.5): calcd. C 64.64, H 8.90; found C 64.57, H 8.86.

X-ray Diffraction Analyses: The reflections were collected with a Bruker Smart CCD diffractometer for **11** and with a Bruker APEX diffractometer for **4a** and **15** (Mo-K_α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using SADABS[20] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated according to stereochemical aspects in the case of **11**, for **4a** and **15** they were refined isotropically. Structure solution and refinement were carried out with SHELXTL

Table 3. Crystal data and structure refinement for compounds **4a**, **11**, and **15**.

	4a	**11**	**15**
Empirical formula	$C_{12}H_{18}O_2$	$C_{25}H_{41}CoO_6S_2$	$C_{26}H_{41}CoO_5$
Formula weight	194.26	560.63	492.52
Crystal color	colorless	yellow	yellow-brownish
Crystal size (mm)	$0.25 \times 0.17 \times 0.12$	$0.26 \times 0.12 \times 0.04$	$0.22 \times 0.12 \times 0.10$
Crystal shape	irregular	irregular	prism
Temperature [K]	100(2)	200(2)	100(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions			
a [Å]	6.1367(6)	10.375(1)	14.041(2)
b [Å]	9.937(1)	13.219(1)	9.8179(1)
c [Å]	9.586(1)	20.457(2)	19.320(3)
α [°]	90.0	90.0	90.0
β [°]	96.283(2)	90.0	98.300(3)
γ [°]	90.0	90.0	90.0
V [Å^3]	581.0(1)	2805.6(5)	2635.5(7)
Z	2	4	4
D_{calc} [g/cm^3]	1.11	1.33	1.24
μ [mm^{-1}]	0.07	0.80	0.68
Max./min. transmission	0.99 and 0.98	0.97 and 0.82	0.93 and 0.86
Θ range for data [°]	3.0 to 28.3	1.8 to 23.3	1.5 to 28.3
Index ranges	$-8 \le h \le 8$	$-10 \le h \le 11$	$-15 \le h \le 18$
	$-13 \le k \le 12$	$-14 \le k \le 9$	$-12 \le k \le 9$
	$-12 \le l \le 12$	$-17 \le l \le 22$	$-17 \le l \le 24$
Reflections collected	5946	6734	8749
Reflections unique	1440 (R_{int} = 0.0224)	4010 (R_{int} = 0.0386)	6139 (R_{int} = 0.0226)
Reflections observed	1271 [$I > 2\sigma(I)$]	3262 [$I > 2\sigma(I)$]	4915 [$I > 2\sigma(I)$]
Observed data/parameters	1440/100	4010/319	6139/453
S (Gof) on F^2	1.05	1.04	1.02
$R(F)$	0.036	0.042	0.040
$R_w(F^2)$	0.096	0.074	0.096
$(\Delta\rho)_{max}$ [e/Å^3]	0.36	0.23	0.89
$(\Delta\rho)_{min}$ [e/Å^3]	–0.16	–0.31	–0.28

(6.12) software package.[20] Details of the crystallographic data and the refinement procedure are given in Table 3.

CCDC-652559 (for **4a**), -652560 (for **11**), and -652561 (for **15**) contain 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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