Inorganic Chemistry
Communication
pubs.acs.org/IC

Novel Triple-Decker Sandwich Complex with a Six-Membered $[B_3Co_2(\mu_4\text{-}Te)]$ Ring as the Middle Deck

Arunabha Thakur, Kiran Kumar Varma Chakrahari, Bijan Mondal, and Sundargopal Ghosh*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

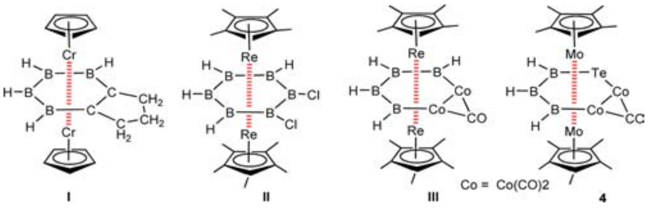
Supporting Information

ABSTRACT: Thermolysis of *nido*-$[(Cp^*Mo)_2B_4TeClH_5]$, with an excess of $Co_2(CO)_8$ at room temperature, afforded a triple-decker sandwich complex $[(Cp^*Mo)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_3H_3TeCo_2(CO)_5\}]$ (**4**), which represents an unsaturated 24-valence-electron sandwich cluster in which the middle deck is composed of B, Co, and a heavy group 16 element.

Since the discovery of ferrocene $[(C_5H_5)_2Fe]$,[1] the chemistry of metal sandwich systems has enjoyed immence research interest in modern organometallic chemistry and continues to attract attention as a result of their structural diversity, unusual properties, and application as special materials.[2] This prototype along with arenes,[3] boranes,[4] carboranes,[5] porphyrins, and polycyclic aromatics[6] has generated numerous organo-transition-metal sandwich complexes. The possibility of extending such sandwich structures to larger molecules, i.e., triple-decker sandwich structures, was first suggested in 1964 by the observation of $Cp_3Ni_2^+$ in the mass spectrum of nickelocene,[7] and subsequently the first triple-decker complex $[Cp_3Ni_2]^+[BF_4]^-$ was isolated in 1972 by Werner and Salzer.[8,9] As a result, the chemistry of triple-decker/multidecker sandwich complexes containing *cyclo*-(η^n-E_n) as the center ring (E = B, P, As, Sb, etc.; n = 5 or 6) has become a well-established field, and the literature in this regard is very extensive.[10−12] Triple-decker sandwiches in which the heteroarene rings are simultaneously and equivalently bonded to two transition-metal atoms lying opposite to each other are particularly rare.[13] Several theoretical studies appeared that discovered some insight into the bonding and electronic structure of this type of molecule.[14] However, because of the lack of convenient synthesis, experimental work in this area has advanced rather slowly.

Recently, we have demonstrated that compounds of the type $[(Cp^*Mo)_2B_4E_2]$ (E = S, Se, or Te; $Cp^* = \eta^5\text{-}C_5Me_5$) are useful metal synthons for the synthesis of cubane-type clusters.[15] Further, a combined theoretical (SI, Figure S1) and experimental[16] study shows that the reactivity of $[(Cp^*Mo)_2B_5H_9]$ with metal carbonyl increases manyfold if one of the boron vertices is replaced by chalcogen atoms. We wonder whether this is due to the availability of the lone pair on the chalcogen, which can coordinate to the metal carbonyl. Thus, we have explored the reactivity of *nido*-$[(Cp^*Mo)_2B_4ECl_mH_{6-m}]$ (**1**: E = S, m = 0; **2**: E = Se, m = 0; **3**: E = Te, m = 1) with various metal carbonyls. In doing so, the reaction of **3** with $Co_2(CO)_8$ at room temperature yielded two boride clusters,[16a] $[(Cp^*MoCO)_2B_3H_2(\mu_3\text{-}Te)(\mu\text{-}CO)\{Co_3(CO)_6\}]$ and $[(Cp^*MoCO)_2B_3H_2(\mu_3\text{-}Te)(\mu\text{-}CO)_4\{Co_6(CO)_8\}]$ as major products along with a byproduct, $[(Cp^*Mo)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_3H_3TeCo_2(CO)_5\}]$ (**4**), which is a novel member of the family of known triple-decker complexes. Consistent with past observations by Fehlner, the ring geometry of this novel triple-decker complex is an isolobal analogue of $[(CpCr)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_4H_4C_2R_2\}]$ (**I**),[17], $[(Cp^*Re)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}1,2\text{-}B_6H_4Cl_2\}]$ (**II**),[4] and $[(Cp^*Re)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_4H_4Co_2(CO)_5\}]$ (**III**)[18] (Chart 1). The tellurium complex **4** is highly significant because it extends the generality of the oblatocloso designation of the $(Cp^*Re)_2(B_nH_n)$ species.

Chart 1. Isoelectronic Triple-Decker Sandwiches I−III and 4



The molecular structure of **4**, shown in Figure 1, contains a nearly planar hexahapto six-membered ring, seen to be $[(Cp^*Mo)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_3H_3TeCo_2(CO)_5\}]$. To the best of our knowledge, this is the first tiple-decker complex in which the middle deck is composed of B, Co, and a heavy group 16 atom. The molecule possesses a planar (sum of the internal angles 718.46°) six-membered B_3TeCo_2 ring sandwiched between two Cp*Mo fragments. However, the accommodation of the five CO ligands of the Co_2 fragment between the Cp* ligands causes the Cp* ligands to incline and produces a conrotatory twist of the two $Co(CO)_2(\mu\text{-}CO)$ fragments around their pseudo-C_3 axes such that the bridging CO lies out of the plane of the $[B_3TeCo_2]$ ring. Although the methyl groups of the Cp* ligands are in the nearly eclipsed orientations, the Cp* rings are nearly coplanar (dihedral angle 1.2°). The Mo−Mo bond length of 2.7520(6) Å is shorter than the sum of the van der waals radii of two Mo atoms, however comparable with other molybdaborane clusters.[19] Although the Mo−B and B−B distances are in the range found for the other molybdaboranes characterized,[19] the Co−Te bond of 2.4471(8) Å is significantly shorter than the corresponding single bond [2.575(5)−2.614(5) Å].[20] Thus, the planarity of the ring and its edge lengths are consistent with

Received: October 12, 2012
Published: February 14, 2013

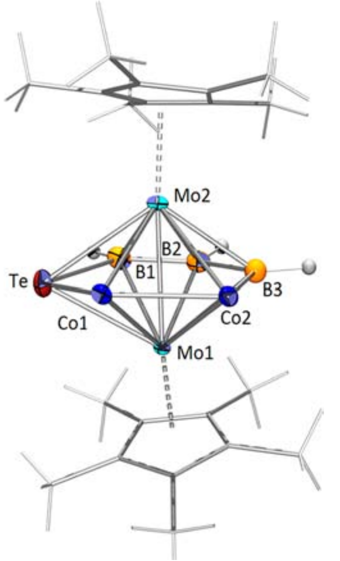


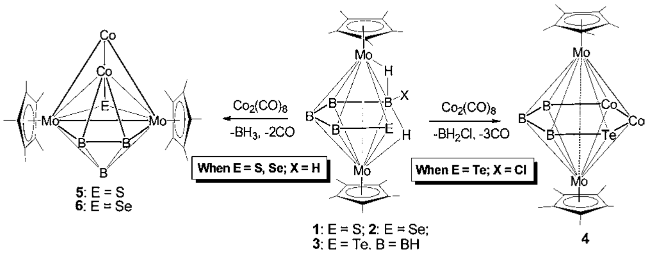
Figure 1. Molecular structure of **4**. The CO groups in $Co_2(CO)_5$ are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1−Mo2 2.7520(6), Mo1−Co2 2.6551(8), Mo1−Te 2.7255(6), Mo2−Te 2.309(10), Mo2−Co1 2.7100(9), Co1−Co2 2.4741(10), Mo2−B2 2.243(7), Co1−Te 2.4471(8), B2−B3 1.727(18); Co1−Co2−Te 114.87(4).

considering **4** as an analogue of a coordinated benzene just like isolobal **I**−**III**, shown in Chart 1.

Alternatively, the geometry of **4** can be viewed as a hexagonal bipyramid, which is rare in metallaborane chemistry and is not one of the polyhedra generally associated with eight-vertex closo clusters.[21,22] Cluster **4** does not have sufficient valence electrons (ve) to meet the requirements for a nine skeleton electron pairs (sep), eight-vertex closo structure. Thus, cluster **4** is better described as a 24-ve triple-decker complex, $[(\eta^5\text{-}C_5Me_5Mo)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_3H_3TeCo_2(\mu\text{-}CO)(CO)_4\}]$, containing a metal−metal bond and a planar 6π-electron $[B_3H_3TeCo_2(CO)_5]^{6-}$ central ring. The $[B_3Co_2Te]$ ring in **4** is not puckered, as observed in 24-ve $\{Cp^*V\}_2\{\mu\text{-}\eta^3{:}\eta^3\text{-}P_6\}$ and $CpTi\text{-}(\mu\text{-}\eta^3{:}\eta^3\text{-}P_6)TiCp$.[23,24] This may be attributed to the better compatibility of B and Mo orbital energies, which favors a nearly planar central ring. Indeed, there is a good match between the energies of the Cp*Mo fragment orbitals and the out-of-plane orbitals of the central ring, which yields a substantial HOMO−LUMO gap without the necessity of ring distortion[17,24] (SI, Figure S1 and Table S1).

During attempts to produce the S and Se analogues of **4**, unusually a new type of compound was isolated (Scheme 1). The analysis and spectroscopic data yielded the composition $[(Cp^*Mo)_2B_3H_3ECo_2(CO)_6]$ (**5**, E = S; **6**, E = Se), which suggests a parallel formulation as **4** except one extra CO ligand. On the other hand, ^{11}B NMR shows three dissimilar boron environments different from that of **4**. In addition, there is no sign of a B−H−Mo bridging H atom. Although related to **4** in terms of composition, both compounds **5** and **6** were defined by a structure determination.[25]

Scheme 1. Synthesis of 4−6 (Carbonyls Are Not Shown for Clarity)



The molecular structures of **5** and **6**, shown in Figure 2, contain qualitatively a similar $[Co_2B_3E]$ (E = S and Se) fragment when the Te atom of **4** is replaced by S and Se. Their overall structure is fascinating, and the core geometry can be viewed as a Mo2CoB3 octahedron. The other cobalt atom (Co2) caps the Mo2Co face of this central Mo2CoB3 octahedron, consistent with the tendency of transition metals to prefer higher degree vertices. The resulting seven-vertex capped octahedron also has an Mo2Co face involving the Co atom that was used for the first capping process. Capping this face with the single chalcogen atom (E) gives the experimentally observed eight-vertex deltahedron. On the basis of the capping principle,[26] the skeletal electron count is determined by the central polyhedron (i.e., Mo2CoB3 octahedron) and amounts to seven sep, required for the octahedron geometry. Thus, **5** and **6** obey Wade−Mingos electron-counting rules[27] for the observed geometry. This geometry may be derived from the closo metal-free borane deltahedra by a diamond−square−diamond process (SI, Chart S1). Alternatively, compounds **5** and **6** can be viewed as an oblatonido cluster derived from $[(Cp^*Re)_2B_7H_7]$ with one missing vertex.[28]

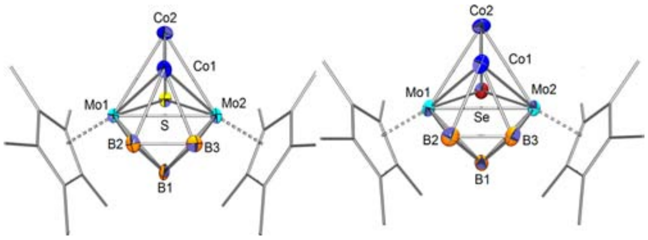


Figure 2. Molecular structures of **5** and **6**. Selected bond lengths (Å) for **5**: Mo1−Mo2 3.0087(4), Mo1−Co1 2.6313(5), Co1−Co2 2.4889(6), Mo1−B1 2.289(4), Mo1−S1 2.3361(9), B1−B2 1.692(6). Selected bond lengths (Å) for **6**: Mo1−Mo2 3.0466(5), Co1−Co2 2.4827(9), Mo1−B1 2.290(5), Co1−B2 2.131(7), B1−B2 1.698(8).

The solution spectroscopic data of all the compounds are fully consistent with the solid-state structure. The IR spectra feature strong bands in the range of 2490−2471 cm^{-1} due to terminal B−H stretches and bands in the region of 2028−1816 cm^{-1} due to the presence of terminal and bridging CO groups. Consistent with the X-ray results, the $^{11}B\{^1H\}$ NMR spectrum of **4** rationalizes the presence of three B atoms at δ 84.4, 53.6, and 25.9 in the ratio of 1:1:1. Similarly, the $^{11}B\{^1H\}$ NMR spectra of **5** and **6** confirm the presence of three B atoms in the ratio of 1:2, at δ 75.7 and 71.7 for **5** and δ 77.4 and 73.4 for **6**. The density functional theory (DFT) calculations using the gauge-independent atomic orbital DFT [GIAO−DFT] method at the B3LYP/SDD/6-31g*[29] level reproduced the ^1H and ^{11}B NMR and IR data satisfactorily (SI, Table S2).

The quantum-chemical calculations with DFT have been used to probe the bonding and electronic structures of compounds **1**−**6**. The DFT studies establish that the cluster $[(Cp^*Mo)_2B_5H_9]$ would show enhanced reactivity if one of the boron vertices in the open face is replaced by a S, Se, or Te ligand. The calculation indicates a large HOMO−LUMO gap (ca. 3 eV) and vertical ionization potential (>6 eV) for **1−3**, which is consistent with their apparent stability (SI, Table S3). The composition of the orbitals,[30] located in the HOMO region, reflects a strong delocalization in both Mo_2B_5 and **1−3** skeletons. Nevertheless, a significant destabilization of HOMOs of clusters **1−3** suggests a higher reactivity compared to their parent molecule. This may be due to the introduction of π-donor chalcogen ligands into the clusters (SI, Figure S1).[31]

The question now arises, why does Te prefer to adopt a triple-decker geometry, whereas S and Se prefer a condensed bicapped trigonal-prism geometry? One may attribute this fact to the electronegativity or size differences of the chalcogen atoms that lead to the formation of different geometries. Further, more spatially extended and diffused p and d orbitals of Te favor the formation of a more flattend geometry over S and Se. Note that Lupan and King[32] recently described the oblate deltahedral geometry of the eight-vertex dirhenaborane, $[Cp_2Re_2B_6H_6]$, which is energetically stable. However, on the basis of DFT studies, we observed that clusters **4−6** prefer a bicapped trigonal-prism geometry over the oblate deltahedral geometry (hexagonal bipyramid). The hypothetical hexagonal-bipyramidal geometry for S and Se congeners, **5a** and **6a**, are less stable by 7 kcal/mol compared to **5** and **6**, respectively. Although cluster **4a**, the Te analogue of **5** or **6**, was found to be surprisingly stable by 17 kcal/mol, we were not able to isolate it experimentally.

In conclusion, a new member of the rare class of 24-electron triple-decker complexes containing a Te ligand has been synthesized and structurally characterized in solution and in the solid state. Clusters **4−6** signify a rare example of hypoelectronic mixed-metal metallaboranes containing a chalcogen atom. The DFT results demonstrate that these clusters with their open face possibly offer further cluster buildup reaction to produce a novel class of compounds. A more detailed chemistry and analysis is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details and DFT calculations, supplementary crystallographic data, and X-ray crystallographic files in CIF format for **2** and **4−6**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sghosh@iitm.ac.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Department of Science and Technology, DST (Project SR/SI/IC-13/2011), New Delhi, India. A.T. and K.K.V.C. are grateful to CSIR and UGC, India, for senior research fellowships. We thank Dr. Babu Varghese and V. Ramkumar for X-ray crystallography analysis.

■ REFERENCES

(1) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039−1040.

(2) (a) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 1−9. (b) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943−958. (c) Eloi, J.-C.; Rider, D. A.; Cambridge, G.; Whittell, G. R.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2011**, *133*, 8903−8913.

(3) (a) Manríquez, J. M.; Ward, M. D.; Reiff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 6182−6193. (b) Bendjaballah, S.; Kahlal, S.; Costuas, K.; Bévillon, E.; Saillard, J.-Y. *Chem.—Eur. J.* **2006**, *12*, 2048−2065.

(4) (a) Ghosh, S.; Noll, B. C.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6568−6571. (b) Alexandrova, A. N.; Birch, K. A.; Boldyrev, A. I. *J. Am. Chem. Soc.* **2003**, *125*, 10786−10787.

(5) Grimes, R. N. *Carboranes*, 2nd ed.; Academic Press: London, 2011.

(6) Munakata, M.; Wu, L. P.; Ning, G. L. *Coord. Chem. Rev.* **2000**, *198*, 171−203.

(7) Schumacher, E.; Taubenest, R. *Helv. Chim. Acta* **1964**, *47*, 1525−1529.

(8) Werner, H.; Salzer, A. *Synth. React. Inorg. Met.−Org. Chem.* **1972**, *2*, 239−248.

(9) Salzer, A.; Werner, H. *Angew. Chem.* **1972**, *84*, 949−950; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 930−932.

(10) (a) Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krueger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479−5480. (b) Siebert, W.; Renk, T.; Kingberger, K.; Bochmann, M.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 779. (c) Siebert, W.; Rothermel, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 333−334.

(11) DiMaio, A.-J.; Rheingold, A. L. *Chem. Rev.* **1990**, *90*, 169−190.

(12) (a) Scherer, O. J. *Angew. Chem.* **1990**, *102*, 1137−1155; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1104−1122. (b) Scheer, M.; Herrmann, E. *Z. Chem.* **1990**, *30*, 41−55.

(13) (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883−1885. (b) Cotton, F. A.; Kibala, P. A.; Wojtczak, W. A. *J. Am. Chem. Soc.* **1991**, *113*, 1462−1463.

(14) (a) Fehlner, T. P.; Halet, J.-F.; Saillard, J.-Y. *Molecular Clusters. A Bridge to Solid-State Chemistry*; Cambridge University Press: New York, 2007. (b) Bowser, J. R.; Bonny, A.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1979**, *101*, 6229−6236. (c) Molina, R. H.; Sykes, A. G. *Coord. Chem. Rev.* **1999**, *187*, 291−302.

(15) (a) Geetharani, K.; Bose, S. K.; Sahoo, S.; Ghosh, S. *Angew. Chem., Int. Ed.* **2011**, *123*, 3994−3997. (b) Thakur, A.; Sahoo, S.; Ghosh, S. *Inorg. Chem.* **2011**, *50*, 7940−7942.

(16) (a) Thakur, A.; Sao, S.; Ramkumar, V.; Ghosh, S. *Inorg. Chem.* **2012**, *51*, 8322−8330. (b) Dhayal, R. S.; Chakrahari, K. K. V.; Varghese, B.; Mobin, S. K.; Ghosh, S. *Inorg. Chem.* **2010**, *49*, 7741−7747.

(17) Kawamura, K.; Shang, M.; Wiest, O.; Fehlner, T. P. *Inorg. Chem* **1998**, *37*, 608−609.

(18) Ghosh, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1999**, *121*, 7451−7452.

(19) Aldridge, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1998**, *120*, 2586−2598.

(20) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 4940−4945.

(21) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: New York, 1990.

(22) (a) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210−214. (b) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446−452.

(23) Scherer, O. J.; Swarowsky, H.; Wolmershauser, G.; Kaim, S.; Kohlmann, W. *Angew. Chem., Int. Ed.* **1987**, *26*, 1153−1155.

(24) Reddy, A. C.; Jemmis, E. D.; Scherer, O. J.; Winter, R.; Heckmann, G.; Wolmershäuser, G. *Organometallics* **1992**, *11*, 3894.

(25) For the crystallographic data of **2** and **4−6**, see the SI

(26) (a) Mingos, D. M. P. *Nature* **1972**, *236*, 99−102. (b) Mason, R.; Thomas, K.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802−3804.

(27) (a) Wade, K. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 559−562. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1−66.

(28) Weller, A. S.; Shang, M.; Fehlner, T. P. *Chem. Commun.* **1998**, 1787−1788.

(29) See the SI for full computational details.

(30) Note that a decrease in the metal character of the HOMO from 71% to 65% for **1−3** was observed (SI, Table S4).

(31) Krishnamoorthy, B. S.; Thakur, A.; Chakrahari, K. K. V.; Bose, S. K.; Hamon, P.; Roisnel, T.; Kahlal, S.; Ghosh, S.; Halet, J.-F. *Inorg. Chem.* **2012**, *51*, 10375−10383.

(32) Lupan, A.; King, R. B. *Inorg. Chem.* **2012**, *51*, 7609−7616.