Inorg. Chem. **1998,** *37,* 5394−5395

Metalation of a Bis(thiophenyl)carborane Giving Both Exo and Endo Products. Synthesis and Structural Characterization of RuCl{7,8-$(SPh)_2$-7,8-*nido*-$C_2B_9H_{10}$}(*p*-cymene) and 1,2-$(SPh)_2$-3-(*p*-cymene)-3,1,2-$RuC_2B_9H_9$[†]

Francesc Teixidor, Clara Viñas,* and Miguel A. Flores

ICMAB−CSIC, Campus de la Universitat Autònoma de
Barcelona, 08193 Bellaterra, Barcelona, Spain

**Georgina M. Rosair, Alan J. Welch,* and
Andrew S. Weller**

Department of Chemistry, Heriot-Watt University,
Edinburgh EH14 4AS, U.K.

Received April 2, 1998

Recent years have witnessed research activity in the synthesis, molecular structures, and catalytic applications of exo-metalated functionalized carboranes[1] and in the preparation, structural study, and spectroscopic properties of *endo*-metallacarboranes which are deliberately overcrowded and either undergo structural deformation[2] or low-temperature polyhedral isomerization.[3] Previously, however, these two areas of interest have had little if any significant overlap.[4] We now report metalation of the $[7,8\text{-}(SPh)_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ carborane anion both without and with prior deprotonation, which on one hand affords a new exo-metal species and on the other hand leads to the first endo-metalated derivative of a bis(SR)-bearing carborane. This latter product displays an unusual cluster deformation believed to result, at least in part, from lone pair···lone pair repulsion between the sulfur substituents.

The bis(thiophenyl)carborane 1,2-$(SPh)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ has been known for many years,[5] but only recently[6] has it been decapitated to the anion $[7,8\text{-}(SPh)_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$, **1**, studied crystallographically as both $[NMe_4]^+$ [6] and $[HNEt_3]^+$ [7] salts.

Heating to reflux an ethanolic solution of $[NMe_4]$**1** and $[RuCl_2(p\text{-cymene})]_2$[8] (*p*-cymene = $C_6H_4Me,{}^iPr$-1,4) affords the orange product **2** in good yield.[9] Characterization by multinuclear NMR spectroscopy and by single-crystal X-ray diffraction[10] confirms the identity of **2** as RuCl{7,8-$(SPh)_2$-7,8-*nido*-$C_2B_9H_{10}$}(*p*-cymene).

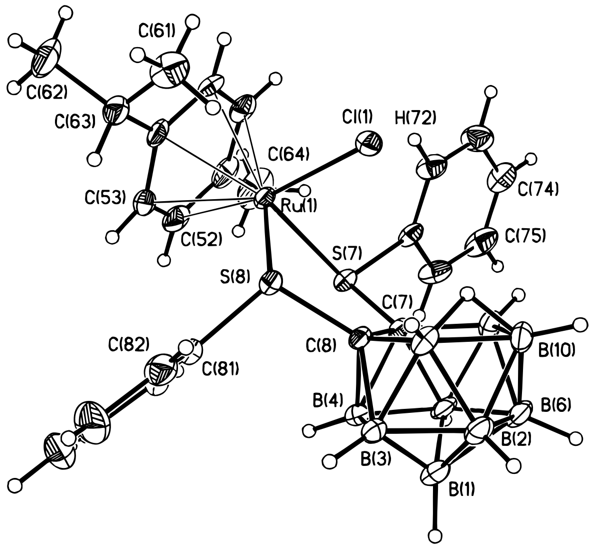

Figure 1. Perspective view of **2**. Selected interatomic distances (Å) and angles (deg): Ru(1)−S(7), 2.363(2); Ru(1)−S(8), 2.382(2); Ru(1)−Cl(1), 2.416(2); C(7)−S(7), 1.821(6); C(8)−S(8), 1.808(6); C(7)−C(8), 1.570(8); S(7)−C(71), 1.790(6); S(8)−C(81), 1.791(6); S(7)−Ru(1)−Cl(1), 91.12(6); S(8)−Ru(1)−Cl(1), 76.96(5); S(7)−Ru(1)−S(8), 85.32(5).

A perspective view of a single molecule is given in Figure 1. The Ru atom is pseudo-octahedrally coordinated to a η^6-*p*-cymene ligand, terminal Cl ligand, and both SPh substituents to the nido carborane. The S-bound Ph rings are oriented in a mutually anti fashion, rendering the overall molecule asymmetric, and at −40 °C in CD_2Cl_2 spectroscopic data are fully in accord with the solid-state structure. Of note in the ^{1}H

[†] Steric effects in Heteroboranes. Part 21. For Part 20 see ref 4.

* Corresponding authors. C.V.: tel., +34 3 580 1853; fax, +34 3 580 5729; e-mail, clara@icmvax.icmab.er. A.J.W.: tel., +44 131 451 3217; fax, +44 131 451 3180; e-mail, a.j.welch@hw.ac.uk.

(1) For recent references, see: Teixidor, F.; Flores, M. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2251. Teixidor, F.; Viñas, C.; Benakki, R.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 1719. Demonceau, A.; Simal, F.; Noels, A. F.; Viñas, C.; Nunez, R.; Teixidor, F. *Tetrahedron Lett.* **1997**, *38*, 4079, 7879. Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Villacampa, M. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 993. Crespo, O.; Gimeno, M. C.; Jones, P. G.; Ahrens, B.; Laguna, A. *Inorg. Chem.* **1997**, *36*, 495.

(2) Brain, P. T.; Bühl, M.; Cowie, J.; Lewis, Z. G.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1996**, 231. Grädler, U.; Weller, A. S.; Welch, A. J.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1996**, 335. Weller, A. S.; Welch; A. J. *Inorg. Chem.* **1996**, *35*, 4538.

(3) Dunn, S.; Rosair, G. M.; Thomas, Rh. Ll.; Weller, A. S.; Welch, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 645.

(4) McWhannell, M. A.; Rosair, G. M.; Welch, A. J.; Teixidor, F.; Viñas, C. *J. Organomet. Chem.*, in press.

(5) Smith, H. D.; Obenland, S.; Papetti, S. *Inorg. Chem.* **1966**, *5*, 1013.

(6) Flores, M. A.; Doctoral Dissertation, Universitat Autonoma de Barcelona, March 1997.

(7) Rosair, G. M.; Weller, A. S.; Welch, A. J. Unpublished results.

(8) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

(9) Synthesis and spectroscopic characterisation of **2**: A suspension of $[NMe_4][7,8\text{-}(SPh)_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]$ (0.100 g, 0.24 mmol) and $[RuCl_2(p\text{-cym})]_2$ (0.072 g, 0.12 mmol) in deoxygenated ethanol (15 mL) was heated to reflux for 3 h. The resulting orange precipitate was isolated by filtration whilst hot, washed with hot ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL). Yield 0.120 g (82%). Anal. Calcd for $C_{24}H_{34}B_9ClRuS_2$: C, 46.46; H, 5.52; S, 10.34. Found: C, 46.12, H, 5.34; S, 10.07. IR (KBr) 2527 cm^{-1} (B−H). NMR: ^{1}H (300.2 MHz, CD_2Cl_2, 25 °C, TMS) δ 7.61−7.54 (br m, 10H, SPh), 5.69, 5.12 (br, 4H, $MeC_6\mathit{H}_4CHMe_2$), 2.73 (qq, app sept, 1H, $^3J_{HH}$ = 7, 7 Hz, $MeC_6H_4C\mathit{H}Me_2$), 1.94 (s, 3H, $\mathit{Me}C_6H_4CHMe_2$), 1.25 (br, 6H, MeC_6H_4-$CH\mathit{Me}_2$), −2.01 (br, 1H, B-*H*-B) ppm; ^{1}H (400.1 MHz, −39 °C) δ 8.66 (m, 1 H, SPh), 7.62−7.40 (m, 9H, SPh), 5.82 (d, 1H, $^3J_{HH}$ = 7 Hz, $MeC_6\mathit{H}_4CHMe_2$,), 5.19 (d, 1H, $^3J_{HH}$ = 7 Hz, $MeC_6\mathit{H}_4CHMe_2$) 5.07 [d, 1H, $^3J_{HH}$ = 7 Hz, $MeC_6\mathit{H}_4CHMe_2$), 4.80 (d, 1H, $^3J_{HH}$ = 7 Hz, $MeC_6\mathit{H}_4CHMe_2$), 2.77 [qq, app sept, 1H, $^3J_{HH}$ = 9, 9 Hz, $MeC_6H_4C\mathit{H}Me_2$)], 1.81 (s, 3H, $\mathit{Me}C_6H_4CHMe_2$), 1.29 (d, 3H, $^3J_{HH}$ = 9 Hz, $MeC_6H_4CH\mathit{Me}_2$), 1.27 (d, 3H, $^3J_{HH}$ = 9 Hz, $MeC_6H_4CH\mathit{Me}_2$) ppm; $^{11}B\{^1H\}$ [96.3 MHz, $(CD_3)_2CO$, 25 °C, $Et_2O{\cdot}BF_3$] δ −3.8 (1B), −5.9 (1B), −9.0 (1B), −14.5 (1B), −19.2 (1B), −23.5 (2B), −29.9 (1B), −31.7 (1B) ppm.

(10) Crystallographic characterization of **2**: Siemens *P*4 diffractometer, 293(2) K. Mo Kα radiation, $\lambda = 0.710\,73$ Å, $2\theta_{max} = 50°$. Corrections for Lorentz and polarization effects, structure solution by direct methods and refined (against F^2) by full-matrix least-squares methods. Crystal data: $C_{24}H_{34}B_9ClRuS_2$, $M_r = 620.44$, crystal size 0.6 × 0.4 × 0.2 mm, triclinic, $P\bar{1}$, $a = 10.8789(13)$ Å, $b = 11.1088(13)$ Å, $c = 14.161(2)$ Å, $\alpha = 76.983(10)°$, $\beta = 98.930(10)°$, $\gamma = 62.303(9)°$, $V = 1473.3(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.398$ g cm^{-3}, $F(000) = 632$, $\mu = 0.778$ mm^{-1}. Of 5110 unique reflections, 3760 were observed [$F_o > 4\sigma(F_o)$], 374 parameters, $R_1 = 0.0546$, w$R_2 = 0.1249$ (for observed data), $S = 1.081$, max and min residual electron density, 0.960 and −1.212 e Å^{-3}.

S0020-1669(98)00370-X CCC: $15.00

spectrum at this temperature is a high frequency integral-1 resonance, 8.66 ppm, assigned to H(72) which is internally H-bonded to Cl(1), 2.575(7) Å.

Progressive warming of the sample causes first (−20 °C) the phenyl signals then (0 °C) the *p*-cymene signals to broaden. At +15 °C the high-frequency resonance disappears into the baseline, reemerging at +30 °C as a broad, integral-2, signal to high frequency of sharper aromatic resonances, indicative of essentially free rotation about the S-Ph bonds. Although the $CHMe_2$ and CH_3 signals of *p*-cymene are relatively sharp at +30 °C, the signals arising from the aromatic C*H* protons of this ligand are still broad up to +40 °C, suggesting only restricted rotation about the ring-Ru axis, probably a consequence of the anti disposition of the S-bound Ph groups. That the molecule as a whole remains asymmetric up to +40 °C is evidenced by the observation of 8 resonances (1 co-incidence) in the $^{11}B\{^1H\}$ NMR spectrum.

In contrast, prior deprotonation of [HNMe$_3$]**1** in thf, by heating to reflux with NaH, followed by reaction with [RuCl$_2$(*p*-cymene)]$_2$ results in the formation of 1,2-(SPh)$_2$-3-(*p*-cymene)-3,1,2-RuC$_2$B$_9$H$_9$, **3**, isolated as a yellow solid after column chromatography.[11] Again, characterization was achieved by NMR spectroscopic and X-ray crystallographic[12] techniques. Figure 2 shows a perspective view of a single molecule.

In **3** the Ru atom occupies a cluster vertex, and, indeed, to our knowledge **3** is the first example of an endo transition-metal complex of a carborane containing two SR substituents. The metallacarborane has an approximately icosahedral geometry (although there is a major distortion, vide infra) and in solution at room-temperature both the ^{1}H and ^{11}B NMR spectra are consistent with C_s molecular symmetry, implying either unhindered rotation or substantial libration of the *p*-cymene ligand about the ring-Ru axis.

The presence of the *endo*-{Ru(*p*-cymene)} fragment causes the two SPh cluster substituents in **3** to be oriented syn with respect to each other. Distances within the metallacarborane are as anticipated, except for a long C(1)−C(2) distance, 2.107(5) Å, and correspondingly short Ru(3)···B(6) distance, 3.198(3) Å. The former is close to that [2.184(7) Å] in 1-(CCPh)-2-Ph-3-(*p*-cymene)-3,1,2-RuC$_2$B$_9$H$_9$, **4**,[13] a "semipseudocloso" species in which steric congestion between the Ph and CCPh units partially opens the C(1)−C(2) connectivity. In solution the cage deformation in **4** is characterized by an average ^{11}B chemical shift ($<\delta^{11}B>$) at +2.4 ppm, to high frequency of that anticipated (ca. −10 ppm) for a nondistorted closo species, although not as high as that previously noted for fully distorted "pseudocloso" metallacarboranes, ca. +5 ppm, with C(1)···C(2) and M(3)···B(6) distances of ca. 2.5 and 2.9 Å, respectively.[2] In **3** $<\delta^{11}B>$ is −2.2 ppm.

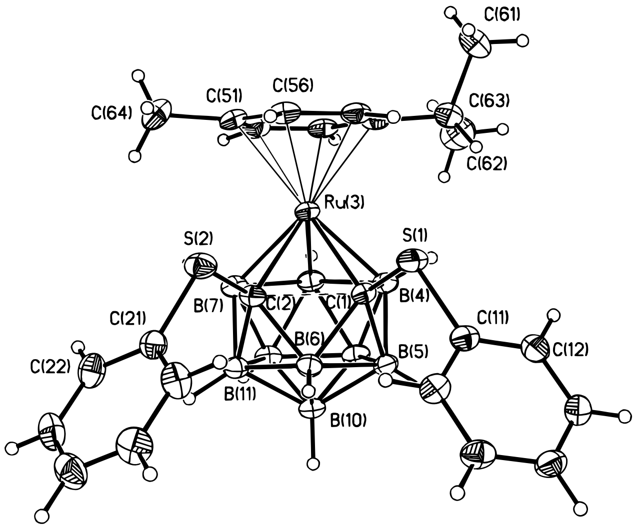

Figure 2. Perspective view of **3**. Selected interatomic distances (Å) and angles (deg): C(1)−C(2), 2.107(5); Ru(3)···B(6), 3.198(3); C(1)−S(1), 1.774(3); C(2)−S(2), 1.770(3); S(1)−C(11), 1.793(3); S(2)−C(21), 1.780(3).

We believe that a contribution to the structural deformation in **3** is S(lone pair)···S(lone pair) repulsion[14] [S···S distance 3.860(1) Å, *cf.* twice the van der Waals radius for S of ca. 3.6 Å], itself a consequence of the orientation of the SPh substituents being fixed by the capping {Ru(*p*-cymene)} unit. At the same time it is possible that an additional contributory factor to the deformation is the electron-withdrawing property of the {SPh} groups.[15] Sterically[2] and nonsterically induced[16] deformations of metallacarboranes are the subject of continuing interest.

Acknowledgment. This work was supported by a fellowship from the EPSRC (A.S.W.) and by the NATO Collaborative Research Grant CRG 971636 (F.T., C.V., and A.J.W.). We thank the Callery Chemical Company for continued gernerous support.

Supporting Information Available: Full data collection and refinement details, atomic coordinates, displacement parameters and interatomic distances and angles have been deposited as a CIF file and are available on the Internet only. Access information is given on any current masthead page.

IC980370C

---

(11) Synthesis and spectroscopic characterisation of **3**: A solution of [HNMe$_3$][7,8-(SPh)$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$] (0.150 g, 0.37 mmol) in thf (20 mL) was heated to reflux with a 3-fold excess of NaH for 15 h, and, after the unreacted NaH had settled, the resulting solution was transferred by cannula to a cooled (−78 °C) solution of [RuCl$_2$(*p*-cym)]$_2$ (0.112 g, 0.18 mmol) in thf (15 mL). The solution was allowed to warm to room temperature and stirred under N$_2$ for 3 h. Concentration and column chromatography (silica; 60−80 petroleum ether/CH$_2$Cl$_2$, 1/1) afforded the bright yellow product as the only mobile band. Yield 0.080 g (76%). Anal. Calcd for $C_{24}H_{33}B_9RuS_2$: C, 49.36; H, 5.70. Found: C, 49.28, H, 5.75. IR (CH$_2$Cl$_2$) 2555 cm^{-1} (B−H). NMR: ^{1}H (400.1 MHz, CDCl$_3$, 18 °C, TMS) δ 7.58 (m, 4H, SPh), 7.37 (m, 6H, SPh), 6.30 [d, 2H, (AB)$_2$, $^3J_{HH}$ = 7 Hz, MeC$_6$*H*$_4$CHMe$_2$], 6.21 [d, 2H, (AB)$_2$, $^3J_{HH}$ = 7 Hz, MeC$_6$*H*$_4$CHMe$_2$], 3.25 (heptet, 1H, $^3J_{HH}$ = 6 Hz, MeC$_6$H$_4$C*H*Me$_2$), 2.56 (s, 3H, *Me*C$_6$H$_4$CHMe$_2$), 1.49 (d, 6H, $^3J_{HH}$ = 6 Hz, MeC$_6$H$_4$CH*Me*$_2$) ppm; $^{11}B\{^1H\}$ (128.4 MHz, CDCl$_3$, 18 °C, Et$_2$O·BF$_3$) d 12.3 (1B), 6.5 (1B), 1.3 (2B), −4.9 (2B), −6.5 (2B), −18.6 (1B) ppm.

(12) Crystallographic characterization of **3**: Experimental details as for **2**. Crystal data: $C_{24}H_{33}B_9RuS_2$, M_r = 583.98, crystal size 0.6 × 0.3 × 0.2 mm, monoclinic, $P2_1/c$. a = 11.0660(6) Å, b = 14.5054(8) Å, c = 17.806(2) Å, β = 99.765(6)°, V = 2785.5(3) Å^3, Z = 4, ρ_{calc} = 1.393 g cm^{-3}. $F(000)$ = 1192, μ = 0.727 mm^{-1}. Of 4910 unique reflections, 3888 were observed [$F_o > 4\sigma(F_o)$], 325 parameters, R_1 = 0.0317, wR_2 = 0.0689 (for observed data), S = 1.054, max and min residual electron density, 0.255 and −0.385 e Å^{-3}.

(13) Thomas, Rh. Ll.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, 631.

(14) Teixidor, F.; Romerosa, A. M.; Ruis, J.; Miravitlles, C.; Casabó, J. *Inorg. Chem.* **1990**, *29*, 149.

(15) Viñas, C.; Pedrajas, J.; Bertran, J.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 2482.

(16) Kim, J. H.; Lamrani, M.; Hwang, J. W.; Do, Y. *Chem. Commun.* **1997**, 1761.