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Divalent Lanthanide Chemistry. Bis(pentamethylcyclopentadienyl)europium(II) and -ytterbium(II) Derivatives: Crystal Structure of Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(II)–Hemitoluene at 176 K

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Red, paramagnetic (7.99 μ_B, 5–50 K) (diethyl ether)bis(pentamethylcyclopentadienyl)(tetrahydrofuran)europium(II), $(Me_5C_5)_2Eu(THF)(Et_2O)$, is isolated from reaction of 3 molar equiv of sodium pentamethylcyclopentadienide and europium trichloride in refluxing tetrahydrofuran, after crystallization from diethyl ether. The mono(tetrahydrofuran) complex $(Me_5C_5)_2Eu(THF)$ may be isolated by use of toluene rather than diethyl ether as the crystallization solvent. Red, diamagnetic bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(II) is isolated from the reaction of ytterbium dichloride and sodium pentamethylcyclopentadienide in refluxing tetrahydrofuran. The diethyl ether complex $(Me_5C_5)_2Yb(OEt_2)$ may be isolated by crystallization of the tetrahydrofuran complex from diethyl ether. The hemitoluene complex $(Me_5C_5)_2Yb(THF)\cdot{}^1/_2$tol can be isolated by recrystallization of the tetrahydrofuran complex from toluene. As these divalent metallocenes are the first hydrocarbon-soluble lanthanide derivatives to be isolated, we have examined the latter complex by X-ray crystallography. Crystals of $(Me_5C_5)_2Yb(OC_4H_8)\cdot{}^1/_2C_6H_5CH_3$ crystallize in the monoclinic system, $P2_1/n$, with a = 11.358 (8) Å, b = 21.756 (19) Å, c = 10.691 (7) Å, and β = 101.84 (5)° at 176 K. For $Z = 4$ the calculated density is 1.37 g cm^{-3}. The ytterbium atom is coordinated to the oxygen atom of a tetrahydrofuran molecule and to two pentamethylcyclopentadienyl rings. The molecule has approximate C_2 symmetry about the Yb–O bond. The Yb–O distance is 2.41 Å, the Yb–C distances average 2.66 Å, and the Yb–Cp(centroid) distances average 2.37 Å. The Me_5C_5 rings are in a staggered configuration with respect to each other. The methyl groups of the Me_5C_5 groups are displaced by 0.03–0.21 Å from the planes of the five-membered rings away from the ytterbium atom. The toluene molecule is not coordinated to the complex and is on a center of symmetry in a disordered configuration. The 3466 data with $F^2 > 3\sigma$ refined by full-matrix least-squares methods to a conventional R factor of 0.036.

Introduction

In contrast to the reasonably extensive literature associated with trivalent lanthanide organometallic compounds, the divalent oxidation state of these metals has been largely ignored.[1] Yellow, paramagnetic (7.63 μ_B) and red, diamagnetic dicyclopentadienyleuropium and -ytterbium, respectively, were first prepared from the metal and cyclopentadiene in liquid ammonia.[2] The compounds are insoluble in solvents with which they do not react, though some coordination complexes with, for example, ammonia have been isolated. The preparation of Cp_2Yb from the metal and diene in liquid ammonia is not straightforward since two other cyclopentadienyl-containing products, Cp_3Yb and a species formulated as $Cp_4Yb_2N_2H_4$, have been isolated.[3] Alternative synthetic schemes have been devised which give Cp_2Yb in good yield.[4] The latter paper also reports that Cp_2Yb is green when pure, rather than red as was initially reported.[2] An insoluble, purple, paramagnetic (3.6 μ_B) derivative of samarium(II), Cp_2Sm(THF), has also been described.[5] The insoluble cyclooctatetraene (COT) derivatives (COT)Eu and (COT)Yb have been briefly mentioned.[6] An ether-soluble (pentafluorophenyl)ytterbium species, $(C_6F_5)_2Yb(THF)_4$,[7] and some insoluble alkynyl derivatives, $(RC{\equiv}C)_2M$, of ytterbium[8,9] and europium[9] have also been described.

The general pattern which dominates the rather meager knowledge of divalent lanthanide organometallic chemistry is their lack of volatility and solubility. This is doubtless due to some type of polymer formation, possibly similar to that found for Cp_2Ca.[10] Use of sterically demanding ligands to stabilize low coordination numbers is a strategy that can be used to prevent polymerization. Replacement of the five hydrogen atoms of a cyclopentadienyl group with five methyl groups, giving the pentamethylcyclopentadienyl group, greatly increases the steric bulk of the ligand. This is shown, by way of example, by the observation that dicyclopentadienylmanganese[11] has a polymeric constitution in the solid state[12] whereas bis(pentamethylcyclopentadienyl)manganese is monomeric.[13] In this paper we describe some coordination complexes of bis(pentamethylcyclopentadienyl)europium(II) and -ytterbium(II) and the crystal structure of one of them, $(Me_5C_5)_2Yb(THF)\cdot{}^1/_2$tol.

Experimental Section

Microanalyses were performed by the microanalytical laboratory of this department. The ^{1}H (90 MHz) and $^{13}C\{^1H\}$ (22.5 MHz) nuclear magnetic resonance spectra were recorded on a JEOL FX-90 spectrometer in toluene-d_8 solution and referenced to Me_4Si (δ 0). Infrared spectra were recorded on a Perkin-Elmer 597 machine as Nujol mulls between cesium iodide windows. The magnetic susceptibility measurements were performed as previously described.[14] All operations were performed under nitrogen.

(Diethyl ether)bis(pentamethylcyclopentadienyl)(tetrahydrofuran)europium(II). Sodium pentamethylcyclopentadienide[15] (9.72 g, 0.0614 mol) in tetrahydrofuran (75 mL) was added to a suspension of europium trichloride (5.30 g, 0.0205 mol) in tetrahydrofuran (75 mL). A blue solution developed immediately which slowly turned brown-red at room temperature. The suspension was refluxed for 12 h. Tetrahydrofuran was removed under vacuum, the residue was extracted with diethyl ether (2 × 150 mL), and the combined extracts were concentrated to ca. 100 mL. Cooling (−10 °C) afforded red

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prisms in 65% yield (7.5 g); mp 181–182 °C. The complex is soluble in aliphatic and aromatic hydrocarbons and in ethereal solvents. The complex decomposed upon attempted sublimation under vacuum at ca. 140 °C. Anal. Calcd for $C_{28}H_{48}EuO_2$: C, 59.1; H, 8.51. Found: C, 59.1; H, 8.43. A sample of the complex was dissolved in benzene and hydrolyzed with water. The ^{1}H NMR spectrum of the benzene solution showed tetrahydrofuran and diethyl ether present in approximately equal amounts. The compound follows Curie behavior from 5–50 K with $\mu_{eff} = 7.99\ \mu_B$ and $C = 7.91$. IR data: 2713 w, 1627 w, 1313 w, 1286 w, 1248 w, 1208 w, 1185 w, 1147 m, 1119 w, 1089 w, 1054 m, 1032 s, 1003 w, sh, 927 w, 896 s, 837 w, 828 w, 818 w, 795 m, 777 m, 766 w, 721 m, 649 w, br, 624 w, 585 m, 506 m, br, 353 w, br, 248 cm^{-1} s, br.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)europium(II). (Diethyl ether)bis(pentamethylcyclopentadienyl)europium (1.5 g, 0.0027 mol) was dissolved in toluene (25 mL), and the solution was concentrated to ca. 10 mL. Cooling (−70 °C) yielded red prisms in quantitative yield; mp 178–181 °C. Anal. Calcd for $C_{24}H_{38}EuO$: C, 58.3; H, 7.74. Found: C, 58.6; H, 7.56. IR data: 2714 w, 1637 w, br, 1292 w, sh, 1281 w, 1243 m, 1209 m, 1027 s, br, 952 w, 928 w, 898 s, br, 834 w, sh, 794 w, 723 m, 691 w, 637 m, br, 587 w, 462 w, 357 m, br, 258 cm^{-1} s, br. Crystallization of the mono(tetrahydrofuran) complex from diethyl ether yields $(Me_5C_5)_2Eu(THF)(OEt_2)$.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(II). Sodium pentamethylcyclopentadienide (3.97 g, 0.0251 mol) in tetrahydrofuran (75 mL) was added to a suspension of ytterbium dichloride[16] (3.06 g, 0.0125 mol) in tetrahydrofuran (75 mL). After refluxing for 12 h, the deep purple suspension was evaporated to dryness, and the residue was extracted with diethyl ether (2 × 100 mL). The combined, green extracts were concentrated to ca. 100 mL and cooled (−10 °C). The red prisms were collected and dried under vacuum; yield 5.5 g (85%). When heated in a sealed capillary, the complex shrank at ca. 120 °C and melted at 206–209 °C. Anal. Calcd for $C_{24}H_{38}OYb$: C, 55.9; H, 7.43. Found: C, 56.2; H, 7.32. The complex is soluble in aliphatic and aromatic hydrocarbons and ethereal solvents. The complex decomposed upon attempted sublimation under vacuum at ca. 125 °C. The ^{1}H nuclear magnetic resonance spectrum (−25 °C) consists of multiplets at δ 3.42 and 1.41 due to the α and β protons of tetrahydrofuran, respectively, and a singlet at δ 2.12 due to the methyl protons of the Me_5C_5 rings in area ratio 4:4:30, respectively. The $^{13}C\{^1H\}$ nuclear resonance spectrum (−25 °C) consists of singlets at δ 111, 69.5, 25.7, and 11.5 due to $(Me_5C_5)_2Yb$, $Yb\overline{O\mathit{CH}_2CH_2CH_2\mathit{CH}_2})$, $Yb(\overline{OCH_2\mathit{CH}_2\mathit{CH}_2CH_2})$, and $(\mathit{Me}_5C_5)_2Yb$, respectively. IR data: 2719 w, 1646 w, br, 1322 w, 1297 w, 1249 m, br, 1221 w, 1151 w, 1093 w, 1067 w, sh, 1034 s, br, 916 w, 882 s, br, 801 w, 783 w, 723 m, 669 m, br, 627 w, 592 m, 483 w, 472 w, 361 m, br, 304 m, 258 cm^{-1} s, br.

(Diethyl ether)bis(pentamethylcyclopentadienyl)ytterbium(II). This complex was crystallized from the mother liquor which yielded the mono(tetrahydrofuran) complex (above). Green needles in ca. 5% yield were isolated after most of the tetrahydrofuran complex had crystallized. The complex decomposed without melting at ca. 145 °C. Anal. Calcd for $C_{24}H_{40}OYb$: C, 55.7; H, 7.79. Found: C, 55.7; H, 7.58. The ^{1}H nuclear magnetic resonance spectrum (PhH-d_6, 35 °C) consisted of a quartet centered at δ 3.15, a singlet at δ 2.16, and a triplet at δ 1.04 due to $CH_3\mathit{CH}_2OYb$, $(\mathit{Me}_5C_5)_2Yb$, and CH_3CH_2OYb in area ratio 4:30:6, respectively. IR data: 2720 w, 1633 w, 1284 w, 1262 w, 1180 w, sh, 1163 w, sh, 1149 s, 1123 w, 1097 w, sh, 1077 s, br, 1041 m, 1019 w, 980 w, sh, 948 w, 929 m, 839 s, 829 w, sh, 797 w, 722 m, 592 m, 552 w, 482 w, 443 w, 355 m, br, 303 m, 268 cm^{-1} s, br.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium-(II)–Hemitoluene. Sodium pentamethylcyclopentadienide (3.52 g, 0.0227 mol) in tetrahydrofuran (75 mL) and ytterbium dichloride (2.71 g, 0.0111 mol) in tetrahydrofuran (75 mL) were refluxed for 12 h. Tetrahydrofuran was removed under vacuum, the residue was extracted with toluene (150 mL), and the solution was concentrated to ca. 80 mL and was cooled to −70 °C. The brown-red prisms were collected and dried under vacuum; yield 4.6 g (74%). When heated in a sealed capillary, the complex darkened at ca. 195 °C and melted at 204–206 °C. Anal. Calcd for $C_{27.5}H_{42}OYb$: C, 58.8; H, 7.54. Found: C, 58.5; H, 7.27. IR data: 2719 m, 1604 m, 1337 w, 1259 m, 1242 w, sh, 1174 m, br, 1079 w, 1022 s, 918 m, 868 s, br, 843 w, sh, 795 w, 730 s, 694 s, 671 m, 589 w, 481 w, sh, 466 m, 360 m, br, 304 s, br, 282 w, sh, 268 cm^{-1}.

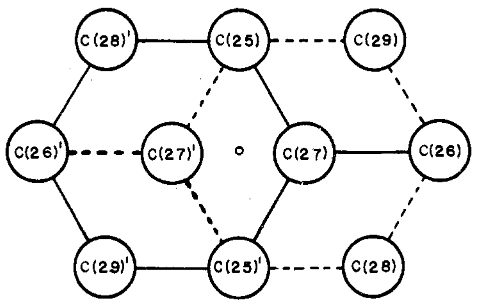

Figure 1. Disordered model for the toluene molecule. Carbons C(25) and C(26) were given full occupancy, and C(27), C(28), and C(29) were given half-occupancy, corresponding to two toluene molecules per unit cell containing four ytterbium ions.

X-ray Data. Crystals were sealed in quartz capillaries and mounted on a Picker FACS-I automated diffractometer equipped with a graphite monochromator, a Mo X-ray tube, and a Syntex LT-1 temperature controller. ω scans of several low-angle reflections had a width at half-height of 0.15°. Least-squares refinement of the setting angles of nine manually centered reflections (40° < 2θ < 50°) using Mo Kα_1 (λ = 0.709 30 Å) radiation gave $a = 11.358$ (8) Å, $b = 21.756$ (19) Å, $c = 10.691$ (7) Å, $\beta = 101.84$ (5)°, and $V = 2585.6$ Å^3 at 176 (5) K. The observed extinctions are unique to space group $P2_1/n$. With $Z = 4$ and a molecular weight of 533.62, the calculated density is 1.37 g cm^{-3}.

Intensity data were collected for two forms to 50° in 2θ by using θ–2θ scans with a scan speed of 2°/min on 2θ, a scan range from 1.5° below the Kα_1 peak to 1.5° above the Kα_2 peak, and backgrounds counted for 10 s at each end of the scan range. Three standard reflections, measured after every 200 reflections, decreased in intensity by 6% during data collection, and the measured intensities were corrected accordingly. Data were collected at low temperature (176 K) to minimize severe crystal movement, which was evident at room temperature. Due to occasional problems with the temperature controller, data for portions of the second form were unreliable and not used. Absorption corrections to the data were not applied, because attempts to fit an analytical absorption correction to the intensity variation of azimuthal scans were unsuccessful as the crystal shape permitted a reentrant beam in some orientations ($\mu = 36.2$ cm^{-1} for Mo Kα radiation and approximate crystal dimensions were 0.12 × 0.16 × 0.22 mm). Intensities of the 8544 reflections measured were corrected for Lorentz and polarization factors, extinctions were removed, and equivalent reflections were averaged to yield a set of 4592 unique reflections.

Trial coordinates for the ytterbium atom were obtained from a three-dimensional Patterson function and were refined by least-squares methods. A Fourier calculation then revealed all nonhydrogen atoms of the pentamethylcyclopentadienyl (Cp) rings and the tetrahydrofuran (THF). A series of isotropic and anisotropic least-squares refinements, followed by a difference synthesis, gave a difference Fourier map with peaks of electron density (3–5 e/Å^3) near a center of symmetry. These peaks could be interpreted in terms of two partially overlapping sets of toluene carbon atoms as shown in Figure 1. In the final cycles of refinement, all nonhydrogen atoms except those for toluene were refined anisotropically; the carbon atoms for toluene were refined isotropically and were not restrained except to assign full occupancy to atoms C(25) and C(26) and half-occupancy to atoms C(27), C(28), and C(29). The refinement converged to the positions given in Table I with the changes in parameters in the last cycle all 0.07σ or less. The data were inspected for evidence of extinction, but an extinction correction was not indicated. Thermal parameters and structure factor amplitudes are included in the supplementary material.

The full-matrix least-squares program minimizes the function $\sum w|\Delta F|^2/\sum wF_o^2$ where the assigned weights, $w = [\sigma(F)]^{-2}$, are derived from $\sigma(F^2) = [S^2 + (pF^2)^2]^{1/2}$, where S^2 is the variance due to counting statistics and $p = 0.04$. Scattering factors for neutral atoms were those of Doyle and Turner[17] corrected for anomalous dispersion.[18]

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Table I. Positional Parameters[a]

atom	*x*	*y*	*z*
Yb	0.68910 (3)	0.64148 (1)	0.30066 (3)
O	0.9038 (43)	0.6472 (2)	0.3172 (5)
C(1)	0.6798 (7)	0.7042 (3)	0.0842 (7)
C(2)	0.6761 (7)	0.7487 (3)	0.1800 (7)
C(3)	0.5646 (6)	0.7425 (3)	0.2186 (7)
C(4)	0.4987 (7)	0.6941 (3)	0.1460 (8)
C(5)	0.5690 (7)	0.6696 (3)	0.0648 (7)
C(6)	0.7800 (9)	0.6958 (4)	0.0100 (9)
C(7)	0.7678 (9)	0.7977 (4)	0.230 (1)
C(8)	0.5228 (9)	0.7833 (4)	0.3187 (9)
C(9)	0.3702 (8)	0.6773 (4)	0.145 (1)
C(10)	0.5317 (9)	0.6187 (4)	−0.0330 (9)
C(11)	0.5689 (7)	0.5485 (3)	0.3764 (7)
C(12)	0.5574 (6)	0.5975 (3)	0.4573 (8)
C(13)	0.6705 (8)	0.6105 (4)	0.5355 (7)
C(14)	0.7541 (7)	0.5678 (4)	0.5021 (7)
C(15)	0.6907 (7)	0.5303 (3)	0.4034 (8)
C(16)	0.4690 (9)	0.5162 (4)	0.287 (1)
C(17)	0.4413 (8)	0.6267 (4)	0.478 (1)
C(18)	0.696 (1)	0.6568 (5)	0.642 (1)
C(19)	0.8853 (8)	0.5611 (5)	0.5679 (9)
C(20)	0.748 (1)	0.4770 (4)	0.343 (1)
C(21)	0.9948 (8)	0.6869 (5)	0.392 (1)
C(22)	1.112 (1)	0.6661 (8)	0.369 (2)
C(23)	1.092 (1)	0.6210 (6)	0.262 (2)
C(24)	0.9642 (7)	0.6009 (4)	0.254 (1)
C(25)	0.0195 (9)	0.4595 (5)	0.077 (1)
C(26)	0.191 (1)	0.5126 (5)	0.020 (1)
C(27)	0.059 (2)	0.5002 (9)	0.005 (2)
C(28)	0.113 (2)	0.5520 (9)	−0.059 (2)
C(29)	0.151 (2)	0.473 (1)	0.090 (2)

[a] The estimated standard deviation of the least significant digit is given in parentheses in this and the following tables.

Discrepancy indices for 255 parameters varied with 3466 data having $F^2 > 3\sigma(F^2)$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.037$$

$$R_w = \sum[w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.049$$

R for all 4592 data is 0.053, and the estimated standard deviation in an observation of unit weight is 1.58. A difference Fourier calculation after the final cycle of least-squares refinement had a maximum electron density of 2.0 e/Å^3 located near the ytterbium atom.

Results and Discussion

Addition of 3 molar equiv of sodium pentamethylcyclopentadienide to europium trichloride in refluxing tetrahydrofuran yields the divalent species $(Me_5C_5)_2Eu(THF)(OEt_2)$ upon crystallization from diethyl ether. In contrast the mono(tetrahydrofuran) complex, $(Me_5C_5)_2Eu(THF)$, is obtained when toluene is used as a solvent for crystallization. These two compounds can be interconverted; e.g., crystallization of the mono(tetrahydrofuran) complex from diethyl ether yields $(Me_5C_5)_2Eu(THF)(Et_2O)$, whereas crystallization of the latter complex from toluene yields $(Me_5C_5)_2Eu(THF)$. Thus the diethyl ether ligand is rather labile, suggesting that it might be present in the solid state as solvent of crystallization. The sensitivity of these compounds to reaction or isolation conditions is further illustrated by our inability to isolate compounds from reaction of europium trichloride with $NaMe_5C_5$ in refluxing toluene or with $LiMe_5C_5$ in refluxing tetrahydrofuran. We have also been unable to isolate compounds from europium dichloride and $NaMe_5C_5$ in refluxing tetrahydrofuran.

The magnetic moment of $(Me_5C_5)_2Eu(THF)(OEt_2)$ (7.99 μ_B) follows Curie behavior from 5–50 K. This is consistent with the $^8S_{7/2}$ ground state expected for a europous (f^7) ion. The ability of sodium pentamethylcyclopentadienide to reduce europium(III) to europium(II) is not surprising as this reduction potential in aqueous acid solution is −0.6 V.[19a] Even lower values (−0.35 V) have been estimated.[19b]

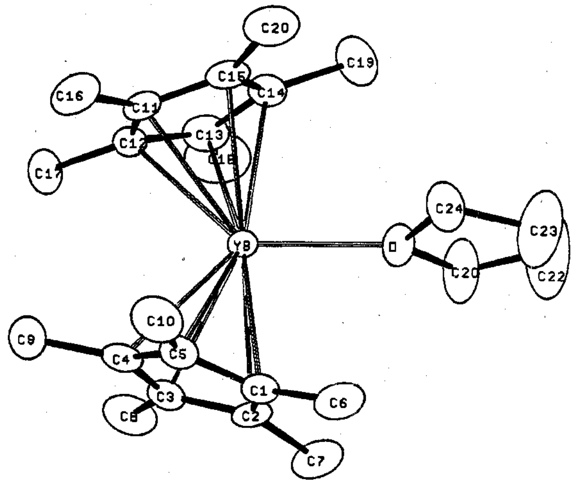

Figure 2. ORTEP diagram showing atom numbering.

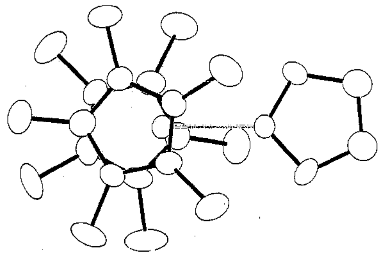

Figure 3. ORTEP diagram showing the staggered configurations of the Cp rings.

The divalent ytterbium derivative, $(Me_5C_5)_2Yb(THF)$, is most readily prepared from sodium pentamethylcyclopentadienide and ytterbium dichloride in refluxing tetrahydrofuran. Again, reaction and crystallization conditions are critical. If diethyl ether is used as crystallization solvent, green $(Me_5C_5)_2Yb(OEt_2)$ and red $(Me_5C_5)_2Yb(THF)$ are isolated by fractional crystallization. If toluene is used for crystallization $(Me_5C_5)_2Yb(THF)\cdot{}^1/_2PhMe$ is isolated. Further, ytterbium dichloride and $NaMe_5C_5$ (1:2 molar ratio) in refluxing diethyl ether or $LiMe_5C_5$ (1:2 molar ratio) in refluxing tetrahydrofuran do not yield any isolable compounds.

The divalent ytterbium(II) species (f^{14}) is rigorously diamagnetic (5–50 K) as expected for a $^1S_0$ ground-state ytterbous ion, and normal, diamagnetic ^1H and $^{13}C\{^1H\}$ nuclear magnetic resonance parameters are observed (see Experimental Section). However, the proton chemical shift of the methyl resonance of the Me_5C_5 group is temperature dependent, ranging from δ 1.98 at 80 °C to δ 2.18 at −50 °C. The tetrahydrofuran resonances are also temperature dependent; between +80 and −50 °C the α protons range from δ 4.02 to 3.30 and the β protons range from δ 1.81 to 1.32.

Atomic positions, distances and angles, and least-squares planes are given in Tables I–IV. The threefold coordination of the Yb(II) ion is planar (see plane 4 in Table IV) with the Yb–Cp(centroid) average distance of 2.37 Å and an angle between the centroids of the two Cp rings of 144°. In addition, the average Cp–Yb–O angle is 108°, giving approximate C_2 symmetry about the Yb–O axis as can be seen in Figure 2. The approximate C_2 symmetry is carried further in the THF molecule and in the staggered conformation of the C_5Me_5

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Table II. Selected Interatomic Distances (Å)

	Pentamethylcyclopentadienyl		
	Ring 1		
Yb-C(1)	2.670 (7)	Yb-C(4)	2.694 (8)
Yb-C(2)	2.654 (7)	Yb-C(5)	2.680 (8)
Yb-C(3)	2.663 (7)	av	2.672
	Ring 2		
Yb-C(11)	2.658 (7)	Yb-C(14)	2.664 (7)
Yb-C(12)	2.643 (7)	Yb-C(15)	2.654 (7)
Yb-C(13)	2.649 (8)	av	2.654
	C(ring)-C(ring)		
C(1)-C(2)	1.42 (1)	C(11)-C(12)	1.40 (1)
C(2)-C(3)	1.42 (1)	C(12)-C(13)	1.41 (1)
C(3)-C(4)	1.43 (1)	C(13)-C(14)	1.42 (1)
C(4)-C(5)	1.40 (1)	C(14)-C(15)	1.41 (1)
C(5)-C(1)	1.45 (1)	C(15)-C(1)	1.41 (1)
av	1.42	av	1.41
	C(ring)-CH_3		
C(1)-C(6)	1.53 (1)	C(11)-C(16)	1.50 (1)
C(2)-C(7)	1.51 (1)	C(12)-C(17)	1.52 (1)
C(3)-C(8)	1.54 (1)	C(13)-C(18)	1.50 (1)
C(4)-C(9)	1.50 (1)	C(14)-C(19)	1.52 (1)
C(5)-C(10)	1.52 (1)	C(15)-C(20)	1.54 (1)
av	1.52	av	1.52
	Tetrahydrofuran		
Yb-O	2.412 (5)	C(21)-C(22)	1.47 (2)
O-C(21)	1.45 (1)	C(22)-C(23)	1.49 (2)
O-C(24)	1.46 (1)	C(23)-C(24)	1.51 (2)
	Toluene		
C(25)-C(27)	1.32 (2)	C(26)-C(27)	1.51 (2)
C(25)-C(27)'	1.42 (2)	C(26)-C(28)	1.39 (2)
C(25)-C(28)'	1.50 (2)	C(26)-C(29)	1.29 (2)
C(25)-C(29)	1.51 (2)		

Table III. Selected Angles (Deg)

	Yb Coordination		
Cp(1)[a]-Yb-Cp(2)	143.5 (3)	Cp(3)-Yb-O	108.8 (3)
Cp(1)-Yb-O	107.7 (3)		
	Tetrahydrofuran		
C(21)-O-C(24)	108.4 (6)	C(22)-C(23)-C(24)	102.8 (9)
O-C(21)-C(22)	106.9 (8)	C(23)-C(24)-O	108.4 (7)
C(21)-C(22)-C(23)	109.5 (10)		
	Toluene		
C(25)-C(29)-C(26)	123 (2)	C(25)'-C(27)-C(25)	122 (2)
C(29)-C(26)-C(28)'[b]	121 (2)	C(27)-C(25)-C(29)	115 (2)
C(28)'-C(25)'-C(27)	119 (2)	av	120

Pentamethylcyclopentadienyl

ring 1		ring 2	
	Internal Angles		
C(5)-C(1)-C(2)	107.8 (6)	C(15)-C(11)-C(12)	107.4 (7)
C(1)-C(2)-C(3)	107.9 (7)	C(11)-C(12)-C(13)	109.3 (6)
C(2)-C(3)-C(4)	108.1 (7)	C(12)-C(13)-C(14)	107.2 (7)
C(3)-C(4)-C(5)	108.5 (7)	C(13)-C(14)-C(15)	107.5 (7)
C(4)-C(5)-C(1)	107.7 (7)	C(14)-C(15)-C(11)	108.6 (7)
av	108.0	av	108.0
	External Angles		
C(2)-C(1)-C(6)	126.4 (7)	C(12)-C(11)-C(16)	126.7 (8)
C(5)-C(1)-C(6)	125.8 (8)	C(15)-C(11)-C(16)	125.6 (8)
C(1)-C(2)-C(7)	128.1 (7)	C(11)-C(12)-C(17)	127.1 (8)
C(3)-C(2)-C(7)	123.9 (7)	C(13)-C(12)-C(17)	122.9 (8)
C(2)-C(3)-C(8)	124.7 (7)	C(12)-C(13)-C(18)	126.3 (8)
C(4)-C(3)-C(8)	127.2 (7)	C(14)-C(13)-C(18)	126.3 (8)
C(3)-C(4)-C(9)	125.8 (8)	C(13)-C(14)-C(19)	126.1 (8)
C(5)-C(4)-C(9)	125.3 (8)	C(15)-C(14)-C(19)	126.3 (8)
C(4)-C(5)-C(10)	126.0 (7)	C(14)-C(15)-C(20)	123.9 (8)
C(1)-C(5)-C(10)	126.1 (7)	C(11)-C(15)-C(20)	127.4 (8)
av	125.9	av	125.9

[a] Cp(1) and Cp(2) represent the centroids of the cyclopentadienyl moieties C(1)-C(5) and C(11)-C(15), respectively. [b] Primed carbon atoms are at positions $-x$, $-y$, $-z$.

Table IV. Perpendicular Distances (Å) from Least-Squares Planes

	Plane 1. Ring 1: C(1)-C(5)		
C(1)[a]	−0.006	C(6)	−0.079
C(2)[a]	+0.002	C(7)	−0.072
C(3)[a]	+0.004	C(8)	−0.028
C(4)[a]	−0.007	C(9)	−0.179
C(5)[a]	+0.008	C(10)	−0.049
		Yb	2.383
	Plane 2. Ring 2: C(11)-C(15)		
C(11)[a]	+0.002	C(16)	+0.137
C(12)[a]	+0.001	C(17)	+0.208
C(13)[a]	−0.003	C(18)	+0.088
C(14)[a]	+0.005	C(19)	+0.108
C(15)[a]	−0.004	C(20)	+0.043
		Yb	−2.367
	Plane 3. Toluene: C(25), C(25)', C(26), C(26)', C(27), C(28), C(29)'		
C(25)[a]	+0.022	C(27)[a]	−0.062
C(25)'[a,c]	+0.001	C(28)[a]	+0.054
C(26)[a]	−0.011	C(29)'[a]	−0.038
C(26)'[a]	+0.034		
	Plane 4. Cp(1)-Cp(2)-Yb-O		
Cp(1)[a,b]	0.008	Yb[a]	−0.020
Cp(2)[a]	0.008	O[a]	0.005

[a] Atoms or groups defining plane. [b] See footnote *a* in Table III. [c] See footnote *b* in Table III.

groups (see Figure 3). The Cp rings are planar and normal to the Yb–Cp axis in both cases as indicated by the lack of significant systematic variation in Yb–C(ring) distances. The methyl groups, however, are bent out of the plane of each Cp ring away from the Yb(II) ion with the largest deviation in each ring (0.18 Å for C(9) and 0.21 Å for C(17)) occurring for those methyl groups with the closest intramolecular contacts. Otherwise, the C_5Me_5 groups have normal geometry. The THF molecule is probably disordered since the root-mean-square amplitudes of displacement for C(22) and C(23) are much larger than for other carbon atoms and are highly anisotropic. Such disorder is normal for THF molecules.[20] Although the apparent bond angles in the disordered toluene molecules are reasonably close to the expected 120°, the apparent bond distances are less satisfactory because they are derived from averaged positions of several atoms that are not necessarily coincident. A better test of the model uses the positions of carbon atoms that are not overlapped by others, C(27), C(28)', and C(29)' in Figure 1, to calculate a C–C bond distance for the toluene ring. With distances of 2.47, 2.43, and 2.32 Å between these atoms, which would form an equilateral triangle if the toluene ring were exactly a hexagon, the calculated C–C bond distance in the ring is 1.39 Å, the expected value.

The average ytterbium–carbon bond lengths in the complex (2.66 Å) less the seven-coordinate ionic radius of the ytterbous ion (1.08 Å)[21] yields 1.58 Å for the effective ionic radius of a pentamethylcyclopentadienide group. This value is similar to those observed for other lanthanide and actinide cyclopentadienyl compounds (1.64 ± 0.04 Å) in which the metal–ring bonding is considered to be primarily ionic.[22–24] Further, the ytterbium–oxygen bond length (2.41 Å) less the ytterbous ionic radius yields 1.33 Å as the ionic radius of a three-coordinate oxygen atom. A value of 1.36 Å has been suggested.[21]

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We have been informed recently that a 1:2 complex, $(Me_5C_5)_2Yb(THF)_2$, has been isolated.[25]

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Registry No. $(Me_5C_5)_2Eu(THF)(OEt_2)$, 74282-44-3; $(Me_5C_5)_2Eu(THF)$, 74282-45-4; $(Me_5C_5)_2Yb(THF)$, 74282-46-5; $(Me_5C_5)_2Yb(OEt_2)$, 74282-47-6; $(Me_5C_5)_2Yb(THF)\cdot{}^1/_2PhMe$, 74282-48-7.

Supplementary Material Available: A listing of atomic thermal parameters and a listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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Bonding of η^2-Sulfur Dioxide: Structures of Tricarbonyl(1,10-phenanthroline)(η^2-sulfur dioxide)molybdenum(0) and Dicarbonyl(2,2′-bipyridyl)bis(η^2-sulfur dioxide)molybdenum(0)

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The structures of the title complexes have been determined by X-ray diffraction techniques. Tricarbonyl(1,10-phenanthroline)(η^2-sulfur dioxide)molybdenum(0) crystallizes in the space group $C2/m$ with cell constants of a = 19.206 (5) Å, b = 12.695 (2) Å, c = 8.025 (1) Å, and β = 129.00 (5)° and refines to an unweighted R value of 3.4% on the basis of 945 observations. Dicarbonyl(2,2′-bipyridyl)bis(η^2-sulfur dioxide)molybdenum(0) crystallizes in $P\bar{1}$ with cell parameters of a = 11.070 (5) Å, b = 7.096 (1) Å, c = 11.043 (6) Å, α = 111.97 (2)°, β = 98.25 (4)°, and γ = 100.02 (3)°. Full-matrix refinements based on 1190 observations resulted in an R value of 3.0%. Both structures contain η^2-type Mo–SO_2 linkages. The first of these complexes exhibits Mo–O and Mo–S distances of 2.223 (7) and 2.532 (3) Å with a dihedral angle between the SO_2 and c-MSO_M planes of 108.1°. The SO_2 is trans to a carbonyl. The corresponding distances in the *trans*-$(SO_2)_2$ complex are 2.113 (4) and 2.109 (4) Å for Mo–O and 2.496 (3) Å for both Mo–S distances with dihedral angles of 103.6 and 103.3°, respectively. The two bound S–O bonds are perpendicular to one another and are in the same plane with a cis carbonyl. The η^2-SO_2 bonding is discussed in relationship to these structures.

Introduction

The "side-on bonded" or η^2-type interaction of sulfur dioxide with transition-metal complexes has now been structurally verified for two different complexes, i.e., $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$[1] and $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$.[2] The first of these exhibits a bent nitrosyl in addition to the η^2-SO_2 and, if one considers the SO_2 to effectively occupy one coordination site, this represents an example of a four-coordinate (d^{10}) tetrahedral coordination complex. We note in passing that the isoelectronic complex $Co(NO)(SO_2)(PPh_3)_2$[3] exhibits a linear nitrosyl and a η^1-planar Co–SO_2 moiety, attesting to the role of the metal center basicity as a contributing factor. The Ru complex represents an example of a (d^8) trigonal-bipyramidal complex with the S–O_M bond (O_M = metal-bound oxygen) in the equatorial plane. At least two of the features these two complexes have in common are (1) the presence of a fairly basic metal center and (2) as far as the SO_2 is concerned, the close proximity of an ancillary ligand with good π-back-bonding capability. As to the latter point, the relative orientation of the nitrosyl and SO_2 ligands in the two complexes shows a striking similarity in that the S–O_M bond is oriented so as to point the sulfur atom toward the nitrosyl ligand. This behavior might be indicative of a ligand–ligand interaction and may suggest that the presence of a good π-accepting ancillary ligand contributes to the stability of the η^2-SO_2 coordination.

Table I. Crystal Data

	I	II
space group	$C2/m$	$P\bar{1}$
a, Å	19.206 (5)	11.070 (5)
b, Å	12.695 (2)	7.096 (1)
c, Å	8.025 (1)	11.043 (6)
α, deg	90.00	111.97 (2)
β, deg	129.00 (5)	98.25 (4)
γ, deg	90.00	100.02 (3)
cell refinement	12 high-order reflections	
Z	4	2
μ(Mo Kα), cm^{-1}	10.4	11.3
developed faces and distances from origin, mm	{20$\bar{1}$}, 0.02; {101}, 0.16; {110}, 0.10	{100}, 0.04; {010}, 0.13; {001}, 0.02
max-min transmission[10]	0.95–0.85	0.92–0.91
data collected	$2\theta \leqslant 40°$	$2\theta \leqslant 40°$
no. of unique reflctns	1061	1453
no. of obsd $I \geqslant 3\sigma(I)$	945	1190
unweighted R value	3.4%	3.0%
diffractometer	Picker FACS-1, P. G. Lenherts' Disk Operating System,[9] Wang encoders, graphite monochromator, 3.5° takeoff angle (1.5° + dispersion), continuous scans, 20-s symmetric background counts, Mo Kα radiation (λ 0.709 30 Å)	

The vibrational spectrum is diagnostic; the Ru and Rh complexes show absorptions at 895 and 948 cm^{-1}, respectively, due to the S–O_M stretching frequency. A survey of the literature revealed that similar frequencies had been observed for a series of sulfur dioxide complexes of molybdenum and tungsten reported by Hull and Stiddard[4] and the η^2 geometry

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