METAL-ORGANIC COMPOUNDS

Acta Cryst. (1996). C**52**, 1875–1877

Benzophenone Adduct of Tris(cyclopentadienyl)dysprosium

XIGENG ZHOU,[a]* HUAIZHU MA,[a] ZHONGZHI WU,[a] XIAOZENG YOU,[b] ZHENG XU,[b] YONG ZHANG[b] AND XIAOYING HUANG[c]

[a]*Institute of Organic Chemistry, Anhui Normal University, Anhui 241000, People's Republic of China,* [b]*Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China, and* [c]*The State Key Laboratory of Structure Chemistry, Fuzhou 350002, People's Republic of China*

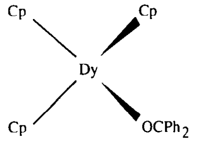
(*Received 4 July 1995; accepted 28 February 1996*)

Abstract

The title compound, (benzophenone-*O*)tris(η^5-cylopentadienyl)dysprosium, [Dy(C$_5$H$_5$)$_3$(C$_{13}$H$_{10}$O)], is a distorted tetrahedral coordination complex. The central dysprosium ion is η^5-bonded to three cyclopentadienyl (Cp) groups and η^1-bonded to one benzophenone molecule. The average Dy—O and Dy—C distances are 2.384 (3) and 2.733 (6) Å, respectively. The Dy—O—C angle is 170.6 (3)°.

Comment

There is currently a rapidly increasing interest in the use of organolanthanides in organic synthesis (Molander, 1992). In the course of our work on the organolanthanide-catalyzed ene reaction of carbonyl compounds, we isolated the title intermediate [Cp$_3$Dy(OCPh$_2$)], (I), in which the benzophenone molecule, acting as a Lewis acid, is attached to the metallocene in an η^1 fashion.



(I)

The overall structure of (I) (Fig. 1) is similar to that of [Cp$_3$Dy(thf)], (II) (Wu, Xu, You, Zhou, Huang & Chen, 1994). The Dy atom has a distorted tetrahedral coordination involving the three cyclopentadienyl groups and the O atom of the benzophenone molecule. The average Dy—C$_{\mathrm{Cp}}$ bond distance of 2.733 (6) Å is not significantly different from the value found in (II) [2.70 (1) Å], but is slightly longer than those observed in [Cp$_2$DyOC(Me)=CHCH$_3$]$_2$ [2.668 (6) Å; Wu, Xu, You, Zhou & Huang, 1994] and [Cp$_2$DyCl]$_2$ (2.63 Å; Lamberts & Lueken, 1987). The difference apparently results from the fact that the steric crowding around the metal centre in compound (I) is greater than that in both [Cp$_2$DyCl]$_2$ and [Cp$_2$DyOC(Me)=CHCH$_3$]$_2$, and this causes unfavourable Cp···*M* interactions. Consistent with this, the ring C atoms adjacent to the benzophenone ligand [C(11), C(15), C(22) and C(23)] are furthest from the Dy atom so that steric interaction is minimized. It is surprising that the Dy—O bond distance of 2.384 (3) Å in (I) is shorter than the Dy—O$_{\mathrm{thf}}$ distance of 2.462 (6) Å in (II), despite the fact that the benzophenone molecule has a larger steric bulk than the tetrahydrofuran molecule, which should cause the interligand repulsions to increase. This indicates that the coordination of the carbonyl O atom to the metal atom is stronger than that of the ether O atom.

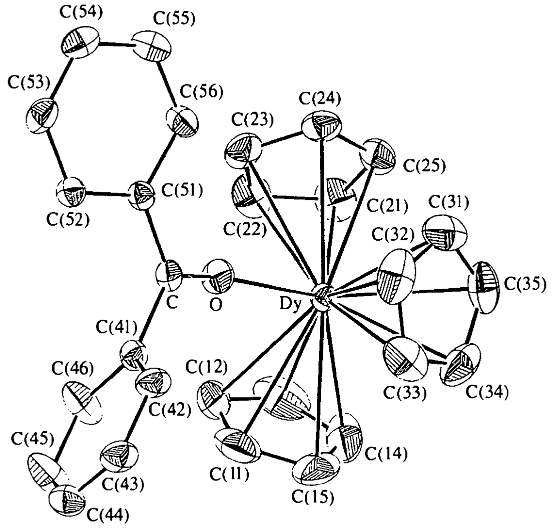


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Taking the difference of metal ionic radii into account (Shannon, 1976), the Dy—O bond length is closer to the values observed in other carbonyl donor adducts, *e.g.* [Cp$_3$Pr(CH$_3$COOCH$_2$CH$_2$CH$_2$CH$_3$)] [2.502 (6) Å; Schulz, Schultze, Reddmann, Link & Amberger, 1992], [Cp$_3$Ce(Me$_2$NCONMe$_2$)] [2.459 (7) Å; Domingos, Marques, Matos, Valenzuela & Zinner, 1993] and [Cp$_3$Nd(Me$_2$NCONMe$_2$)] [2.437 (1) Å; Domingos, Marques, Matos, Valenzuela & Zinner, 1993]. The Dy—O—C angle of 170.6 (3)°, however, is considerably larger than those observed in the above compounds (153–156°). The C—O bond distance of the coordinated benzophenone ligand is comparable to the corresponding value reported for free benzophenone [1.23 (1) Å; Fleischer, Sung & Hawkinson, 1968], but is clearly shorter than those reported for η^2-benzophenone–metal complexes [1.39 (6)–1.43 (1) Å; Hou, Yamazaki, Kobayashi, Fujiwara & Taniguchi, 1992; Erker, Dorf, Czisch & Petersen, 1986].

Experimental

The title compound was prepared under a purified argon atmosphere, with rigorous exclusion of oxygen and moisture, by reaction of Cp_3Dy and Ph_2CO (molar ratio 1:1) in CH_2Cl_2. Red crystals suitable for X-ray diffraction analysis were obtained by the cooling of a saturated solution of (I) in dichloromethane at 243 K.

Crystal data

[$Dy(C_5H_5)_3(C_{13}H_{10}O)$]
$M_r = 540.00$
Triclinic
$P\bar{1}$
$a = 8.387 (8)$ Å
$b = 12.111 (2)$ Å
$c = 12.619 (2)$ Å
$\alpha = 111.27 (2)°$
$\beta = 102.06 (3)°$
$\gamma = 99.81 (5)°$
$V = 1125 (1)$ Å^3
$Z = 2$
$D_x = 1.59$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.94–14.92°$
$\mu = 3.367$ mm^{-1}
$T = 296$ K
Prism
0.52 × 0.40 × 0.20 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (*TEXSAN*; Molecular Structure Corporation, 1987)
$T_{min} = 0.798$, $T_{max} = 1.000$
4229 measured reflections
3931 independent reflections

3921 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.01$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 300 reflections frequency: 60 min intensity decay: 1.1%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.039$
$S = 1.34$
3640 reflections
272 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.02$

$\Delta\rho_{max} = 1.28$ e Å^{-3}
$\Delta\rho_{min} = -1.53$ e Å^{-3}
Extinction correction: type 2, Gaussian isotropic (Zachariasen, 1967)
Extinction coefficient: 8.90×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Dy	0.36506 (2)	0.65574 (2)	0.84567 (2)	2.80 (1)
O	0.3014 (5)	0.7852 (3)	0.7478 (3)	4.2 (1)
C	0.2649 (5)	0.8370 (4)	0.6824 (4)	3.0 (1)
C(11)	0.6332 (9)	0.6791 (9)	0.7547 (8)	7.0 (3)
C(12)	0.6936 (8)	0.7549 (6)	0.8701 (8)	6.5 (3)
C(13)	0.7011 (8)	0.679 (1)	0.9302 (8)	8.1 (3)
C(14)	0.635 (1)	0.5615 (9)	0.850 (1)	8.6 (4)
C(15)	0.5999 (9)	0.5624 (8)	0.744 (1)	8.3 (3)
C(21)	0.4346 (8)	0.7354 (6)	1.0872 (5)	5.6 (2)
C(22)	0.4812 (9)	0.8442 (6)	1.0721 (5)	5.9 (2)
C(23)	0.3346 (8)	0.8661 (5)	1.0173 (5)	5.1 (2)
C(24)	0.1963 (8)	0.7718 (6)	0.9988 (5)	4.8 (2)
C(25)	0.2602 (8)	0.6919 (5)	1.0428 (5)	4.9 (2)
C(31)	0.0388 (8)	0.5115 (7)	0.7655 (7)	6.7 (2)
C(32)	0.0627 (8)	0.5356 (6)	0.6731 (7)	6.6 (2)
C(33)	0.173 (1)	0.4759 (8)	0.6322 (6)	7.2 (3)
C(34)	0.2180 (8)	0.4148 (6)	0.7015 (8)	6.8 (2)
C(35)	0.1374 (9)	0.4374 (6)	0.7831 (6)	6.1 (2)
C(41)	0.3447 (5)	0.8254 (4)	0.5852 (4)	3.1 (1)
C(42)	0.2482 (6)	0.7636 (4)	0.4675 (4)	3.9 (1)
C(43)	0.3238 (7)	0.7545 (5)	0.3782 (4)	4.4 (2)
C(44)	0.4905 (7)	0.8074 (5)	0.4063 (5)	4.8 (2)
C(45)	0.5881 (8)	0.8663 (7)	0.5221 (5)	6.6 (2)
C(46)	0.5163 (7)	0.8758 (6)	0.6121 (5)	5.6 (2)
C(51)	0.1492 (5)	0.9159 (4)	0.7016 (3)	2.9 (1)
C(52)	0.1445 (5)	1.0009 (4)	0.6511 (4)	3.3 (1)
C(53)	0.0490 (7)	1.0825 (5)	0.6810 (5)	4.3 (2)
C(54)	−0.0404 (7)	1.0824 (5)	0.7606 (5)	4.6 (2)
C(55)	−0.0389 (7)	0.9972 (5)	0.8086 (5)	4.7 (2)
C(56)	0.0543 (6)	0.9143 (5)	0.7806 (4)	3.9 (1)

Table 2. *Selected geometric parameters (Å, °)*

*Cnt*1, *Cnt*2 and *Cnt*3 are the centroids of rings C(11)–C(15), C(21)–C(25) and C(31)–C(35), respectively.

Dy—O	2.384 (3)	Dy—C(21)	2.737 (5)
Dy—C(11)	2.749 (6)	Dy—C(22)	2.770 (6)
Dy—C(12)	2.717 (6)	Dy—C(23)	2.774 (5)
Dy—C(13)	2.724 (6)	Dy—C(24)	2.750 (5)
Dy—C(14)	2.702 (7)	Dy—C(25)	2.721 (5)
Dy—C(15)	2.753 (7)	Dy—C(32)	2.726 (6)
Dy—C(31)	2.737 (6)	Dy—C(34)	2.707 (6)
Dy—C(33)	2.708 (6)	Dy—*Cnt*1	2.471 (2)
Dy—C(35)	2.720 (6)	Dy—*Cnt*3	2.465 (1)
Dy—*Cnt*2	2.482 (1)	C—C(51)	1.470 (6)
O—C	1.227 (5)	C—C(41)	1.491 (6)
C—O—Dy	170.6 (3)	O—C—C(51)	121.0 (4)
O—C—C(41)	120.0 (4)	C(51)—C—C(41)	118.8 (3)
C(42)—C(41)—C	120.4 (4)	C(46)—C(41)—C	120.2 (4)
C(52)—C(51)—C	120.8 (4)	C(56)—C(51)—C	119.6 (4)
*Cnt*1—Dy—*Cnt*2	117.1 (3)	*Cnt*1—Dy—*Cnt*3	118.1 (3)
*Cnt*2—Dy—*Cnt*3	117.7 (4)	O—Dy—*Cnt*1	101.7 (2)
O—Dy—*Cnt*2	98.8 (3)	O—Dy—*Cnt*3	96.3 (3)

The structure of (I) was solved by the heavy-atom method. The H atoms were placed in calculated positions, with C—H = 0.95 Å, but were not included in the refinement. All calculations were carried out on a MicroVAX 3100 computer using programs *MITHRIL* (Gilmore, 1983) and *TEXSAN* (Molecular Structure Corporation, 1987). *ORTEP*II (Johnson, 1976) was used to produce the figure. Data collection and cell refinement used *CAD*-4 *Software* (Enraf–Nonius, 1989).

This research is supported by a grant for a key research project from the State Science and Technology Commission of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Domingos, A., Marques, N., Matos, A. P., Valenzuela, M. G. S. & Zinner, L. B. (1993). *Polyhedron*, **12**, 2545–2549.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Erker, G., Dorf, U., Czisch, P. & Petersen, J. L. (1986). *Organometallics*, **5**, 668–676.

Fleischer, E. B., Sung, N. & Hawkinson, S. (1968). *J. Phys. Chem.* **72**, 4311–4317.

Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Department of Chemistry, University of Glasgow, Scotland.

Hou, Z., Yamazaki, H., Kobayashi, K., Fujiwara, Y. & Taniguchi, H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 722–724.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lamberts, W. & Lueken, H. (1987). *Inorg. Chim. Acta*, **132**, 119–122.

Molander, G. A. (1992). *Chem. Rev.* **92**, 29–68.

Molecular Structure Corporation (1987). *TEXSAN. TEXRAY Structure Analysis Package*, revised. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Schulz, H., Schultze, H., Reddmann, H., Link, M. & Amberger, H. D. (1992). *J. Organomet. Chem.* **424**, 139–152.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Wu, Z., Xu, Z., You, X., Zhou, X. & Huang, X. (1994). *J. Organomet. Chem.* **481**, 107–113.

Wu, Z., Xu, Z., You, X., Zhou, X., Huang, X. & Chen, J. (1994). *Polyhedron*, **13**, 379–384.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1996). C**52**, 1877–1879

Di-μ-chloro-bis{chloro[2-(*N*-propylaminomethyl)pyridine-*N*,*N*′]copper(II)}

Daphne Wahnon, Curtis Keith, Jik Chin and Rosemary C. Hynes

Chemistry Department, McGill University, 801 Sherbrooke Street West, Montreal, Canada H3A 2K6. E-mail: jik_chin@maclan.mcgill.ca

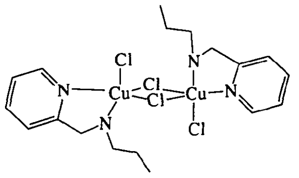
(*Received 6 November 1995; accepted 8 March 1996*)

Abstract

The structure of the title compound, $[Cu_2Cl_2(C_9H_{14}N_2)_2(\mu\text{-}Cl)_2]$, has been determined. The geometry about the Cu atom is square pyramidal. The complex exists as a dimer about an inversion centre with the Cu atoms linked by two asymmetric chlorine bridges. The dimeric structure of this complex differs from the polymeric dihalo-bridged chain of CuLX_2 complexes, where L is 2-(aminomethyl)pyridine.

Comment

The *cis*-diaquo complexes of copper(II) generated in aqueous solution from the corresponding dichloro complexes have been studied (Morrow & Trogler, 1988; Chin, Jubian & Mrejan, 1990; Wahnon, Hynes & Chin, 1994) for their potential as functional enzyme models of phosphodiesterases and peptidases. We have prepared $[Cu_2Cl_2(C_9H_{14}N_2)_2(\mu\text{-}Cl)_2]$, (I), as part of our interest in the reactivity and structure of such complexes.



(I)

The title complex exists as a dimer which is well separated from the other dimers in the cell. The dimer exists about an inversion centre. The bridging Cu_2Cl_2 unit is planar with a Cu···Cu′ distance of 3.4137 (13) Å. The chlorine bridges are unsymmetrical, with a Cu—Cl(1) distance of 2.2705 (14) Å and a Cu—Cl(1′) distance of 2.8336 (16) Å. The geometry about the Cu atom is distorted square pyramidal, with atoms N(1), N(2), Cl(1) and Cl(2) defining the basal plane, and Cl(1′) located in the apical position.

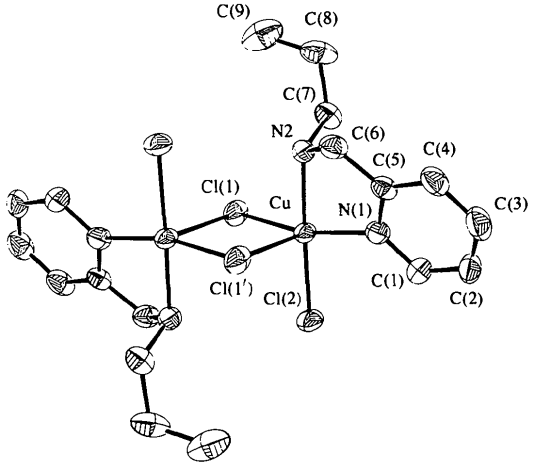


Fig. 1. *ORTEP*II plot (Johnson, 1976) of the title complex showing the atom-numbering scheme. Ellipsoids are shown at the 50% probability level.

The geometry about the Cu atom and the structural characteristics of (I) are similar to other CuLX_2 complexes, where L is a bidentate diammine ligand such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Estes,