Synthesis and Crystal Structures of the Dithiolato Complexes $[W(SPh)_2(CO)_2(PEt_3)_2]$ and $[M\{S(CH_2)_nS\}(CO)_2(PEt_3)_2]$ ($M = Mo$ or W, $n = 2$; $M = W$, $n = 3$)

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Introduction

Molybdenum complexes containing thiolate, thioether, or sulfide as models for the molybdenum center in nitrogenase have become increasingly important because of the recently reported[1−3] crystal structure of the active site of nitrogenase. We have previously described the reaction of $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W) with dithioether,[4] trithioether,[4,5] and tetrathioether[6] ligands to give a wide range of thioether complexes of these metals. In this paper we describe the synthesis and crystallographic characterization of a series of new 16-electron dithiolate complexes $[W(SPh)_2(CO)_2(PEt_3)_2]$ and $[M\{S(CH_2)_nS\}(CO)_2(PEt_3)_2]$ ($M = Mo$ or W, $n = 2$; $M = W$, $n = 3$).

Although a large number of molybdenum(II) and tungsten(II) carbonyl complexes containing dithiocarbamates and related species as coligands have been reported,[7−16] very few thiolate complexes of this type have been described. Stiefel et al.[17,18] have described a number of molybdenum(II) complexes containing multidentate thiolate thioether ligands and nitrogenase-relevant coligands ranging from CO via N_2H_3 to NH_2. Other examples of such complexes are the anionic complex $[Mo(CO)_2(TiPT)_3]^-$ (TiPT = triisopropylthiophenolate)[19] and the norbornadiene complex $[WBr(SC_6H_5)(CO)_2(\eta^4\text{−nbd})]$,[20] both of which were crystallographically characterized. The closely related complexes $[M(SR)_2(CO)_2(PR'_3)_2]$ ($M = Mo$ or W; $R = C_6H_2\text{-}Me_3\text{-}2,4,6$ or $C_6H_2Pr^i_3\text{-}2,4,6$; $PR'_3 = PMePh_2$ or PMe_2Ph) have also been previously described.[21]

Results

The reaction of $[MI_2(CO)_3(PEt_3)_2]$ ($M = Mo$ or W, prepared in situ as reported elsewhere[22]) with either 2 equiv of NaSPh or 1 equiv of $Na_2[S(CH_2)_nS]$ at room temperature afforded high yields of the six-coordinate complexes $[W(SPh)_2(CO)_2(PEt_3)_2]$ (**1**) and $[M\{S(CH_2)_nS\}(CO)_2(PEt_3)_2]$ ($M = Mo$ or W, $n = 2$; $M = W$, $n = 3$) (**2**−**4**) by metathesis of two iodide ligands and loss of a carbonyl ligand. The new complexes **1**−**4** have all been characterized by elemental analysis, IR spectroscopy (Table 1), ^1H NMR spectroscopy (Table 2), and also X-ray crystallography. The structures of **1**, **2**, **3**, and **4** are illustrated in Figures 1−3, together with the atomic numbering scheme. Crystal data are given in Table 3, together with refinement details. Dimensions in the metal coordination spheres of **1**, **2**, **3**, and **4** are given in Table 4. Conductivity measurements in acetone solution showed complexes **1**, **3**, and **4** to be nonelectrolytes (conductivities of 23, 20, and 18 S cm^2 mol^{-1} for **1**, **3**, and **4**, respectively). All of the complexes are very soluble in chlorinated solvents, soluble in diethyl ether, and slightly soluble in hexane. The complexes can be stored in the solid state under dinitrogen; however, they are very air-sensitive in solution.

The IR spectrum of $[W(SPh)_2(CO)_2(PEt_3)_2]$ (**1**) shows a single carbonyl band both in the solid state and in solution, consistent with the *trans*-carbonyl crystallographically observed structure shown in Figure 1. In contrast, the IR spectra of complexes **2**−**4**, both in solution and in the solid state, showed two carbonyl bands, again in agreement with the *cis*-carbonyl ligands observed in the crystallographically determined structures shown in Figures 2 and 3. It is interesting to note that the capping carbonyl ligand in $[WI_2(CO)_3(PEt_3)_2]$[22] is lost when iodides are replaced by SR groups to give the 16-electron complexes **1**−**4**. This seems more likely to be due to electronic rather than steric effects, given that coordination number 7 is retained in closely related complexes such as $[W(S_2COPr^i\text{-}S)(S_2COPr^i\text{-}S,S')(CO)_2(PMe_3)_2]$.[23]

The structure of **1** contains a crystallographic center of symmetry. The metal geometry is octahedral with dimensions to the carbonyl groups 2.04(3) Å, to the triethylphosphine 2.563(6) Å, and to the phenylsulfide 2.402(5) Å. The cis angles are all within 5.2 of 90°.

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Table 1. Physical, Analytical,[a] and IR[b] Data for the Complexes

			anal. (%)			IR (cm^{-1})	
complex	color	yield (%)	C	H	S	ν(CO) CH_2Cl_2	ν(CO) KBr
1 $[W(SPh)_2(CO)_2(PEt_3)_2]$	dark green	60	45.1 (44.9)	5.9 (5.8)	9.0 (9.2)	1839(br)	1833(br)
2 $[Mo\{S(CH_2)_2S\}(CO)_2(PEt_3)_2]$	dark red	91	40.2 (40.0)	7.7 (7.1)	14.7 (13.4)	1919(s), 1832(br)	1906(s), 1810(br)
3 $[W\{S(CH_2)_2S\}(CO)_2(PEt_3)_2]$	dark red	85	33.4 (33.8)	5.5 (5.6)	12.0 (11.3)	1912(s), 1830(br)	1910(s), 1832(br)
4 $[W\{S(CH_2)_3S\}(CO)_2(PEt_3)_2]$	dark red	80	35.1 (35.0)	5.7 (6.2)	10.3 (11.0)	1909(s), 1834(br)	1908(s), 1831(br)

[a] Calculated values in parentheses. [b] s = strong, br = broad.

Table 2. ^1H NMR Data[a] for Complexes **1**−**4** at 25 °C Referenced to $SiMe_4$

complex	^1H δ (ppm)
1	7.4 (br, m, 10H, PhS); 2.5 (m, 12H, CH_2P); 0.9 (m, 18H, CH_3)
2	2.8 (s, 4H, CH_2S); 2.15 (m, 12H, CH_2P); 1.0 (m, 18H, CH_3)
3	2.7 (s, 4H, CH_2S); 2.15 (m, 12H, CH_2P); 1.1 (m, 18H, CH_3)
4	2.9 (t, J_{P-H} = 18 Hz, 4H, CH_2S); 2.3 (m, 2H, CH_2); 2.25 (m, 12H, CH_2P); 1.1 (m, 18H, CH_3)

[a] All spectra recorded in $CDCl_3$. s = singlet, t = triplet, m = multiplet, br = broad.

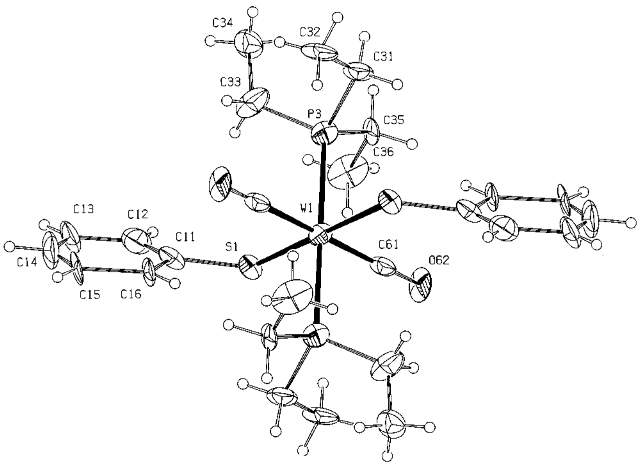

Figure 1. The structure of **1** showing the atomic numbering scheme. Ellipsoids are drawn at 30% probability. Hydrogen atoms are included as small circles of arbitrary radii.

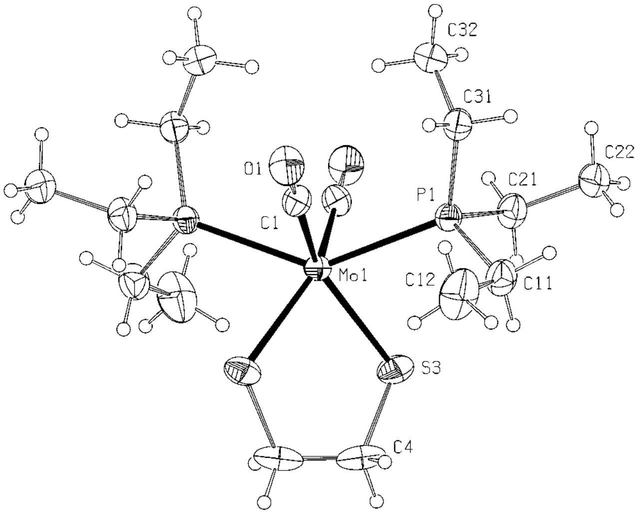

Figure 2. The structure of **2** showing the atomic numbering scheme. Ellipsoids are drawn at 30% probability. Hydrogen atoms are included as small circles of arbitrary radii. Compound **3** is isomorphous.

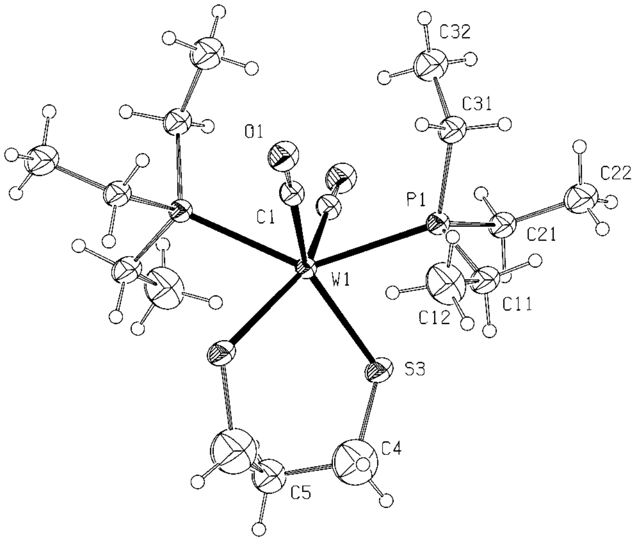

Figure 3. The structure of **4** showing the atomic numbering scheme. Ellipsoids are drawn at 30% probability. Hydrogen atoms are included as small circles of arbitrary radii.

By contrast, in **2**, **3**, and **4**, which are isomorphous, the metal atoms exhibit distorted trigonal prismatic structures. The structure of **2** is shown in Figure 2 (**3** is equivalent), and **4** is shown in Figure 3 together with the common atomic numbering scheme. In each structure, the metal atom is bonded to two carbonyls, two sulfur atoms of the bidentate ligand, and two phosphorus atoms of the triethylphosphine ligands. In projection looking down the approximate threefold axis of the trigonal prism, the two sulfur atoms superimpose as does each carbon with a phosphorus atom (Figure 4).

Distortions in the geometry of six-coordinate dicarbonyl complexes of molybdenum(II) and tungsten(II) have recently been analyzed.[21,24] Apart from structures only slightly distorted from the ideal forms of octahedron and trigonal prism, there is a complete range of intermediate geometries characterized by the twist angle between the two triangular faces. This is 60° for the ideal octahedron and 0° for the ideal trigonal prism. These angles are 13.7, 13.2, and 13.5° in **2**, **3**, and **4**, respectively. These structures conform to the pattern of geometries noted in refs 21 and 24 and also found by us[25] in characterization of other structures of the type $[W(S{\wedge}S)(CO)_2(PEt_3)_2]$, with $S{\wedge}S$ = 1,3-dithiole-2-thione-4,5-dithiolate or bdt = benzene-1,2-dithiolate, although the angles in those two structures were 23° and 20°, respectively. It is not clear why there should be a difference between the present three structures and these latter two, although it could well be an electronic effect as, in the two sets of structures, the sulfur atoms are linked

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Table 3. Crystal Data and Structure Refinement for **1**, **2**, **3**, and **4**

	1	**2**	**3**	**4**
empirical formula	$C_{26}H_{40}S_2P_2O_2W$	$C_{16}H_{34}MoO_2P_2S_2$	$C_{16}H_{34}O_2P_2S_2W$	$C_{16}H_{36}O_2P_2S_2W$
fw	694.5	480.4	568.34	570.36
temp (K)	293(2)	293(2)	293(2)	293(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst system	monoclinic	tetragonal	tetragonal	tetragonal
space group	$P2_1/a$	$P4_22_12$	$P4_22_12$	$P4_22_12$
unit cell dimens				
a Å	10.402(9)	14.514(9)	14.343(9)	14.318(9)
b Å	16.263(14)	14.514(9)	14.343(9)	14.318(9)
c Å	10.029(8)	11.006(11)	10.900(11)	11.206(9)
β °	112.69(1)	(90)	(90)	(90)
V	1565(2)	2319(3)	2242(3)	2297(3)
z	2	4	4	4
density (calcd) Mg cm^{-3}	1.474	1.376	1.683	1.649
abs coeff (mm^{-1})	3.945	0.889	5.486	5.355
F(000)	696	1000	1128	1136
cryst size (mm)	0.25 × 0.25 × 0.30	0.35 × 0.15 × 0.20	0.35 × 0.25 × 0.25	0.20 × 0.25 × 0.25
θ range for data collection	2.70−24.90	2.32−25.07	2.01−24.85	2.71−24.73
index ranges	$0 \le h \le 12$	$-14 \le h \le 14$	$0 \le h \le 16$	$-16 \le h \le 16$
	$-19 \le k \le 19$	$-14 \le k \le 14$	$16 \le k \le 16$	$-16 \le k \le 16$
	$-11 \le l \le 10$	$0 \le l \le 11$	$-12 \le l \le 12$	$0 \le l \le 13$
reflns collected	4117	6423	6291	4499
indep reflns (R_{int})	2260(0.0655)	1868(0.0452)	6291(0.0572)	4449(0.0862)
data/restraints/parameters	2260/0/155	1868/0/215	1900/0/215	1865/0/209
goodness-of-fit on F^2	1.257	1.168	1.092	1.056
weighting scheme $(a,b)^a$	0.0825, 42.247	0.0735, 1.7536	0.0304, 26.116	0
final *R* indices [$I > 2\sigma(I)$]				
R1	0.0915	0.0444	0.0460	0.0551
wR2	0.2548	0.0901	0.0906	0.1382
R indices (all data)				
R1	0.1008	0.0603	0.0512	0.0585
wR2	0.2593	0.0998	0.0932	0.1437
extinction coeff	0.042(5)	0.016(2)	0.000(1)	0.0145(11)
largest diff peak and hole (e $Å^{-3}$)	1.937, −1.227	0.640, −1.403	0.777, −0.753	1.191, −2.103

[a] Weighting scheme $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 4. Dimensions in the Metal Coordination Spheres of **1**, **2**, **3**, and **4**

Bond Lengths (Å) and Angles (deg) for **1**

W(1)−C(61)	2.04(3)
W(1)−S(1)	2.402(5)
W(1)−P(3)	2.563(6)
C(61)−W(1)−S(1)	84.8(6)
C(61)−W(1)−P(3)	89.8(5)
S(1)−W(1)−P(3)	87.5(2)

Bond Lengths (Å) and Angles (deg) for **2**−**4**

	2 (M = Mo)	**3** (M = W)	**4** (M = W)
M(1)−C(1)	1.973(7)	1.950(10)	1.989(13)
M(1)−S(3)	2.430(2)	2.386(3)	2.403(3)
M(1)−P(11)	2.515(2)	2.492(3)	2.494(4)
C(1)−M(1)−C(1) #1[a]	105.7(5)	105.6(6)	104.9(8)
C(1)−M(1)−S(3)	146.9(2)	147.0(3)	147.8(4)
C(1)−M(1)−S(3) #1	93.6(2)	93.7(4)	90.2(3)
C(1)−M(1)−P(1) #1	76.4(2)	76.1(3)	76.3(5)
C(1)−M(1)−P(1)	79.4(2)	79.4(3)	78.0(4)
S(3)−M(1)−S(3) #1	83.7(1)	83.5(1)	91.6(1)
S(3)−M(1)−P(1) #1	134.6(1)	134.7(1)	135.5(4)
S(3)−M(1)−P(1)	79.3(1)	79.6(1)	78.3(3)
P(1)−M(1)−P(1) #1	139.3(1)	139.0(2)	137.8(2)

[a] #1 is symmetry element *y*, *x*, −*z*.

by different types of carbon atoms, being aliphatic and aromatic, respectively.

The dimensions are compared in Table 4 and show that the bond lengths in **2** (M = Mo) are significantly longer than those for **3** and **4** (M = W) by ca. 0.02−0.03 Å. There are also differences in the angles subtended at the metal. There is very little difference between the angles in **2** and **3** (maximum difference is less than 1°), but the increased size of the thiolate ligand in **4** over **3** is reflected in the increased S−W−S angle: 91.6(1)° in **4** and 83.5(1)° in **3**. This also affects the other angles which include sulfur, and these change by ca. 3−5°, but the angles involving just phosphorus and carbon are little changed. It seems likely that the difference in structure between the trigonal prismatic structures **2**, **3**, and **4** and the octahedral structure (**1**) is a consequence of the different denticities of the sulfur ligands in these complexes.

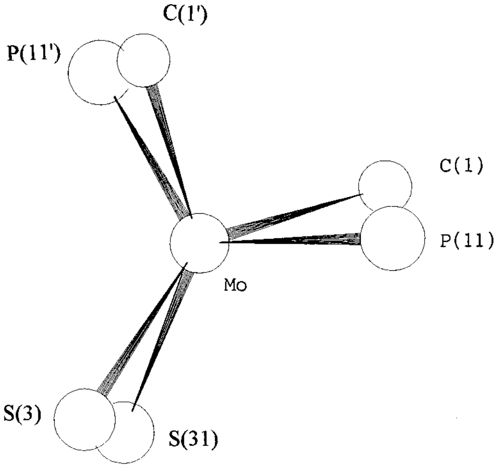

Figure 4. A view of the coordination sphere of the molybdenum atom in **2**, showing the trigonal prismatic geometry.

The ^1H NMR spectra (Table 2) of complexes **1**−**4** conform with the solid-state structures shown in Figures 1−4. The room temperature $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2) of complexes **1**, **3**, and **4** have carbonyl resonances at $\delta = 228$ ($J_{P-C} = 7$ Hz), 236 (J_{P-C} = 8 Hz), and 236 (J_{P-C} = 8 Hz), respectively, suggesting a single isomer for each in solution at room temperature.

Several attempts were made to isolate a tricarbonyl complex by saturating CH_2Cl_2 solutions of **1**−**4** with carbon monoxide, but they were unsuccessful, with no evidence for the seven-coordinate complexes $[M(SPh)_2(CO)_3(PEt_3)_2]$ and $[M\{S(CH_2)_nS\}(CO)_3(PEt_3)_2]$ (M = Mo or W, *n* = 2; M = W, *n* = 3).

Conclusions

In conclusion, we have successfully prepared and characterized four neutral bis(dithiolate) phosphine carbonyl complexes of molybdenum(II) and tungsten(II) and compared and contrasted the molecular structures of these complexes in the solid state.

Experimental Section

All experimental work was carried out under an atmosphere of dry dinitrogen using standard Schlenk-line techniques. Ethanol was dried over magnesium/iodine and distilled before use. Tetrahydrofuran (THF) was dried by distillation over sodium. Diethyl ether was dried over sodium. The thiolates NaSPh and $Na_2[S(CH_2)_nS]$ (*n* = 2 or 3) were prepared by reacting HSPh (in ethanol) and $HS(CH_2)_nSH$ (in THF) with the appropriate molar quantity of sodium. The complexes $[MI_2(CO)_3(PEt_3)_2]$ (M = Mo or W) were prepared by a published method.[22] All other chemicals used were purchased from commercial sources.

Elemental analyses (C, H, N, and S) were recorded on a Carbo Erba elemental analyzer MOD 1106 (using helium as a carrier gas). Conductivity measurements were measured using a Portland Electronics conductivity bridge. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer, and all spectra were referenced to $SiMe_4$.

Syntheses. $[W(SPh)_2(CO)_2(PEt_3)_2]$ (1). To a stirred suspension of $[WI_2(CO)_3(NCMe)_2]$ (0.27g, 0.44 mmol) in Et_2O (50 cm^3) was added a 1.0 M solution of PEt_3 in THF (0.88 cm^3, 0.88 mmol). The resulting yellow solution was stirred for 5 min and then filtered. Solid NaSPh (0.13 g, 0.98 mmol) was added, and the solution was stirred for 18 h to give a green solution, which was filtered twice through Celite to remove any insoluble inorganic impurities. The solvent was reduced to approximately 5 mL in vacuo, and after the mixture was cooled to 0 °C, green single crystals of $[W(SPh)_2(CO)_2(PEt_3)_2]$ (**1**) were obtained (yield = 0.20 g, 60%), which were suitable for X-ray crystallography.

$[Mo\{S(CH_2)_2S\}(CO)_2(PEt_3)_2]$ (2). To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.25 g, 0.48 mmol) in Et_2O (50 cm^3) was added a 1.0 M THF solution of PEt_3 (0.95 cm^3, 0.95 mmol). The resulting solution was stirred for 30 s and then filtered. Solid $Na_2[S(CH_2)_2S]$ (0.07 g, 0.48 mmol) was added, and the solution was stirred for 2 h to give a wine-red solution, which was filtered twice through Celite to remove any insoluble inorganic impurities. The solvent was reduced to approximately 5 mL and the mixture was cooled to −17 °C, affording dark red crystals of $[Mo\{S(CH_2)_2S\}(CO)_2(PEt_3)_2]$ (**2**) (yield = 0.21 g, 91%), which were suitable for X-ray crystallography.

$[W\{S(CH_2)_2S\}(CO)_2(PEt_3)_2]$ (3). To a filtered yellow solution of $[WI_2(CO)_3(PEt_3)_2]$ prepared from $[WI_2(CO)_3(NCMe)_2]$ (0.27 g, 0.44 mmol) and a 1.0 M solution of PEt_3 in THF (0.88 cm^3, 0.88 mmol), as above, was added solid $Na_2[S(CH_2)_2S]$ (0.06 g, 0.44 mmol). The mixture was stirred for 18 h to give a wine-red solution, which was filtered twice through Celite to remove any insoluble inorganic impurities. The solvent was removed in vacuo to give a dark red oil, which was recrystallized from Et_2O at −17 °C, affording dark red crystals of $[W\{S(CH_2)_2S\}(CO)_2(PEt_3)_2]$ (**3**) (yield = 0.21 g, 85%), which were suitable for X-ray crystallography.

$[W\{S(CH_2)_3S\}(CO)_2(PEt_3)_2]$ (4). To a filtered yellow solution of $[WI_2(CO)_3(PEt_3)_2]$ prepared from $[WI_2(CO)_3(NCMe)_2]$ (0.22 g, 0.37 mmol) and a 1.0 M solution of PEt_3 in THF (0.74 cm^3, 0.74 mmol), as above, was added solid $Na_2[S(CH_2)_3S]$ (0.06 g, 0.37 mmol). The solution was stirred for 18 h and then filtered twice through Celite to remove any insoluble inorganic impurities. The solvent was reduced to approximately 5 mL and the mixture was cooled to −17 °C, affording dark red crystals of $[W\{S(CH_2)_3S\}(CO)_2(PEt_3)_2]$ (**4**) (yield = 0.17 g, 80%), which were suitable for X-ray crystallography.

Crystallography. Crystal data are given in Table 3, together with refinement details. Dimensions in the coordination spheres of **1**, **2**, **3**, and **4** are given in Table 4. Data for all four crystals were collected with Mo Kα radiation using the MAR research image plate system. The crystals were positioned at 75 mm from the image plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[26] The structures were then solved using direct methods with the Shelx86 program.[27] Compound **1** contained a crystallographic center of symmetry. Compounds **2**, **3**, and **4** were isomorphous. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions, methyl groups are rigid groups, with a thermal parameter equal to 1.2 times that of the carbon atom to which they were attached. An empirical absorption correction was applied to **1**, **3**, and **4**.[28] Structures were then refined on F^2 using Shelxl.[29] All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading.

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Supporting Information Available: For **1**, **2**, **3**, and **4**, tables of remaining molecular dimensions not included in the paper, anisotropic and isotropic thermal parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs@acs.org.

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