Dithiolene transfer from nickel to a dimolybdenum centre: the first dithiolene alkyne complex

Harry Adams, Michael J. Morris [*], Sarah A. Morris, Jeffrey C. Motley

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

Abstract

Transfer of dithiolene ligands from $[Ni(S_2C_2Ph_2)_2]$ to the dimolybdenum complex $[Mo_2(\mu\text{-}C_2R_2)(CO)_4Cp_2]$ (R = CO_2Me, Cp = $\eta\text{-}C_5H_5$) affords the first example of a dithiolene alkyne complex, $[Mo_2(\mu\text{-}C_2R_2)(\mu\text{-}S_2C_2Ph_2)_2Cp_2]$, together with $[Mo_2(\mu\text{-}SCR\text{=}CR)(\mu\text{-}SCPh\text{=}CPh)Cp_2]$ in which sulfur transfer from dithiolene to alkyne has occurred.
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Keywords: Molybdenum; Dithiolene; Alkyne; Nickel; Sulfur transfer

1. Introduction

The chemistry of metal dithiolene complexes is currently undergoing something of a renaissance, with their electrochemical properties leading to widespread applications in materials chemistry and, more recently, a renewed interest in the selective separation of olefins from mixed gas streams [1]. Extensive investigations in the 1960s resulted in the synthesis of dithiolene complexes of virtually all the transition metals, many of which were homoleptic species [2]. Heteroleptic complexes containing co-ligands such as carbonyls, nitrosyls and phosphines are relatively widespread, and cyclopentadienyl dithiolene complexes are also prevalent in the literature [3]. In contrast however, the organometallic chemistry of dithiolene complexes with other organic ligands has very rarely been explored [4]. Remarkably, for example, given the fact that dithiolene complexes have often been prepared either by the reaction of alkynes with metal sulfido complexes [5] or conversely by the combination of coordinated alkynes with sulfur [6], it appears that there is no reported example of a compound which contains both dithiolene and alkyne ligands.

Recently we have shown that treatment of $[Mo_2(\mu\text{-}C_2R_2)(CO)_4Cp_2]$ (R = H, alkyl, aryl, CO_2Me, etc.) with elemental sulfur results in oxidative decarbonylation to the Mo(V) species $[Mo_2S(\mu\text{-}S)_2(SCR\text{=}CRS)Cp_2]$, in which the dithiolene ligand arises through insertion of sulfur into the Mo–alkyne bonds [6]. In attempting to introduce dithiolene ligands into the dimolybdenum centre in the absence of additional sulfur, we were inspired to adapt the method of Schrauzer (recently improved by Holm) for the synthesis of $[Mo(CO)_2(S_2C_2Ph_2)_2]$, involving dithiolene transfer from $[Ni(S_2C_2Ph_2)_2]$ to $[Mo(CO)_6]$ or $[Mo(CO)_3(NCMe)_3]$ [7,8]. Here we report that this approach is also successful in the dimolybdenum system and leads to the isolation of the first dithiolene-alkyne complex.

2. Results and discussion

Heating a toluene solution of $[Mo_2(\mu\text{-}C_2R_2)(CO)_4Cp_2]$ (1; R = CO_2Me) with two equivalents of $[Ni(S_2C_2Ph_2)_2]$ for 5 h produced a new olive-green molybdenum-containing product, $[Mo_2(\mu\text{-}C_2R_2)(\mu\text{-}S_2C_2Ph_2)_2Cp_2]$ 2, in 47% yield, accompanied by a brown compound which appears identical to Schrauzer's $[Ni(S_2C_2Ph_2)]_n$ [7,9]. Complex 2 shows no remaining $v(CO)$ absorptions in its IR spectrum, but the presence of an ester peak at 1698 cm^{-1} confirms the retention of the alkyne ligand. The

[*] Corresponding author. Tel.: +44-114-2229363; fax: +44-114-2738673.

E-mail address: m.morris@sheffield.ac.uk (M.J. Morris).

^{1}H NMR spectrum contains peaks for phenyl, Cp and methyl protons in a ratio of 20:10:6, suggesting the incorporation of two dithiolene moieties. Mass spectrometry and analytical data were in agreement with this assessment. The ^{13}C NMR spectrum provided the additional information that two peaks are observed for the dithiolene carbons at δ 163.3 and 116.0.

The structure of **2** determined by X-ray diffraction is shown in Fig. 1, with important bond lengths given in Table 1. The Mo–Mo bond [2.7233(8) Å] is bridged by the alkyne in a transverse manner, with a C(11)–C(12) distance of 1.341(7) Å, not significantly changed from the 1.33 Å typically found in the [Mo$_2$(μ-alkyne)-(CO)$_4$Cp$_2$] complexes [10]. In accord with their ^{13}C NMR shifts, the two dithiolene ligands are each bonded such that one sulfur atom bridges the two molybdenums whereas the other is bonded only to one metal; this

coordination mode is well known in Mo chemistry [11]. Each CpMo unit therefore achieves a four-legged piano-stool environment consisting of three dithiolene sulfurs and the alkyne. The bridging sulfurs are asymmetrically bonded: S(3) is closer to Mo(1) and conversely S(4) is nearer to Mo(2).

When the reaction between **1** and [Ni(S$_2$C$_2$Ph$_2$)$_2$] was carried out with a 1:1 ratio of reagents, the yield of **2** dropped to 23% and a second new compound could be isolated in 17% yield (Scheme 1). This orange complex was identified as [Mo$_2$(μ-SCR=CR)(μ-SCPh=CPh)Cp$_2$] **3** by a combination of spectroscopy and crystallography. Again its IR spectrum revealed complete decarbonylation, but in this case the ^{1}H NMR spectrum contained peaks for inequivalent Cp ligands and methyl groups, implying a less symmetrical structure. The ratio of Ph:Cp:Me protons was 10:10:6, indicating
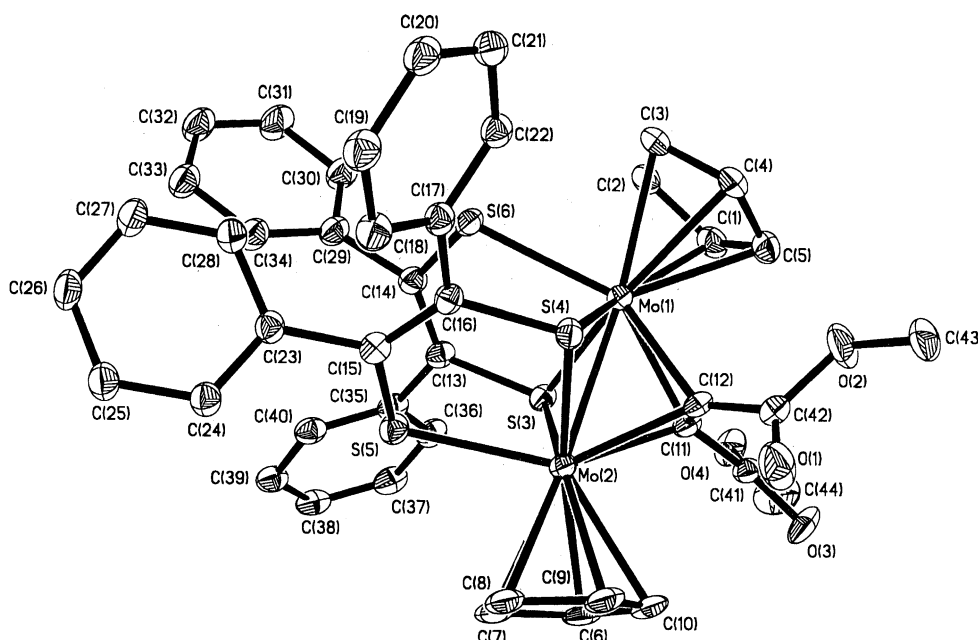

Fig. 1. Molecular structure of complex **2** in the crystal showing the atomic numbering scheme.

Table 1
Selected bond lengths [Å] and angles [°] for complex **2**

Mo(1)–C(11)	2.143(5)	Mo(1)–C(12)	2.192(6)
Mo(1)–S(3)	2.4276(14)	Mo(1)–S(6)	2.4751(16)
Mo(1)–S(4)	2.5265(16)	Mo(1)–Mo(2)	2.7233(8)
Mo(2)–C(12)	2.149(6)	Mo(2)–C(11)	2.181(6)
Mo(2)–S(4)	2.4467(17)	Mo(2)–S(5)	2.4824(16)
Mo(2)–S(3)	2.5104(16)	C(11)–C(12)	1.341(7)
C(13)–C(14)	1.337(7)	C(15)–C(16)	1.354(7)
S(3)–Mo(1)–S(6)	79.61(5)	S(3)–Mo(1)–S(4)	107.05(6)
S(6)–Mo(1)–S(4)	82.71(5)	S(4)–Mo(2)–S(5)	78.97(5)
S(4)–Mo(2)–S(3)	106.97(5)	S(5)–Mo(2)–S(3)	84.22(5)
Mo(1)–S(3)–Mo(2)	66.92(4)	Mo(2)–S(4)–Mo(1)	66.38(4)
C(12)–C(11)–C(41)	130.7(6)	Mo(1)–C(11)–Mo(2)	78.1(2)
C(11)–C(12)–C(42)	138.7(6)	Mo(2)–C(12)–Mo(1)	77.70(19)
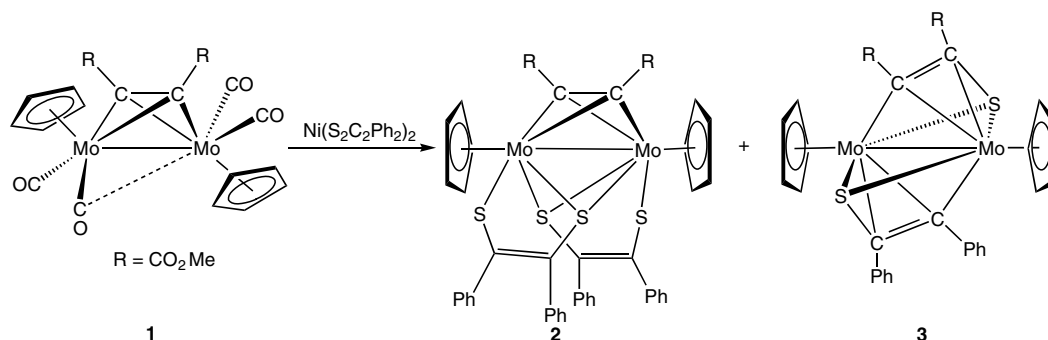
Scheme 1. Synthesis of complexes **2** and **3**.

the incorporation of only one dithiolene unit, again confirmed by the mass spectrum and analysis. Because this information was not sufficient to establish the structure of the compound, an X-ray diffraction study was carried out, the result of which is shown in Fig. 2.

The structure of **3** contains a dimolybdenum core in which the Mo–Mo bond length of 2.6048(4) Å is considerably shorter than that in **2** (Table 2). It is clear that transfer of a sulfur atom from a dithiolene ligand to the original alkyne must have occurred during the reaction, as this bond is bridged by two different β-thiovinyl ligands: one SCPh=CPh and one SCR=CR. A direct comparison of these two molybdenathiacyclobutene metallacycles reveals, as expected, that the Mo–C bond lengths in the latter are shorter than those in the former. The sulfur atoms are again asymmetrically disposed, with S(1) closer to Mo(2) and S(2) to Mo(1), but of the bridging carbon atoms, C(14) is almost symmetrically bridging. The atoms S(1), S(2), C(12) and C(14) adopt

the familiar orthogonal paddle-wheel arrangement observed in $[Mo_2(\mu-S)_2(\mu-SMe)_2Cp_2]$ [12] and other related compounds [13]. The metallacyclic unit present in **3** has been observed previously in di-iron complexes [14]; indeed one such complex was prepared by Schrauzer through the reaction of the methylated nickel dithiolene complex $[Ni(MeSCPh=CPhSMe)(SCPh=CPhS)]$ with iron pentacarbonyl [15]. More recently the reaction of the cluster $[Mo_2Rh(\mu_3-S)(\mu-S)_3(\mu-Cl)(S_2CNEt_2)_2-(PPh_3)_2]$ with phenylacetylene was shown to produce three such units coordinated to the trinuclear centre [16].

The mechanism of the reaction may proceed either by substitution of CO ligands of **1** by free dithiobenzil liberated from the nickel precursor or through the intermediacy of a Ni–S–Mo bridged species. The monodithiolene intermediate so formed could then undergo further substitution to give **2** or sulfur transfer to give **3**. In a separate reaction, we verified that **3** is not formed by the conproportionation of **1** and **2**: after heating a
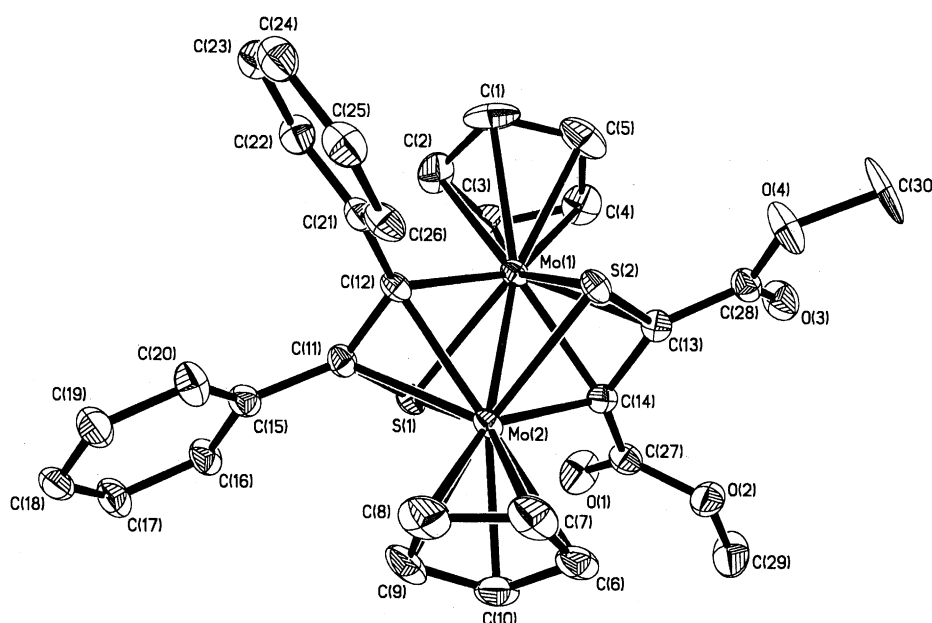

Fig. 2. Molecular structure of complex **3** in the crystal showing the atomic numbering scheme.

Table 2
Selected bond lengths [Å] and angles [°] for complex **3**

Mo(1)–C(12)	2.169(3)	Mo(1)–C(14)	2.185(3)
Mo(1)–C(13)	2.238(3)	Mo(1)–S(2)	2.4162(8)
Mo(1)–S(1)	2.4556(8)	Mo(1)–Mo(2)	2.6048(4)
Mo(2)–C(14)	2.154(3)	Mo(2)–C(12)	2.253(3)
Mo(2)–C(11)	2.306(3)	Mo(2)–S(1)	2.3958(8)
Mo(2)–S(2)	2.4577(8)	C(11)–C(12)	1.403(4)
C(13)–C(14)	1.413(4)		
C(12)–Mo(1)–S(2)	75.90(8)	C(14)–Mo(1)–S(2)	67.60(8)
C(12)–Mo(1)–S(1)	66.61(8)	C(14)–Mo(1)–S(1)	75.84(8)
S(2)–Mo(1)–S(1)	114.85(3)	C(14)–Mo(2)–S(1)	77.69(8)
C(12)–Mo(2)–S(1)	66.47(7)	C(14)–Mo(2)–S(2)	67.28(8)
C(12)–Mo(2)–S(2)	73.61(7)	S(1)–Mo(2)–S(2)	115.52(3)
Mo(2)–S(1)–Mo(1)	64.93(2)	Mo(1)–S(2)–Mo(2)	64.60(2)
C(12)–C(11)–S(1)	105.7(2)	Mo(1)–C(12)–Mo(2)	72.14(10)
C(14)–C(13)–S(2)	106.7(2)	Mo(2)–C(14)–Mo(1)	73.78(10)

toluene solution of equimolar amounts of **1** and **2** for 24 h, both compounds were recovered essentially unchanged, with only minute traces of other products observable. Heating **1** with Schrauzer's P_4S_{10}/benzoin reagent causes mainly decomposition, and no trace of **2** (or **3**) is formed. It is notable that reaction of **1** with the analogous dithiolene complex $[Ni(S_2C_2Me_2)_2]$ results in complete consumption of both starting materials but does not give any tractable products, perhaps indicating that the less stable free ligand does not survive the reaction conditions. The reaction of $[Ni(S_2C_2Ph_2)_2]$ with $[Mo_2(\mu\text{-}C_2H_2)(CO)_4Cp_2]$, which contains a less strongly bound alkyne ligand, also produced only decomposition. The formation of **2** constitutes only the second known reaction in which all four carbonyl ligands of **1** are lost while the transverse coordination of the alkyne is retained, the first being the oxidation of **1** with Me_3NO to give the Mo(IV) species $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}C_2R_2)Cp_2]$ [17].

Preliminary studies indicate that the reactivity of the alkyne ligand in **2** is much reduced compared to that in **1**. Thus, refluxing a toluene solution of **2** with an excess of sulfur caused a very slow reaction, the major product of which was the mono-dithiolene complex $[Mo_2S(\mu\text{-}S)_2(SCPh=SCPh)Cp_2]$; and in contrast to the well-known sequence of alkyne oligomerisation reactions which take place from **1** [18], heating **2** with an excess of $MeO_2CC\equiv CCO_2Me$ produced mainly decomposition. We attribute this to the lack of readily labile ligands in **2**, coupled with the large steric bulk of the dithiolene ligands.

3. Experimental

3.1. General

All reactions were carried out under nitrogen using standard Schlenk techniques. The products described are relatively air stable and work-up procedures can be carried out without special precautions. Toluene and light petroleum were dried by distillation from sodium. Light petroleum refers to the fraction boiling between 60 and 80 °C. Dichloromethane and other solvents were used as received unless otherwise stated. Chromatographic separations were performed under a slight positive pressure of nitrogen on silica columns (Merck Kieselgel 60, 230–400 mesh) of varying length. Thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.20 mm layer of silica.

Infra-red spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer 1600 FT-IR machine using 0.5 mm NaCl cells. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or an AMX400 spectrometer. Chemical shifts are given on the δ scale relative to $SiMe_4 = 0.0$ ppm. The $^{13}C\{^1H\}$ NMR spectra were recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry. Complex **1** was prepared by a slight adaptation of the literature procedure [10,19].

CAUTION! Although we have no evidence for the formation of toxic $[Ni(CO)_4]$ during these reactions, this possibility should be borne in mind during work-up.

3.2. Preparation of $[Mo_2(\mu\text{-}C_2R_2)(\mu\text{-}S_2C_2Ph_2)_2Cp_2]$ (**2**)

A solution of complex **1** (499 mg, 0.87 mmol) and $[Ni(S_2C_2Ph_2)_2]$ (940 mg, 1.74 mmol) in toluene (175 ml) was heated to reflux for 5 h with TLC monitoring. After cooling, silica (5 g) was added and the solvent was removed under vacuum. The solid residue was then loaded

onto a silica chromatography column made up in light petroleum. Elution with CH_2Cl_2-light petroleum (4:1) separated a green band which was finally eluted with a 2:3 mixture of the same solvents; it proved to be unreacted Ni complex (248.8 mg, 26% recovery). Elution with a 1:1 mixture gave a brown band of $[Ni(S_2C_2Ph_2)]_n$ (231.6 mg), and a minor unidentified green band (19.5 mg) was eluted with a 7:3 mixture. Finally elution with CH_2Cl_2-acetone (99:1) produced a large olive-green zone due to complex **2** (387.3 mg, 47%).

2: M.p. 263 °C (dec.). IR(CH_2Cl_2): 1698 (CO_2Me) cm^{-1}. ^{1}H NMR δ 7.09–6.69 (m, 20 H, Ph), 5.92 (s, 10 H, Cp), 3.84 (s, 6 H, Me). ^{13}C NMR δ 172.6 (CO_2Me), 163.3 (CPh), 141.2 (C_{ipso} of Ph), 140.5 (C_{ipso} of Ph), 129.5–125.5 (m, Ph), 116.0 (CPh), 102.1 (Cp), 74.1 (CCO_2Me), 52.9 (Me). Anal. Found: C, 55.33; H, 3.92; S, 13.23. Calc. for $C_{44}H_{36}Mo_2O_4S_4$: C, 55.70; H, 3.80; S, 13.50%. Mass spectrum m/z 951 (M$^+$).

3.3. Preparation of [Mo$_2$(μ-SCR=CR)(μ-SCPh=CPh)Cp$_2$] (3)

A solution of complex **1** (256 mg, 0.444 mmol) and $[Ni(S_2C_2Ph_2)_2]$ (237 mg, 0.444 mmol) in toluene was heated to reflux for 18 h. The solvent was removed and the residue chromatographed as above. After elution of a small amount of starting Ni complex and brown $[Ni(S_2C_2Ph_2)]_n$ (87 mg) as above, and a faint blue band, complex **2** (98 mg, 23%) was collected with an eluent of

CH_2Cl_2–acetone (49:1). Continued elution with the same solvent mixture provided a faint orange band of **1** followed by a further orange band containing **3** (54 mg, 17%).

3: M.p. 221–223 °C. IR(CH_2Cl_2): 1704, 1698 sh cm^{-1}. ^{1}H NMR δ 7.22–6.68 (m, 10 H, Ph), 5.24 (s, 5 H, Cp), 5.02 (s, 5 H, Cp), 3.70 (s, 3 H, Me), 3.61 (s, 3 H, Me). ^{13}C NMR δ 178.1, 166.9 (CO_2Me), 149.6 (μ-CCO_2Me), 139.7 (μ-CPh), 129.4–124.8 (m, Ph), 126.7 (C_{ipso}), 116.4 (C_{ipso}), 112.4 (CCO_2Me), 96.8 (CPh), 95.9, 95.5 (Cp), 52.4, 51.8 (Me). Anal. Found: C, 49.54; H, 3.64; S, 8.68. Calc. for $C_{30}H_{26}Mo_2O_4S_2$: C, 50.10; H, 3.68; S, 9.07%. Mass spectrum m/z 707 (M$^+$).

3.4. X-ray crystal structure determinations

The crystal data for **2** and **3** are given in Table 3. General procedures were as described in a previous publication [20]; a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system was used for data collection. Complex scattering factors were taken from the program package SHELXTL [21] as implemented on the Viglen Pentium computer.

Crystallographic data for the structure determinations have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 207387 and 207388 for **2** and **3** respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2

Table 3
Summary of crystallographic data for complexes **2** and **3**

	2	**3**
Empirical formula	$C_{44}H_{36}Mo_2O_4S_4$	$C_{30}H_{26}Mo_2O_4S_2$
Formula weight	948.85	706.51
T/K	150(2)	150(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2(1)$	$P2_1/c$
a/Å	36.803(3)	10.4749(11)
b/Å	9.4742(8)	19.994(2)
c/Å	10.8485(9)	12.8890(14)
α/°	90	90
β/°	90	94.147(2)
γ/°	90	90
V/Å^3	3782.6(5)	2692.4(5)
Z	4	4
Density (calcd)/Mg m^{-3}	1.666	1.743
μ/mm^{-1}	0.929	1.122
F(0 0 0)	1920	1416
Crystal size/mm^3	$0.34 \times 0.23 \times 0.09$	$0.43 \times 0.32 \times 0.18$
θ range for data collection/°	1.11–23.30	1.88–28.31
Reflections collected	27678	16633
Independent reflections	5442 [$R_{int} = 0.0853$]	6445 [$R_{int} = 0.0407$]
Data/restraints/parameters	5442/1/487	6445/0/343
Goodness-of-fit on F^2	0.952	0.938
Final R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0517$	$R_1 = 0.0343$, $wR_2 = 0.0747$
(all data)	$R_1 = 0.0497$, $wR_2 = 0.0556$	$R_1 = 0.0494$, $wR_2 = 0.0799$
Largest diffraction peak and hole/e Å^{-3}	0.465 and −0.421	1.237 and −1.056

1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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