

새로운 트리오스뮴 붕소 클러스터 $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$ 의 합성 및 그 특성 연구

류택형 · 정장훈*
명지대학교 이과대학 화학과
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Synthesis and Characterizations of a Novel Tri-Osmium Carbonyl Boride Cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$

Taek-Hyoung Ryu, Jang-Hoon Chung*

Department of Chemistry, Myongji University, Yongin, Kyunggido 449-728, Korea
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Recently, metal-rich osmium carbonyl boride cluster complexes containing boron have been intensively studied^{1,2} and thus tri-, tetra-, penta-, and hexa-osmium carbonyl boride clusters, $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$,¹ $\text{H}_2\text{Os}_3(\text{CO})_8\text{BH}_3$,³ $\text{HOs}_3(\text{CO})_{12}\text{BH}_2$,⁴ $\text{HOs}_3(\text{CO})_{16}\text{B}$,⁴ and $\text{H}_2\text{Os}_3(\text{CO})_{16}\text{B}$ ⁵ have been reported. The possibility of preparing other osmium-rich carbonyl boride clusters is of continuing interest and we find that $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ can serve as a precursor to such clusters. The boron atom in $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ caps a triangle of osmium atoms and is bonded to a carbonyl group. This observation encouraged us to examine the preparation of the other osmium-rich boride carbonyl cluster using $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ as a precursor.

Here we reported the result of reaction of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ with toluene which led to the preparation of the novel tri-osmium carbonyl boride cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$.

EXPERIMENTAL SECTION

General Data

All reactions were performed under inert-atmosphere conditions. Standard vacuum line and inert-

atmosphere techniques were employed.⁶ Toluene was dried with P_2O_5 , distilled, and stored in a sealed flask. $(\mu\text{-H})_3\text{Os}_3(\text{CO})_{10}$ was prepared according to published procedure.⁷ ^{13}C (Isotec, 99.99%) was used without further purification. Thin layer chromatography plates (J.T. Baker, 250 μm , plastic-backed) were heated in a 45 °C oven for 24 h before use. IR spectrum was obtained with a Mattson Polaris FT-IR spectrometer. ^1H , ^{11}B , and ^{13}C NMR spectra were obtained using a Bruker AM-250 and WH-500 spectrometers. NMR chemical shifts are referenced to $\text{Si}(\text{CH}_3)_4$ (^1H , $\delta=0.00$ ppm) and BF_3OEt_2 (^{11}B , $\delta=0.00$ ppm). FAB mass spectrum was obtained on VG 70-250s mass spectrometer.

Preparation of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$

$(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ (310 mg, 0.34 mmole) was added to a 100 mL flask equipped with a Kontes vacuum adaptor and then toluene (30 mL) was condensed into the flask at -78 °C. The solution was stirred at 110 °C for 12 hours. Then solvent was removed by means of dynamic high vacuum leaving a brown solid in the flask. The product was separated by preparative TLC on 2 mm silica using a mixed solvent toluene/hexane as an eluent. A pale

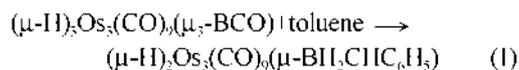
yellow band ($R_f=0.50$) in the preparative TLC on silica above was identified and characterized as $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$ (15 mg, 0.0011 mmole, 5% yield based on $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$). ^1H NMR (CDCl_3 , 30 °C) 7.35 (s), 7.23 (s), 7.14 (s), 2.35 (s), -12.1 (br), -12.2 (br), -19.7 (s) ppm. $^1\text{H}\{^{11}\text{B}\}$ NMR (CDCl_3 , 30 °C) 7.35 (s), 7.23 (s), 7.14 (s), 2.35 (s), -12.1 (s), -12.2 (s), -19.7 (s) ppm. ^{11}B NMR (CDCl_3 , 30 °C) 36.1 (br) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 30 °C) 36.1 (s) ppm. ^{13}C NMR (CDCl_3 , -40 and 30 °C) 174.5 (d of d, $J_{\text{BC}}=16\text{Hz}$), 172.4 (s), 168.0 (d, $J_{\text{BC}}=10\text{Hz}$), 167.6 (s), 163.5 (s) 146.0 (br), 137.5 (s), 133.6 (d, $J_{\text{BC}}=85\text{Hz}$), 129.7 (d, $J_{\text{BC}}=19\text{Hz}$), 127.8 (d, $J_{\text{BC}}=63\text{Hz}$), 21.35 (d, $J_{\text{BC}}=50\text{Hz}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , -40 and 30 °C) 174.5 (s), 172.4 (s), 168.0 (s), 167.6 (s), 163.5 (s) 146.0 (br), 137.5 (s), 133.6 (s), 129.7 (s) 127.8 (s), 21.35 (s) ppm. IR(ν_{CO}) 2101(m), 2077(s), 2070(s), 2022(s), 2015(s) cm^{-1} . FAB mass spectrum calculated m/e 940, obs. m/e 942.

Preparation of ^{13}C enriched $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$

$\text{Os}_3(\text{CO})_{12}$ (41% ^{13}C) prepared by a published procedure⁸ was the starting point in the preparation of ^{13}C enriched $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$. The enriched $\text{Os}_3(\text{CO})_{12}$ was converted to $\text{H}_2\text{Os}_3(\text{CO})_{10}$ by hydrogenation of the $\text{Os}_3(\text{CO})_{12}$. The $\text{H}_2\text{Os}_3(\text{CO})_{10}$ was converted to ^{13}C labeled $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ by reacting it with B_2H_6 . Thermolysis of the $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ by the procedure described above yielded ^{13}C labeled $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$.

RESULTS AND DISCUSSIONS

Reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ with toluene at 110 °C for 12 hours yielded a novel tri-osmium carbonyl boride cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$ in 5% yield based upon $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ (reaction 1). The osmium cluster is an



air-stable solid at room temperature. However, it decomposes at 110 °C. The cluster was characterized by ^1H , ^{11}B & ^{13}C NMR spectroscopies at various temperatures from -40 to 30 °C. ^1H NMR spectrum at

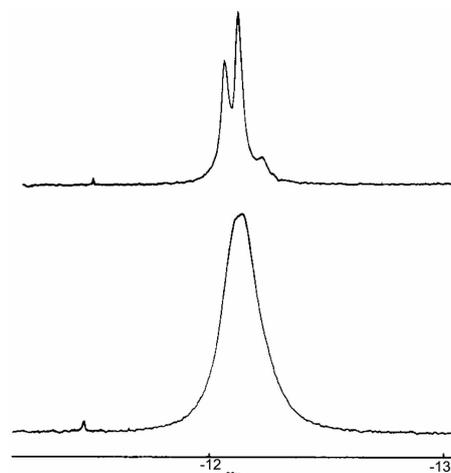


Fig. 1. ^1H and $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$.

30 °C shows a sharp singlet at -19.7 ppm and two broad signals at -12.1 and -12.2 ppm which are partially overlapped. The boron decoupled $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum at 30 °C shows the reduction of the broad signals to two sharp singlets at the same chemical shifts as shown in Fig. 1. Generally, the signal of hydrogen bridging between boron and transition metal atom in ^{11}B NMR spectrum is broad at room temperature due to coupling with boron atom and the signal in the boron decoupled $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum is sharpened to be a singlet. Therefore these two signals can be assigned to two non-equivalent hydrogens which bridge between osmium and boron atoms and thus couple with a boron atom. This is consistent with the signal in ^1H NMR spectrum of bridge hydrogens B-H-Os of tri-osmium carbonyl boride cluster $\text{H}_2\text{Os}_3(\text{CO})_9\text{BH}_2$ previously reported. The slight difference between two chemical shift values shows that this molecule has asymmetric structure but two hydrogens have very close electronic environments. ^{11}B NMR spectrum at -40 °C consists of two distinct sharp signals at -12.1 and -12.2 ppm which show two different non-equivalent hydrogens. The sharp singlet at -19.7 ppm can be assigned to Os-H-Os bridge hydrogens. This chemical shift is a typical value for bridge hydrogen between osmium and osmium atoms. The integration of ^1H NMR spectrum shows that the ratio of the

intensity of the signals at -12.1, -12.2, and -19.7 ppm is 1:1:2. Therefore, the signal at -19.7 ppm can be assigned to two bridge hydrogens. ^1H NMR spectrum at 30 °C does not show any broad signal at downfield which may be assigned to terminal hydrogen bonded to boron atom. However, it shows a singlet at 2.35 ppm assigned to aliphatic hydrogen bonded to carbon and three signals at 7.35, 7.23, and 7.14 ppm which are attributed to aromatic hydrogens. ^{11}B NMR spectrum at 30 °C shows a broad signal at 36.10 ppm. This chemical shift, which is at a lower field than the resonance of typical trigonal boron compounds,⁹ as the manner of that seen for carbides in ^{13}C NMR spectroscopy,¹⁰ suggests that this cluster has boridic character.¹¹ The chemical shift in ^{11}B NMR spectrum of transition metal boride is usually shown at the far downfield. For example, penta-osmium carbonyl boride cluster $\text{HOs}_5(\text{CO})_9\text{B}$ with an interstitial boron atom bonded to five osmium atoms has typical boridic nature. The value of the chemical shift of the cluster is 184.4 ppm. However, the chemical shift of this new cluster is not that far downfield. Therefore, ^{11}B NMR spectrum suggests that the cluster should have a boron atom bonded to three osmium atoms. The proton decoupled $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum at 30 °C shows a sharp signal. This means the cluster has a boron atom bonded to hydrogen atoms. Therefore, the signal can be assigned to boron which is bonded to hydrogen atoms which bridge osmium and boron atoms.

^{13}C NMR spectrum of the tri-osmium borane cluster at room temperature is shown in Fig. 2. It consists of a quartet at 174.5, a doublet at 168.0, three singlets at 172.4, 167.6, and 163.5, a broad signal at 146.0, a singlet at 137.5, three doublets at 133.6, 129.7, 127.8, and 21.35 ppm. The five signals from 174.5 to 163.5 ppm are due to terminal carbonyls bonded to osmium atoms. The ^{13}C NMR spectrum of the cluster at -40 °C shows no change of the chemical shifts, indicative of no rapid exchange of the terminal carbonyls. The proton decoupled $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the cluster shows five singlets at the same chemical shifts. That is, it shows the reductions of the quartet to a singlet and the doublet to a singlet at the same chemical shifts, 174.5 and 168.2 ppm

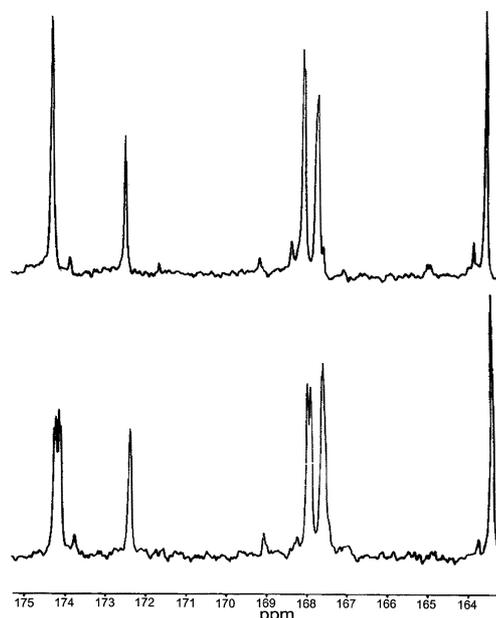


Fig. 2. $^{13}\text{C}\{^1\text{H}\}$ and ^{13}C NMR spectra of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BI})\text{C}(\text{H})_2$.

respectively. It suggests that the carbonyls couple with Os-H-Os bridge hydrogens. The ratio of five singlets at 174.5, 172.4, 168.0, 167.6, and 163.5 ppm in the proton decoupled ^{13}C NMR spectrum is approximately 2 : 1 : 2 : 2 : 2. This cluster may have *pseudo* C_s symmetry with a tetrahedral Os_3B core based on the spectra. The nine terminal carbonyls can be assigned based on the intensity and the characterization of the spectra as shown in Fig. 2. The quartet at 174.5 ppm reflecting coupling with two non-equivalent hydrogens can be assigned to two terminal carbonyls CO(5) which are trans to two hydrogens bridging osmium atoms. The singlet at 172.3 ppm can be assigned to carbonyl CO(2). The doublet at 168.0 ppm coupled with a hydrogen can be assigned to two carbonyls CO(3) which are trans to one hydrogen. The two singlets at 167.6 and 163.5 ppm can be assigned to two carbonyls CO(4) and two carbonyls CO(1), respectively, which do not have trans hydrogen. The broad signal at 146.0 ppm shows that the carbon couples with a boron atom and thus the signal can be assigned to an vinylidene carbon which is bonded to a boron, aliphatic carbon and osmium atoms. This chemical

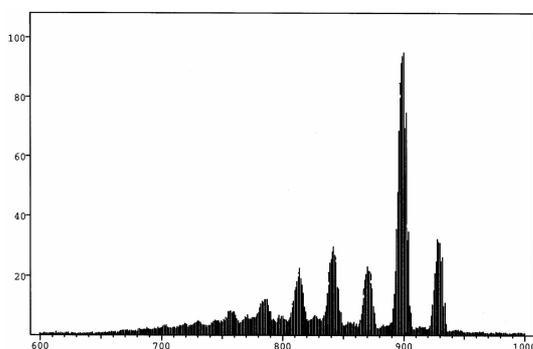


Fig. 3. FAB mass spectrum of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$.

shift value is similar to that of the carbon atom bonded to boron and osmium atoms in $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9[(\mu_3\text{-}\eta^2\text{-C}(\text{OBC}_6\text{H}_4)_2\text{B}(\text{Cl}))]$.¹² Four signals from 137.5 to 127.8 ppm are due to aromatic carbons and a signal at 21.35 ppm to an aliphatic carbon. The singlet at 137.5 ppm can be assigned to a aromatic carbon which has no hydrogen, and three doublets at 133.6, 129.7, and 127.8 ppm, to aromatic carbons coupling with a hydrogen. The doublet at 21.35 ppm can be assigned to an aliphatic carbon coupling with a hydrogen.

The FAB mass spectrum of the cluster is shown in Fig. 3. The highest intensity peak in the parent envelope calculated for $\text{H}_{10}\text{BC}_{17}\text{O}_9\text{Os}_3$ is $m/e=940$ and the value found $m/e=942$. The sequential loss of the carbonyl ligands was observed in the mass spectrum. The parent envelope and the distribution of peak intensities in the envelope in general are in accord with those predicted for natural abundance isotope distribution. IR spectrum shows typical vibration absorbance for terminal carbonyls and aliphatic and aromatic carbon-hydrogen and carbon-

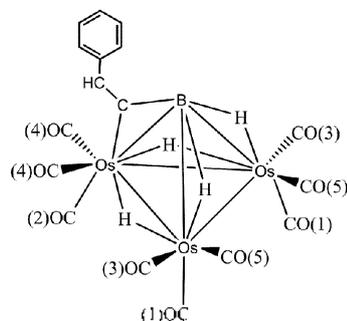


Fig. 4. Proposed molecular structure of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$.

carbon bonds. The solid state structure of was not characterized by the single crystal X-ray diffraction analysis. However, the molecular structure of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu\text{-BH}_2\text{CHC}_6\text{H}_5)$ may be proposed as shown in Fig. 4 based on ^1H , ^{11}B , and ^{13}C NMR, infrared and FAB mass spectra. The molecule has *pseudo* C_3 symmetry with a tetrahedral Os_3B core where the boron atom is bonded to three osmium atoms. It has nine terminal CO's of which three terminal CO's are bonded to each osmium atom. A vinylidene carbon bonded by benzyl group is bonded to a boron and osmium atoms and the cluster has two B-H-Os bridge hydrogens and two Os-H-Os bridge hydrogens.

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REFERENCES

- Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.
- (a) Jan, D.-Y.; Workman, D. P.; Hsu, L.-Y.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1992**, *31*, 5123. (b) Jan, D.-Y.; Shore, S. G. *Organometallics* **1987**, *6*, 428. (c) Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Kennedy, S.; Hoffman, J. C.; Line Wang, T.-C.; Marshall, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 392.
- Chung, J.-H.; Boyd, E. P.; Liu, J.; Shore, S. G. *Inorg. Chem.* **1997**, *36*, 4778.
- Chung, J.-H.; Knoepfel, D.; McCarthy, D.; Columbie, A.; Shore, S. G. *Inorg. Chem.* **1993**, *32*, 3391.
- Chung, J.-H.; Jordan, G.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2000**, *39*, 568.
- Shriver, D. F.; Drezdron, M. A. *The Manipulation of Air Sensitive Compounds; 2nd ed.*; John Wiley & Sons: New York, **1986**.
- Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.
- Brieker, J. C.; Payne, M. W.; Shore, S. G. *Organometallics* **1987**, *6*, 2545.
- Rath, N. P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 345.
- Chini, R.; Heaton, B. T. *Top. Cur. Chem.* **1977**, *71*, 1.
- (a) Chini, R.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285. (b) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37.
- Workman, D. P.; Jan, D.-Y.; Shore, S. G. *Inorg. Chem.* **1990**, *29*, 3518.