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[(CO)H(PPh3)2-Arachno-OsB3H8]

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L. Barton

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[(CO)H(PPh₃)₂-arachno-OsB₃H₈]

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Abstract

A single-crystal X-ray diffraction study of the species 2-carbonyl-2-hydrido-trans-2,2-bis(triphenylphosphine)-2-osma-arachno-tetraborane confirms the structure as a tetraborane(10) butterfly with a trans-[(CO)H(PPh₃)₂Os] group replacing a BH₂ group at a wing-tip or 2-position. It is compared with the previously reported ruthenaborane analogue (CO)H(PPh₃)₂-arachno-RuB₃H₈ (Alcock et al., 1992) (Table 3), with some small differences.

Comment

During our investigations of the chemistry of metallaboranes, we have prepared the osmahexaborane (CO)(PPh₃)₂OsBsH₉, which is available in ca. 80% yield from the reaction of LiBsH₈ and OsHCl(CO)(PPh₃)₃ (Bould, Greenwood & Kennedy, 1983). We have found that the residues from the preparation show, from ¹¹B NMR, evidence of other metallaborane products and we have attempted to identify some of these. The products include the title compound, (I), an arachno-osmatetrahydroborane, and what appear to be a novel arachno-osmapentaborane cluster and a novel nido-osmadecaborane cluster. Compound (I) is formed in a very low yield (2%) and is more conveniently available in 65% yield from the reaction of TiB₃H₈ and OsHCl(CO)(PPh₃)₃ (Bould et al., 1983).

The M—B(1) and M—B(3) distances in the osmaborane are equal whereas the ruthenaborane shows a lengthening of the Ru—B vector trans to the metal hydride of 0.045 Å, which has been attributed by Alcock et al. (1992) to the trans effect of the hydride.
The slightly larger e.s.d.'s for the osmaborane could possibly obscure a similar but smaller trans effect in the osmaborane. The P(1)—M(2)—P(2) angle for the trans phosphine ligands is significantly closer to 180° in the osmaborane [172.21 (7)°] than in the ruthenaborane [161.8 (1)°] although, as with the latter compound, the deviations from the ideal octahedral angles are greater for the phosphine [P(2)] in the cis position with respect to the endo-terminal H atom H(4') (Fig. 2).

Experimental

The reaction between LiB₃H₆ and [OsHCl(CO)(PPh₃)₃] was carried out on a 0.5 mmol scale in tetrahydrofuran (thf) solution essentially according to the literature method (Bould et al., 1983) using the same conditions and similar procedures. Compound (I) was obtained as follows: the thf was removed under vacuum, the solid obtained redissolved in CH₂Cl₂/pentane solution (1:3), filtered through silica gel, the filtrate applied to a preparative thin-layer-chromatography plate and developed using diethyl ether/pentane (1:1) as the mobile phase giving two bands (under UV illumination) at Rᵣ = 0.8 (identified by NMR spectroscopy as Ph₃PBH₃) and Rᵣ = 0.5 [compound (I), 9 mg, 0.011 mmol, 2% yield]. Colourless crystals of (I) were obtained by slow diffusion of pentane into a dichloromethane solution of the compound at 273 K.

Crystal data

[Os(B₃H₆)(H)(CO)]

(C₁₈H₁₅P₂)₃

Mₒ = 784.25

Monoclinic

P₂₁/n

a = 17.116 (4) Å

b = 9.960 (3) Å

γ = 108.59 (2)°

V = 3460 (2) Å³

Z = 4

Dₐ = 1.505 Mg m⁻³

Data collection

Siemens R3/mw diffractometer

ω/2θ scans

Absorption correction: Siemens SHELXLA, Sheldrick, 1993

Tₘₐₓ = 0.319, Tₘᵣₐₜ = 0.756

6347 measured reflections

6129 independent reflections

4231 observed reflections  

[F > 4σ(F)]

Reefinement

Reefinement on F²

wR(F²) = 0.1129

S = 0.935

6129 reflections

x

y

z

U₁₁

Uₐₐ

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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Table 2. Selected geometric parameters (Å, °)

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Table 3. Atomic displacement parameters (Å², %)
trans-(S)-(S-Methyl-d-penicillaminato)(d-penicillaminesulfinate)cobalt(III) Monohydrate

TOSHIKAI YONEMURA, TAKAJI YASUI, KEN-ICHI OKAMOTO, AND JINSAI HIDAKA

Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780, Japan, and Department of Chemistry, University of Tsukuba, Ibaraki 305, Japan, and Department of Industrial Chemistry, Faculty of Engineering, Kinki University in Kyushu, Iizuka, Fukuoka 820, Japan

(Rceived 25 April 1995; accepted 17 November 1995)

Abstract

The title complex \([\text{Co}([\text{CsH9NO4S})(\text{CsH12NO2S})](\text{H}_2\text{O})]\), containing thioether and/or sulfinate groups because of the influence of these donor S atoms. Moreover, reports the investigation of Co\textsuperscript{III} complexes containing two different types of donor S atoms are scarce. In order to elucidate the geometry adopted by (I), we have determined its structure crystallographically.

Comment

In the course of our investigations on the stereochemical and spectrochemical properties of Co\textsuperscript{III} complexes with sulfur-containing ligands, we have recently prepared the title complex, (I). It is difficult to prepare stably the trans(S) isomer of a Co\textsuperscript{III} complex with two thiolate and/or sulfinate groups because of the trans influence of these donor S atoms. Moreover, reports on the investigation of Co\textsuperscript{III} complexes containing two different types of donor S atoms are scarce. In order to elucidate the geometry adopted by (I), we have determined its structure crystallographically.

Table 3. A comparison of selected distances (\AA) and angles (°) for \([\text{CO})\text{H}(\text{PPhs})_2\text{OsB}_2\text{H}_8\] and \([\text{CO})\text{H}(\text{PPhs})_2\text{RuB}_2\text{H}_8\]

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<tr>
<th>Bond</th>
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<th>Angle</th>
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<td>P(I)--M(2)--P(3)</td>
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<td>124.4</td>
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The structure was solved by the Patterson method. Full-matrix least-squares refinement was carried out by minimizing \(\sum w(F_o^2 - F_c^2)^2\). The non-H atoms were refined anisotropically to convergence. All H atoms connected to B atoms were located from the difference Fourier synthesis and were included in the final refinement. The positional parameters of the hydride H(2) were refined. The phenyl H atoms were calculated using a riding model (AFFIX43 in SHELXL93; Sheldrick, 1993b). All H atoms were assigned fixed isotropic displacement parameters of 0.08 Å². Attempts were made to resolve the disorder resulting in larger displacement ellipsoids for C(33)–C(36), but the disorder models could not be refined successfully.

Data reduction and structure solution were carried out using the SHELXTL-Plus (VMS) software package (Sheldrick, 1991). Least-squares refinement was achieved by using SHELXL93.