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Stable *exo-nido*-Metallacarboranes (M = Os^{IV}) that Incorporate *meta*-Carborane-Based Dicarbollide Ligands

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Abstract: Reactions of the $[K]^+$ salts of the [*nido*-7,9-$C_2B_9H_{12}]^-$ anion (**2**) and its C-phenylated derivative [7-Ph-*nido*-7,9-$C_2B_9H_{11}]^-$ (**4**) with $[OsCl_2(PPh_3)_3]$ (**3**) proceed in benzene at ambient temperature with the formation of 16-electron chlorohydrido-Os(IV) *exo-nido* complexes, [*exo-nido*-10,11-$\{(Ph_3P)_2OsHCl\}$-10,11-(μ-H)$_2$-7-R-7,9-$C_2B_9H_8$] (**5**: R = H; **6**: R = Ph), along with the small amounts of the charge-compensated *nido*-carboranes [*nido*-7,9-$C_2B_9H_{11}PPh_3$] (**7**) and [7-Ph-*nido*-7,9-$C_2B_9H_{10}PPh_3$] (**8**) as byproducts. However, when carried out under mild heating in ethanol, the reaction of **2** with **3** selectively afforded a 16-electron dihydrido-Os(IV) *exo-nido* complex [*exo-nido*-10,11-$\{(Ph_3P)_2OsH_2\}$-10,11-(μ-H)$_2$-7,9-$C_2B_9H_9$] (**9**). Structures of both complexes **5** and **9** have been confirmed by single-crystal X-ray diffraction studies, which revealed that *nido*-carboranes in these species function as a bidentate dicarbollide ligands [7-R-*nido*-7,9-$C_2B_9H_{10}]^{2-}$ linked to the Os(IV) center via two B−H···Os bonds involving adjacent B−H vertices in the upper CBCBB belt of the carborane cage. Thus, compounds **5** and **9** represent the first structurally characterized *exo-nido*-metallacarboranes based on *meta*-dicarbollide-type ligands. Variable-temperature ^1H and $^{31}P\{^1H\}$ NMR experiments indicate that complex **9** is fluxional in solution and shows an unusual exchange between terminal Os−$(H)_2$ and bridging $\{B-H\}_2$···Os hydrogen atoms. Upon heating in d_8-THF at 65 °C, complex **9** converts irreversibly to its *closo* isomer [2,2-$(PPh_3)_2$-2,2-H_2-*closo*-2,1,7-$OsC_2B_9H_{11}$] (**13**), which could thus be obtained as a pure crystalline solid. The structure of **13** has been established on the basis of analytical and multinuclear NMR data and a single-crystal X-ray diffraction study.

Introduction

Since the mid 1980s, much progress has been made in the studies of a new class of complexes which became known as *exo-nido*-metallacarboranes. The metal-containing moiety in these complexes is attached to the {*nido*-C_2B_9} carborane cage either through multiple 2e,3c $\{B-H\}_n$···M (n = 2, 3) bonds[1] or via one or two *exo*-polyhedral M−E bonds (E is a heteroatom-containing cage substituent), which may be supported by one or two B−H···M linkages, depending on the nature of the d metal and the number of heteroatom substituents.[2] The *exo-nido*-metallacarborane complexes of the d-block metals together with their *closo* isomers are known to play an important role in the field, frequently representing efficient precatalysts for organic reactions[3] and, in some cases, useful building-block reagents for the construction of novel mono- and binuclear metallacarboranes of different types and structures.[4] Although *exo-nido* species are, at present, well documented and there are about three dozen of the structurally studied *exo-nido*-metallacarboranes of p-, d-, and f-block elements,[1,2,5] none of these species found in the literature involved any carborane ligands other than those derived from the [*nido*-7,8-$C_2B_9H_{12}]^-$ anion,

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(1) (a) Doi, J. A.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 80. (b) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2979. (c) Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2990. (d) Hewes, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 5757. (e) Brew, S. A.; Jeffery, J. C.; Mortimer, M. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1365. (f) Chizhevsky, I. T.; Lobanova, I. A.; Bregadze, V. I.; Petrovskii, P. V.; Antonovich, V. A.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T. *Mendeleev Commun.* **1991**, 47. (g) Lobanova, I. A.; Bregadze, V. I.; Timofeev, S. V.; Petrovskii, P. V.; Starikova, Z. A.; Dolgushin, F. M. *J. Organomet. Chem.* **2000**, *597*, 48. (h) Timofeev, S. V.; Lobanova, I. A.; Petrovskii, P. V.; Starikova, Z. A.; Bregadze, V. I. *Russ. Chem. Bull.* **2001**, *50*, 2245. (i) Kolomnikova, G. D.; Petrovskii, P. V.; Sorokin, P. V.; Dolgushin, F. M.; Yanovsky, A. I.; Chizhevsky, I. T. *Russ. Chem. Bull.* **2001**, *50*, 706. (j) Cheredilin, D. N.; Balagurova, E. V.; Godovikov, I. A.; Solodovnikov, S. P.; Chizhevsky, I. T. *Russ. Chem. Bull.* **2005**, *54*, 2535. (k) Cheredilin, D. N.; Dolgushin, F. M.; Korlyukov, A. A.; Godovikov, I. A.; Kadyrov, R.; Balagurova, E. V.; Solodovnikov, S. P.; Chizhevsky, I. T. *J. Organomet. Chem.* **2006**, *691*, 3989.

(2) (a) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabo, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1281. (b) Teixidor, F.; Viñas, C.; Casabo, J.; Romerosa, A. M.; Rius, J.; Miravitlles, C. *Organometallics* **1994**, *13*, 914. (c) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabo, J. *Organometallics* **1994**, *13*, 2751. (d) Viñas, C.; Nuñez, R.; Flores, M. A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1995**, *14*, 3952. (e) Viñas, C.; Nuñez, R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1996**, *15*, 3850. (f) Teixidor, F.; Flores, M. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2251. (g) Viñas, C.; Flores, M. A.; Nuñez, R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1998**, *17*, 2278. (h) Viñas, C.; Nuñez, R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1998**, *17*, 2376. (i) Teixidor, F.; Benakki, R.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1998**, *17*, 4630. (j) Teixidor, F.; Flores, M. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1998**, *17*, 4675. (k) Barberà, G.; Viñas, C.; Teixidor, F.; Rosair, G. M.; Welch, A. J. *J. Organomet. Chem.* **2002**, *663*, 221.

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the most common representative among the 11-vertex *nido*-carborane isomers.

We are aware of several previous attempts to synthesize *exo-nido*-metallacarborane complexes (M = Rh) based on the related {*nido*-7,9-C_2B_9} carborane derivatives and, in particular, via the direct reaction of [$RhCl(PPh_3)_3$] with the [Me_3NH]$^+$ salt of the [*nido*-7-Me-9-Ph-7,9-$C_2B_9H_{10}$]$^-$ anion in hot ethanol.[6] Although one would expect that the steric effects associated with the bulky C,C′ cage substituents in the starting {*nido*-7,9-C_2B_9} carborane salt should enhance the stability of the desired Rh(I) *exo-nido* species, the isomeric Rh(III) *closo* complex identified as [*closo*-2,2-$(Ph_3P)_2$-2-H-1-Me-7-Ph-2,1,7-$RhC_2B_9H_9$] (**1**) was, unexpectedly, isolated instead in moderate yield.[6] Further attempts to stabilize *exo-nido*-rhodacarborane isomers by the replacement of PPh_3 ligands in **1** with phosphine groups having larger cone angles, such as, P(*m*-tolyl)$_3$, P(*o*-tolyl)$_3$, and PCy_3, failed, although in the case of the substitution reaction with PCy_3, the formation of the species which presumably retained an *exo-nido* structure in solution has been detected by the $^{31}P\{^1H\}$ NMR spectroscopy.[6] At last, when the carborane ligand exchange reaction of the Cs^+ salt of the [*nido*-7,9-$C_2B_9H_{12}$]$^-$ anion (**2**), employed as the nucleophilic reagent, with the [*exo-nido*-4,9-{$(PPh_3)_2Rh$}-4,9-(μ-H)$_2$-7-Me-8-Ph-7,8-$C_2B_9H_8$] was monitored by the $^{31}P\{^1H\}$ NMR spectroscopy, the kinetically unstable unsubstituted *exo-nido* intermediate was initially observed along with its conversion to the more stable *closo* isomer [*closo*-2,2-$(Ph_3P)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$].[4a]

In the present work, the synthesis of a short series of three stable 16-electron *exo-nido*-osmacarborane complexes of the general formula [*exo-nido*-{$(Ph_3P)_2HXOs$}-10,11-(μ-H)$_2$-7-R-7,9-$C_2B_9H_{10}$] (**5**: R = H, X = Cl; **6**: R = Ph, X = Cl; **9**: R = X = H) is described. In each of these complexes, the dianionic [*nido*-7-R-7,9-$C_2B_9H_{10}$]$^{2-}$ cage ligand is bound to the Os(IV)-containing moiety via the bidentate $\{B-H\}_2\cdots Os$ bonding interaction, and an *exo-nido* structure of all species is retained both in the solid state and in solution.

Results and Discussion

Synthesis of *exo-nido*-Osmacarborane Complexes 5, 6, and 9. As a part of our ongoing studies on the chemistry[1f,i−k,4b,c,f,g] and catalytic activity[3c,k] of "three-bridge" *exo-nido*-metallacarboranes, we have previously developed a convenient synthetic procedure allowing one to obtain a series of new 18-electron *exo-nido*-metallacarboranes of the type [*exo-nido*-5,6,10-{$(Ph_3P)_2ClM$}-5,6,10-(μ-H)$_3$-10-H-7-R-8-R′-7,8-$C_2B_9H_6$] (M = Ru,[1f] Os;[1i] R, R′ = H, Me, $PhCH_2$) in modest to high yields. This was based on the room-temperature reaction in benzene between [$RuCl_2(PPh_3)_3$] or [$OsCl_2(PPh_3)_3$] (**3**) and the [K]$^+$ salts of the corresponding [*nido*-7-R-8-R′-7,8-$C_2B_9H_{10}$]$^-$ anions. Since all three-bridge *exo-nido* complexes thus prepared were quite stable both in the solid state and in solution, we decided to use this mild and efficient method to try to generate *exo-nido*-osmacarborane complexes incorporating "carbons-apart" {*nido*-7,9-C_2B_9} carborane ligands, which, as yet, have not been known within this particular category of metallacarborane complexes. Accordingly, similar reactions in benzene of osmium reagent **3** with the [K]$^+$ salts of the [*nido*-7,9-$C_2B_9H_{12}$]$^-$ anion **2** or its C-phenylated derivative [*nido*-7-Ph-7,9-$C_2B_9H_{11}$]$^-$ (**4**) were carried out, and each has been found to afford "two-bridge" 16-electron *exo-nido*-osmacarboranes that were analyzed correctly for [*exo-nido*-10,11-{$(Ph_3P)_2OsHCl$}-10,11-(μ-H)$_2$-7-R-7,9-$C_2B_9H_8$] (**5**: R = H; **6**: R = Ph), respectively.

These electron-deficient complexes **5** and **6** were isolated, after silica gel column chromatography, in 56 and 62% yield, respectively, along with small amounts of [*nido*-7-R-7,9-$C_2B_9H_{10}PPh_3$] (**7**: R = H; **8**: R = Ph) formed as byproducts and a trace of an initially unidentified dark-green solid in the case of the former reaction. Remarkably, when the reaction of **3** with a 10% molar excess of the [K]$^+$ salt of an unsubstituted anion **2** was carried out in hot ethanol (50 °C, ca. 2.5 h) instead of benzene, the dark-green species was isolated in 68% yield, and this, on the basis of analytical and multinuclear NMR data, was formulated as a dihydrido-osmium complex [*exo-nido*-10,11-{$(Ph_3P)_2OsH_2$}-10,11-(μ-H)$_2$-7,9-$C_2B_9H_9$] (**9**) (Scheme 1). Complexes **5**, **6**, and **9** were all stable microcrystalline solids soluble in CH_2Cl_2, THF, and moderately in C_6H_6 and could thus be purified by recrystallization from CH_2Cl_2/*n*-hexane upon cooling. Further support for the *exo-nido* structure of the complexes so obtained and their precise connectivity pattern was provided by X-ray diffraction studies of two selected complexes **5** and **9**. Zwitterionic triphenylphosphine-cage-substituted *nido*-carboranes **7** and **8** were identified as such using NMR spectroscopy by their characteristic ^1H, $^{11}B/^{11}B\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra and by comparison of the data obtained with those found in the literature for [*nido*-9-PPh_3-7,8-$C_2B_9H_{11}$].[7]

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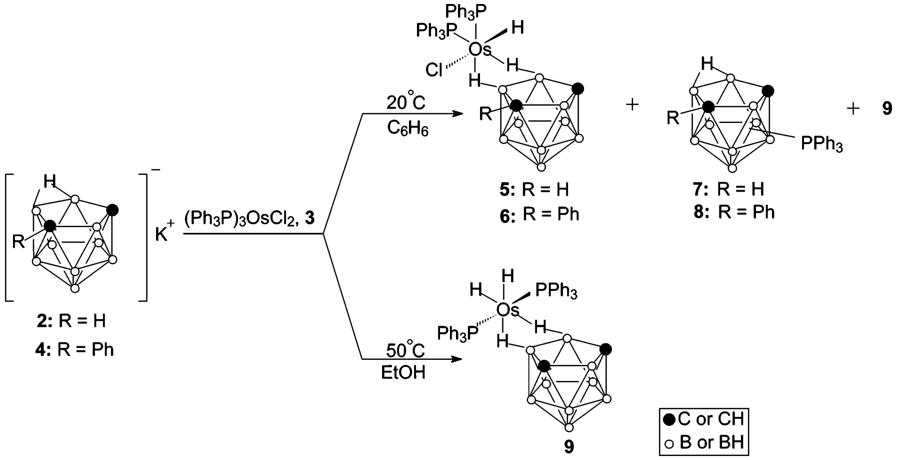
(3) See, for instance: (a) Belmont, J. A.; Soto, J.; King, R. E., III; Donaldson, A. J.; Hewes, J. D.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1989**, *111*, 7475 and references therein. (b) Kang, H. C.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2327. (c) Demonceau, A.; Saive, E.; de Froidmont, Y.; Noels, A. F.; Hubert, A. J.; Chizhevsky, I. T.; Lobanova, I. A.; Bregadze, V. I. *Tetrahedron Lett.* **1992**, *33*, 2009. (d) Demonceau, A.; Simal, F.; Noels, A. F.; Viñas, C.; Nuñez, R.; Teixidor, F. *Tetrahedron Lett.* **1997**, *38*, 4079. (e) Demonceau, A.; Simal, F.; Noels, A. F.; Viñas, C.; Nuñez, R.; Teixidor, F. *Tetrahedron Lett.* **1997**, *38*, 7879. (f) Simal, F.; Sebille, S.; Demonceau, A.; Noels, A. F.; Nuñez, R.; Teixidor, F.; Viñas, C. *Tetrahedron Lett.* **2000**, *41*, 5347. (g) Teixidor, F.; Flores, M. A.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *J. Am. Chem. Soc.* **2000**, *122*, 1963. (h) Brunner, H.; Apfelbacher, A.; Zabel, M. *Eur. J. Inorg. Chem.* **2001**, 917. (i) Tutusaus, O.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Viñas, C.; Teixidor, F. *Tetrahedron Lett.* **2003**, *44*, 8421. (j) Yinghuai, Z.; Carpenter, K.; Bun, C. C.; Bahnmueller, S.; Ke, C. P.; Srid, V. S.; Kee, L. W.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3792. (k) Kolyakina, E. V.; Grishin, I. D.; Cheredilin, D. N.; Dolgushin, F. M.; Chizhevsky, I. T.; Grishin, D. F. *Russ. Chem. Bull.* **2006**, *55*, 89. (l) For the latest reviews, see: Teixidor, F.; Nuñez, R.; Flores, M. A.; Demonceau, A.; Viñas, C. *J. Organomet. Chem.* **2000**, *614−615*, 48; Grimes, R. *Coord. Chem. Rev.* **2000**, *200−202*, 773; Teixidor, F.; Viñas, C.; Demonceau, A.; Nuñez, R. *Pure Appl. Chem.* **2003**, *75*, 1305.

(4) (a) Long, J. A.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 3004. (b) Lobanova, I. A.; Chizhevsky, I. T.; Petrovskii, P. V.; Bregadze, V. I. *Russ. Chem. Bull.* **1996**, *45*, 241. (c) Chizhevsky, I. T.; Lobanova, I. A.; Petrovskii, P. V.; Bregadze, V. I.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T.; Chistyakov, A. L.; Stankevich, I. V.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1999**, *18*, 726. (d) Ellis, D. D.; Couchman, S. M.; Jeffery, J. C.; Malget, J. M.; Stone, F. G. A. *Inorg. Chem.* **1999**, *38*, 2981. (e) Lobanova, I. A.; Timofeev, S. V.; Kudinov, A. R.; Meshcheryakov, V. I.; Petrovskii, P. V.; Starikova, Z. A.; Bregadze, V. I. *Russ. Chem. Bull.* **2002**, *51*, 517. (f) Cheredilin, D. N.; Kadyrov, F. M.; Dolgushin, F. M.; Balagurova, E. V.; Godovikov, I. A.; Solodovnikov, S. P.; Chizhevsky, I. T. *Inorg. Chem. Commun.* **2005**, *8*, 614. (g) Chizhevsky, I. T.; Yanovsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1997**, *536−537*, 51 (a review).

(5) In addition to refs 1 and 2, see: (a) Churchill, M. R.; Reis, A. N., Jr.; Young, D. A. T.; Willey, G. R.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1971**, 298. (b) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 5687. (c) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046. (d) Kim, J.; Kim, S.; Do, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 938. (e) Park, Y.-W.; Kim, J.; Kim, S.; Do, Y. *Chem. Lett.* **1993**, 121. (f) Park, Y.-W.; Kim, J.; Do, Y. *Inorg. Chem.* **1994**, *33*, 1. (g) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403. (h) Xie, Z.; Liu, Z.; Chiu, K.-y.; Xue, F.; Mak, T. C. W. *Organometallics* **1997**, *16*, 2460. (i) Kwong, W.-C.; Chan, H.-S.; Tang, Y.; Xie, Z. *Organometallics* **2004**, *23*, 4301.

(6) Hewes, J. D.; Thompson, M.; Hawthorne, M. F. *Organometallics* **1985**, *4*, 13.

Scheme 1



Single-Crystal X-ray Diffraction Studies of the "Two-Bridge" *exo-nido*-Osmacarboranes 5 and 9. The molecular structures of **5** and **9** are shown in Figures 1 and 2, respectively, and selected geometrical parameters (bond distances and angles) are listed in Table 1.

The crystallographic studies of **5** and **9** established these species to be the first currently known *exo-nido*-metallacarboranes incorporating the carbons-apart [*nido*-7,9-$C_2B_9H_{11}$]$^{2-}$ ligand. The metal atom in **5** is bound to the two PPh_3 groups (2.355(2) and 2.343(2) Å), one terminal hydride ligand (1.64 Å), and a chlorine (2.442(2) Å). Complex **9** is similar in composition to **5** except for the replacement of the Cl ligand by the terminal H ligand. However, these small structural changes cause a substantial difference in the architecture of the *exo* polyhedrally bound osmium-containing moieties and the metal-hydride orientation with respect to the open face of the carborane cage ligand in these species (vide infra).

It has become apparent from the X-ray diffraction data that the {*nido*-7,9-C_2B_9} carborane cage in both species **5** and **9** acts as a bidentate ligand forming two B−H···M linkages; it is particularly noteworthy that boron atoms, B(10) and B(11), involved in the B−H···Os bonding interaction with the metal center are both from the upper CBCBB belt of the *nido*-carborane cage. In both structures **5** and **9**, there is a quite noticeable folding of the {C_2B_3} open face about the C(7)···C(9) line of the cage ligand with the corresponding dihedral angles between the B_2C_2 and C_2B planes being equal to 26.4 and 27.0°, respectively. This, however, appears to be a typical feature of the carbons-apart {*nido*-7,9-C_2B_9} cluster geometry. For example, in the crystal structure of the protonated proton sponge salt of an unsubstituted [*nido*-7,9-$C_2B_9H_{12}$]$^-$ monoanion, the boron atom between the two carbon atoms on the open face is above the plane containing the other four atoms by 0.246 Å.[8]

A similar **5** and **9** metal-to-carborane cage "two-bridge" bonding pattern was previously observed for only a few *exo-nido*-metallacarborane species, which are all, however, derived from the "carbons-adjacent" [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion and, in particular, [*exo-nido*-9,10-{$W(CO)_2(\eta\text{-}C_5Me_5)$}-9,10-($\mu$-H)$_2$-7,8-$Me_2$-7,8-$C_2B_9H_8$] (**10**),[1e] [*exo-nido*-9,10-{$Al(CH_3)_2$}-9,10-(μ-H)$_2$-7,8-$C_2B_9H_{10}$] (**11**),[5a,b] and [*exo-nido*-9,10-{$Cu(PPh_3)_2$}-9,10-(μ-H)$_2$-7,8-$C_2B_9H_{10}$] (**12**).[5d] In many other currently known *exo-nido*-metallacarboranes of d-block metals, where the *nido*-carborane ligand is connected with an *exo*-metal-containing unit via the two B−H···M linkages,[1a−d] those boron vertices involved in such an interaction were from different belts of the cage framework. It should also be noted that, among the crystallographically studied complexes **10**−**12**, the position of the *endo*-hydrogen atom postulated as a bridge between two adjacent boron atoms on the pentagonal C_2B_3 open face was clearly defined only for complex **10**,[1e] whereas in the other two complexes, the position of the H-bridging atom was determined by NMR spectroscopy.[5a,d] Interestingly, in our case, the X-ray diffraction experiments showed that there are no *endo*-hydrogen atoms in complexes **5** and **9**; all other hydrogen positions, including those of the terminal osmium hydrides and the cluster B−H units, have been objectively located in these structures. Thus, the {*nido*-7,9-C_2B_9} carborane ligand in each structure **5** and **9** was defined as the dicarbollide dianion. As such, the *exo-nido*-osmacarboranes obtained represent rare examples of 16-electron complexes with the osmium atom in the 4^+ oxidation state. To the best of our knowledge, there are only a few structurally studied examples of "two-bridge" and mixed "two/three-bridge" *exo-nido* species that originated from dicarbollide dianion derivatives,[5f−h] and among these, complexes **5** and **9** are the first having the carbons-apart dicarbollide system. The facile formation and stability of such electron-deficient osmium species, where the metal atom exists in the rather uncommon oxidation state of 4, is surprising indeed since, within the family of osmium complexes, the only precedent was reported to be the sterically crowded osmium−phosphine complexes OsH_3X-(i-Pr_3P)$_2$[9] and $OsH_2X_2(R_3P)_2$[10] (where X = halides; R = i-Pr or t-Bu_2Me).

In relation to this, it is necessary to discuss a specific structural detail of complex **5** regarding the orientation of the metal hydride with respect to the pentagonal open face of the carborane cage. It is seen from Figure 1 that the osmium hydride H(1M) in **5**, although located near the metal atom (Os···H, 1.64 Å), could, in principle, be involved in a weak four-center (OsHBB) bonding interaction between the osmium center and the two

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[7] Kim, K. M.; Do, Y., Knobler, C.; Hawthorne, M. F. *Bull. Korean Chem. Soc.* **1989**, *10*, 321.
[8] Fox, M. A.; Geoeta, A. E.; Hughes, A. K.; Johnson, A. L. *J. Chem. Soc., Dalton Trans.* **2002**, 2132.
[9] Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.
[10] Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.

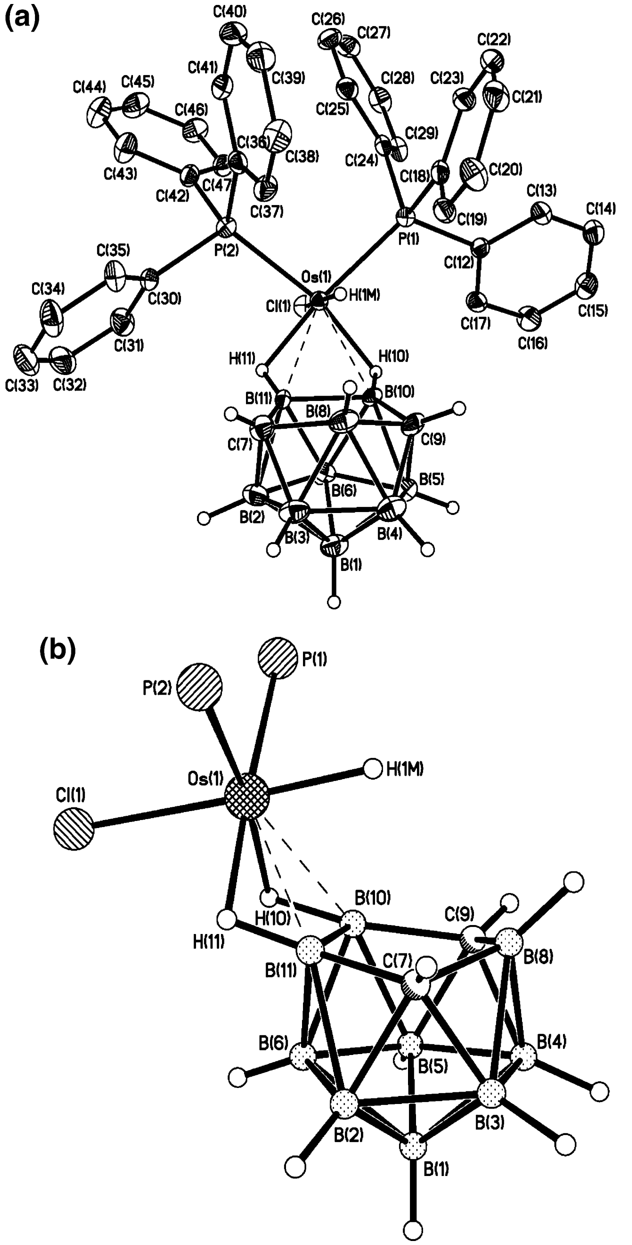

Figure 1. Perspective view of a single molecule of complex **5** with thermal ellipsoids drawn at the 30% probability level (hydrogen atoms of the phenyl substituents are omitted for clarity) (top) and schematic view of **5** with the phenyl groups at the Os atom omitted for clarity (bottom).

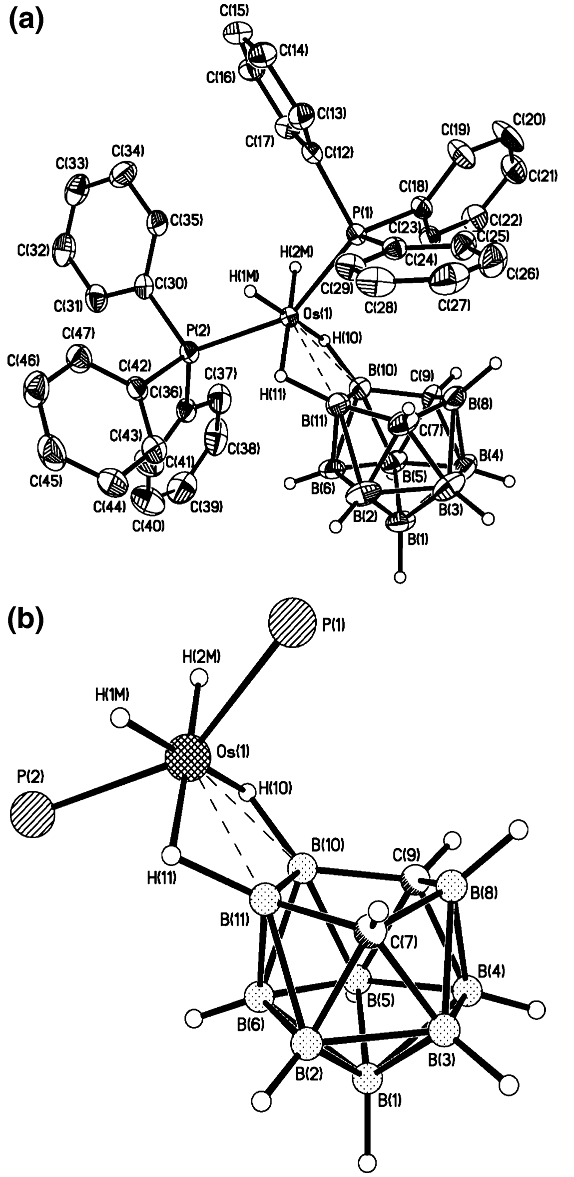

Figure 2. Perspective view of a single molecule of complex **9** with thermal ellipsoids drawn at the 30% probability level (hydrogen atoms of the phenyl substituents are omitted for clarity) (top) and schematic view of **9** with the phenyl groups at the Os atom omitted for clarity (bottom).

cage boron atoms B(10) and B(11). If we then assume that such a bridging B(10)···H···B(11) fragment, through the agostic-like B_2H···Os interaction, contributes two electrons to the metal center, complex **5** might formally be considered as a zwitterionic Os(II) species with the metal atom having a saturated 18-electron shell. If this were the case, the noticeable strengthening of the bridging B(10)···H···B(11) bonds occurring in the structure of **5** (B(10)···H(1M), 2.20; B(11)···H(1M), 2.34 Å) could have been explained by the four-center bridging nature of the hydrogen H(1M) and, in addition, by its purely trans position with respect to the chlorine ligand in the octahedral coordination sphere of the Os(II) atom. Note, in all crystallographically studied 18-electron Os(II) and Ru(II) *exo-nido*-{$MCl(PPh_3)_2$}-metallacarboranes[1f−j] and the related *exo-nido*-{$RuCl(PPh_3)_2$}-metallaheteroboranes[2] as well, the longest of all of the B−H bonds involved in the interaction with a metal center is that lying trans to the Cl ligand. Although the mode of the B(10)-B(11)···H···M interaction postulated in **5** has not been exemplified in the metallacarborane chemistry, at least several more or less similar examples of smaller-cage metallacarborane clusters published by Grimes and co-workers are known,[11b] where the metal-bound hydrogen atom acts as a bridge between the metal center and two neighboring cage boron atoms. It seemed probable, therefore, that, to generate an electronically favored Os(II) species in the case of complex **9**, a similar bonding to **5** of the metal hydride to the C_2B_3 open face should take place. In the solid-state structure of **9**, metal-hydride ligands (Os−H, 1.52 and 1.40 Å), nevertheless, adopt a different orientation with respect to the *nido*-carborane open face from that postulated. One of the PPh_3 groups (not the metal hydride) lies over the

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(11) (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 252. (b) Stephan, M.; Davis, J. H., Jr.; Meng, X.; Chase, K. J.; Hauss, J.; Zenneck, U.; Pritzkow, H.; Siebert, W.; Grimes, R. N. *J. Am. Chem. Soc.* **1992**, *114*, 5214.

Table 1. Selected Bond Lengths (Å) and Angles (°) for Complexes **5** and **9**

bond	**5**	**9**	angle	**5**	**9**
Os(1)−P(1)	2.355(2)	2.303(2)	P(1)−Os(1)−P(2)	100.58(6)	150.34(5)
Os(1)−P(2)	2.343(2)	2.367(2)	P(1)−Os(1)−Cl(1)	93.03(6)	
Os(1)−Cl(1)	2.442(2)		P(2)−Os(1)−Cl(1)	99.78(6)	
Os(1)−H(1M)	1.64	1.40	H(1M)−Os(1)−Cl(1)	172	
Os(1)−H(2M)		1.52	H(10)−Os(1)−P(2)	167	
Os(1)−H(10)	1.85	1.75	H(11)−Os(1)−P(1)	173	
Os(1)−H(11)	1.74	1.69	H(10)−Os(1)−H(11)	81	118
Os(1)−B(10)	2.194(6)	2.227(6)	H(1M)−Os(1)−H(2M)		110
Os(1)−B(11)	2.169(6)	2.217(7)	H(1M)−Os(1)−H(10)		169
B(10)−H(10)	1.29	1.45	H(2M)−Os(1)−H(11)		179
B(11)−H(11)	1.08	1.33	B(11)−C(7)−B(8)	97.1(5)	97.7(5)
C(7)−B(8)	1.651(10)	1.620(10)	C(7)−B(8)−C(9)	119.5(5)	120.9(5)
C(7)−B(11)	1.590(8)	1.587(9)	B(10)−C(9)−B(8)	97.0(5)	96.6(5)
B(8)−C(9)	1.650(10)	1.638(9)	C(9)−B(10)−B(11)	110.7(5)	110.5(5)
C(9)−B(10)	1.582(8)	1.569(8)	C(7)−B(11)−B(10)	110.1(5)	108.4(5)
B(10)−B(11)	1.747(9)	1.784(9)			

BBCBC open face, while both terminal hydrides are positioned cisoid to one another (H(1M)⋯H(2M), 2.39 Å), being, in fact, far away from either of the boron atoms of the *nido*-carborane ligand. At the same time, the crystal structure of **9** shows tight interatomic distances between two pairs of osmium-bound and boron-bound terminal hydrogen atoms, that is, between H(1M) and H(11) (1.79 Å) and H(2M) and H(10) (1.70 Å), a feature that will be discussed further in the following sections.

NMR Characterization of *exo-nido*-Osmacarboranes 5, 6, and 9. Study of Dynamic Behavior of Complex 9 in Solution. Parallel examination of the solution structures of complexes **5**, **6**, and **9** by a combination of multinuclear NMR spectroscopic methods showed that 16-electron Os(IV) formulation has to be made for all of these *exo-nido* clusters. Thus, in the ^{1}H NMR spectrum of **5**, no high-field resonance in the range between δ +0.5 and −2.5 ppm that might be attributed to the bridging B⋯H⋯B hydrogen atom was observed. However, in the upper field of this spectrum, there are two separate resonances at δ −5.85 and −13.60 ppm in a 2:1 intensity ratio, respectively. The 2H resonance at δ −5.85 ppm, due to its broad and unresolved character, was assigned to the two equivalent bridging hydrogen atoms arising from the B−H⋯Os fragments, and the 1H resonance at δ −13.60 ppm, seen as a sharp triplet with $^2J(H,P) = 30.0$ Hz, appears to be representative of the terminal osmium hydride. The line width of the latter resonance was indeed too narrow to consider the presence of even a weak bonding interaction between this terminal hydride and the adjacent boron atoms B(10) and B(11), and this fact allowed us to rule out a hypothetical 18-electron structure for complex **5**. This is also supported by the selective boron-decoupled ^{1}H-{^{11}B(10,11)} NMR spectrum of **5** where no additional sharpening of this resonance had occurred. At the same time, the broad 2H resonance at δ −5.85 ppm collapsed upon boron decoupling to a significantly sharpened doublet with $^2J(H,P) = 42.8$ Hz due, apparently, to a long-range coupling of the two equivalent B−H⋯Os bridging hydrogens to the two equivalent PPh_3 groups positioned trans to them. Accordingly, the ^{31}P{^{1}H} NMR spectrum of **5** shows a single resonance at δ 2.36 ppm, supporting the equivalence of two PPh_3 groups in this molecule. The ^{11}B{^{1}H} NMR spectrum of **5** shows a set of five resonances ranging from δ +5.0 to −21.0 ppm with the relative intensities 2:1:3:1:2. Of these resonances, one at δ +5.2 ppm, integrating as a 2B peak, was seen in the ^{11}B NMR spectrum as a broadened singlet for which no $J(B,H)$ coupling was observed, while the other four resonances were doublets showing $J(B,H)$ coupling of ca. 150−160 Hz. Due to the low chemical shift and the observed line shape, the resonance at δ +5.2 ppm was attributed to two equivalent B(10) and B(11) atoms both involved in the relatively strong[1i,12] B−H⋯Os bonding interaction in **5**. Such an assignment correlates well with the data obtained from the selective ^{1}H{^{11}B(10,11)} NMR experiment discussed previously in this paper.

In accordance with the lack of the mirror plane symmetry in the C-phenylated *nido*-carborane ligand in **6**, the ^{1}H NMR spectrum of this species displays three separate resonances in a high-field region, each of 1H relative intensity. Two of these resonances centered at δ −4.83 and −7.37 ppm due to their broad and unresolved character were readily assigned to nonequivalent B−H⋯Os bridging hydrogen atoms. The third resonance appears as a sharp doublet of doublets at δ −14.24 ppm and was, therefore, attributed to the terminal osmium hydride. The observed multiplicity of this resonance is due to coupling of the osmium hydride to the two nonequivalent, in this case, PPh_3 groups ($^2J(H,P_1) = 30.0$ Hz and $^2J(H,P_2) = 31.0$ Hz). Accordingly, the ^{31}P{^{1}H} NMR spectrum of **5** exhibits a pair of equal-intensity doublets at δ 5.88 and 0.04 ppm with $^2J(P,P) = 12.0$ Hz. The ^{11}B/^{11}B{^{1}H} spectra of **6** proved to be more complex than those of **5** displaying a set of seven partially overlapping resonances of a 1:2:1:2:1:1:1 intensity ratio.

An examination of complex **9** both by ^{1}H and ^{31}P{^{1}H} NMR spectroscopic methods provided evidence for the dynamic process occurring in this species in solution. This is shown by a series of temperature-dependent ^{1}H and ^{31}P{^{1}H} NMR spectra of **9** in the temperature range between −20 and +65 °C (Figure 3a,b), where the high-field region of the ^{1}H NMR spectrum was especially informative.

The room-temperature ^{1}H NMR spectrum of **9** in d_8-THF exhibits two separate resonances of bridging (2H, δ −6.68 ppm) and terminal (2H, δ −8.47 ppm) hydrides. Although the latter resonance might be expected to have doublet of doublets multiplicity, due to nonequivalency of the osmium-bound PPh_3 ligands in the crystal structure of **9**, at the observation temperature (+20 °C), it displays as a broad triplet-like signal, which only at −20 °C splits into the anticipated doublet of doublets with $^2J(H,P_1) = 30.7$ Hz and $^2J(H,P_2) = 22.0$ Hz. As the temperature is raised above room temperature, both bridging and terminal hydride resonances become more broadened and,

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(12) Fernandez, J. R.; Helm, G. F.; Haward, J. A. K.; Pilotti, M. U.; Stone, F. J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 1747.

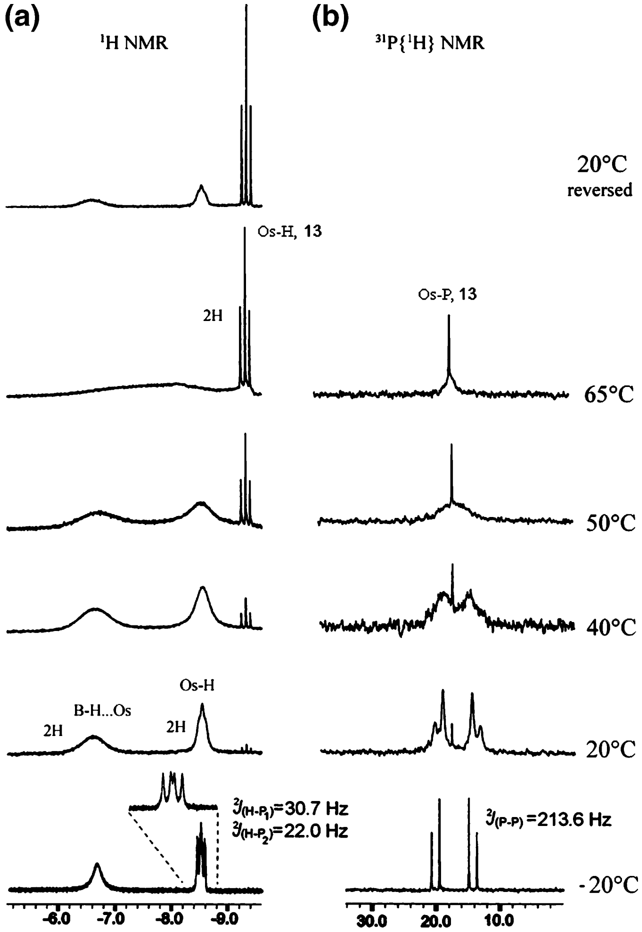
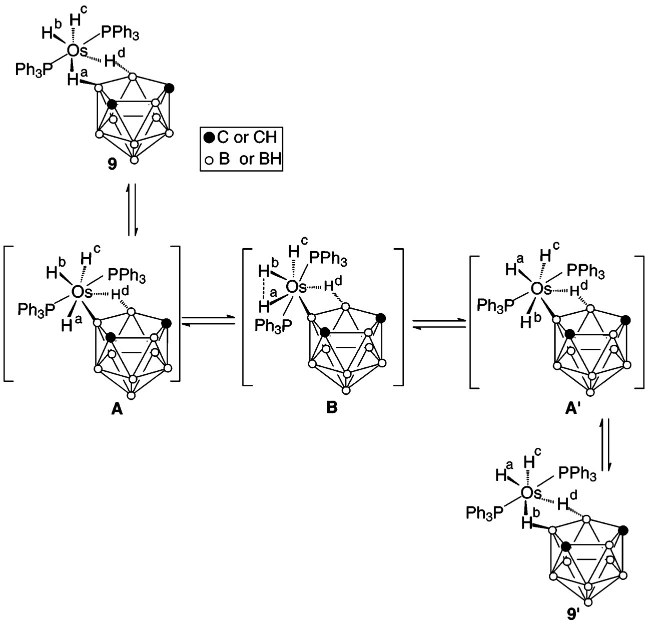


Figure 3. A series of a variable-temperature ^{1}H NMR (a) and $^{31}P\{^{1}H\}$ NMR (b) spectra for **9** from −20 to +65 °C in a d_8-THF solution (only the hydride region of the ^{1}H NMR spectrum is displayed).

at +65 °C (the highest temperature limit attained experimentally), eventually coalesce into a very broad hump, indicating that full exchange between these hydrogens does occur (Figure 3a). This hump at a higher temperature would presumably transform into the 4H sharp resonance, but this, however, was not achieved in the ^{1}H NMR experiment due to the d_8-THF boiling point limitation.

The $^{31}P\{^{1}H\}$ NMR spectrum of **9**, measured at room temperature, exhibits a broad AB quadruplet with the doublet components centered at δ ca. 20.0 and 14.0 ppm (Figure 3b). Like the variable-temperature proton spectra, the $^{31}P\{^{1}H\}$ NMR spectra of **9** in the temperature range from 0 to +65 °C exhibited the dynamic behavior resulting from an intramolecular H/H exchange process. Thus, increasing the temperature above +20 °C causes the AB pattern to broaden to give, primarily, a broad doublet resonance, in which no discernible coupling constants were observed; this doublet then merges into a broad singlet resonance. Decoalescence of this resonance occurs at −20 °C and results in the formation of a nicely resolved AB quadruplet with $^{2}J(P_1,P_2)$ coupling of 213.6 Hz. A high value of $^{2}J(P_1,P_2)$ is indicative of the PPh_3 ligands lying trans to each other, in accordance with the results of the X-ray diffraction data for **9**. We, therefore, concluded that the fluxional process occurring in a solution of **9** is frozen out, and both the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra at the observation (−20 °C) temperature represent the "static" structure of **9**.

Scheme 2. The Simplified Representation of the Reaction Pathway (One Cycle) to Give B−Os−H Oxidative Addition Products Affecting the H/H Exchange in Complex **9** in Solution



Although the two-electron, three-center B−H···M bonds in metallacarborane compounds may be highly fluxional,[1b,4a,13] so far, there are no reports on the direct spectroscopic evidence for the exchange occurring between bridging B−H···M and terminal M−H hydrides in *exo-nido*-metallacarboranes having hydrido ligands at the *exo*-positioned metal center.[1a,2e] Perhaps, very close location of both terminal and bridging hydrogen atoms H(1M) and H(11) as well as H(2M) and H(10), as it is observed in the crystal structure of **9**, may force such an unusual H/H exchange in this complex in solution. The dynamic features observed for **9** indicate that, at an earlier stage, there must be an alternating intramolecular oxidative addition of the B(10)−H···Os and B(11)−H···Os bonds, giving rise, through the formation of a new B−Os−H fragment, to a third terminal hydride at the Os center. The Os atom in such a transient trihydrido complex (species A in Scheme 2) would be seven-coordinate and adopt an entirely unfavorable high oxidation state. However, both of these negative factors in A may be relieved via coupling between two closely spaced terminal hydrides at the Os center, either H(1M) and H(11) or H(2M) and H(10), with subsequent formation of a coordinatively more favorable dihydrogen 16-electron Os(IV) intermediate (species B in Scheme 2), through which, by rapid spinning of the dihydrogen ligand or via another viable mechanism,[14] the mutual H/H exchange in **9** could be operative.

Synthesis of [*closo*-2,2-$(PPh_3)_2$-2,2-H_2-2,1,7-$OsC_2B_9H_{11}$] (13) via Thermal *exo-nido* to *closo* Rearrangement of Complex 9. Interestingly, when the high-temperature NMR experiment on complex **9** in d_8-THF was carried out, some changes were observed both in the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra and, in particular, as can be seen from Figure 3a,b, one new proton triplet at δ −9.33 ppm and a sharp phosphorus singlet

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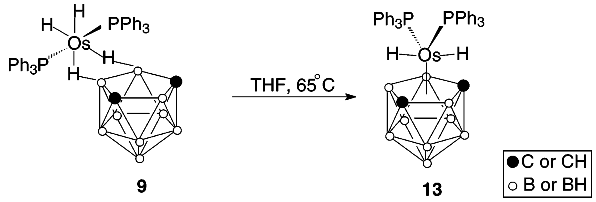
(13) (a) Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009. (b) Ellis, D. D.; Franken, A.; Jelliss, P. A.; Kautz, J. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **2000**, 2509. (c) Pisareva, I. V.; Konoplev, V. E.; Petrovskii, P. V.; Vorontsov, E. V.; Dolgushin, F. M.; Yanovsky, A. I.; Chizhevsky, I. T. *Inorg. Chem.* **2004**, *43*, 6228.

(14) Gusev, D. G.; Berke, H. *Chem. Ber.* **1996**, *129*, 1143.

Scheme 3



resonance at δ 17.90 ppm appeared in these spectra, respectively. Furthermore, once these new resonances had emerged, they could not be reversed by recooling the solution down to room temperature (Figure 3a, see the reversed ^{1}H NMR spectrum). These observations led us to believe that, during VT NMR spectroscopic experiments, an irreversible thermal conversion of **9** to produce a new PPh$_3$-containing hydrido (or dihydrido)-osmacarborane complex had occurred. Accordingly, we made an attempt to obtain this new species in a quantitative manner starting from complex **9**. It has been found that mild heating of **9** in a THF solution at 65 °C for 3.5 h, followed by column chromatography, yields white-grayish crystals in 62% yield, and this compound, on the basis of analytical, IR, and NMR spectral data, was formulated as *closo*-2,2-(PPh$_3$)$_2$-2,2-H$_2$-2,1,7-OsC$_2$B$_9$H$_{11}$ (**13**).The ^{1}H and ^{31}P{^{1}H} NMR spectra of complex **13** in CD$_2$Cl$_2$ exhibited patterns similar to those seen in the spectra of **9** in d_8-THF at a high temperature. In particular, the ^{1}H NMR spectrum showed a sharp triplet at δ −9.51 ppm with J(H,P) ~ 32 Hz, arising from two equivalent terminal metal hydrides, and a somewhat broadened singlet resonance at δ 1.23 ppm, assigned to the carborane cluster CH protons. The spectrum of **13** also contained aromatic resonances centered at δ 7.48, 7.27, and 7.22 ppm with a total 15:1 intensity ratio relative to the metal-hydride 2H resonance; these appeared as two triplet-like and one quadruplet-like multiplets and correspond to phenyl *m*-, *p*-, and *o*-protons of PPh$_3$ ligands. The ^{31}P{^{1}H} NMR spectrum of **13** in CD$_2$Cl$_2$ showed the only singlet at δ 17.65 ppm, which reflects the equivalence of the respective phosphine groups in this molecule. The ^{11}B{^{1}H} NMR spectrum of **13** revealed the presence of five somewhat-broadened resonances of relative areas 1:3:3:1:1 and was indicative of an overall C_s symmetry of complex **13**. Accordingly, the IR spectrum of **9** showed absorptions consistent with the presence of a carborane unit (ν 2549 cm^{-1}) and terminal metal hydrides (2166, 2096 cm^{-1}) in the molecule.

Since little attention has been given in the literature to *closo*-hydrido-osmacarborane clusters[15] and no examples with the carbons-apart {*nido*-7,9-C$_2$B$_9$} ligands were reported, a single-crystal X-ray diffraction study of **13** has been undertaken. This study confirmed the *closo* structure of **13** and made clear some details of its cluster geometry and the arrangement of ligands at the metal vertex. Figure 4 depicts the molecular structure of **13** with selected bond lengths and angles. The dicarbollide [*nido*-7,9-C$_2$B$_9$H$_{11}$]$^{2-}$ ligand is bound to the metal atom in an η^5-fashion with osmium-to-boron/carbon (upper belt) distances ranging from 2.222(8) to 2.318(7) Å. As expected, the Os atom is additionally coordinated to two PPh$_3$ ligands (Os−P(1) 2.316(2), Os−P(2) 2.329(2) Å) and two terminal hydrides (Os−H(1M) 1.67, Os−H(2M) 1.56 Å); the terminal hydride atoms were located in **13** from difference Fourier maps, and their position proved to be nearly symmetrical between two PPh$_3$ groups. Thus, **13** can be regarded as a neutral seven-coordinated Os(IV) complex in which the osmium atom has the stable 18-electron configuration. At present, a few metallacarborane complexes with seven-coordinate Os(IV)[15] and Ru(IV),[16] closely related to **13**, are known, and among these, one species, [*closo*-2,2-(PPh$_3$)$_2$-2,2-H$_2$-2,1,7-RuC$_2$B$_9$H$_{11}$], studied long ago by Hawthorne and co-workers,[16b] happens to be the ruthenium congener of **13**.

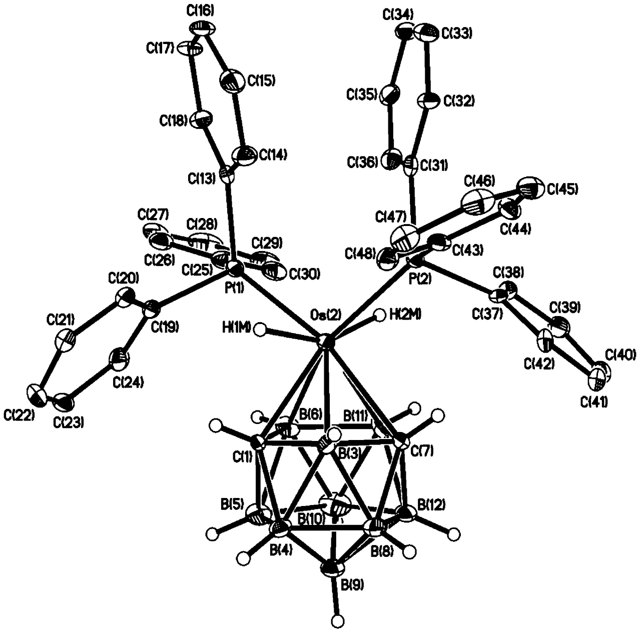


Figure 4. ORTEP representation of the molecular structure with the numbering scheme for complex **13**; ellipsoids are drawn at the 30% probability level (hydrogen atoms of the phenyl substituents are omitted for clarity). Selected bond lengths (Å): Os(2)−P(1) 2.316(2), Os(2)−P(2) 2.329(2), Os(2)−H(1M) 1.67, Os(2)−H(2M) 1.56, Os(2)−C(1) 2.248(7), Os(2)−C(7) 2.318(7), Os(2)−B(3) 2.269(8), Os(2)−B(6) 2.222(8), Os(2)−B(11) 2.283(9), C(1)−B(3) 1.714(11), C(1)−B(6) 1.725(11), B(3)−C(7) 1.690(11), C(7)−B(11) 1.690(12), B(6)−B(11) 1.831(13).

A facile thermal *exo-nido* to *closo* conversion of **9** should be associated directly with its fluxionality in solution. Clearly, the isomerization reaction would proceed through intermediates similar in nature to the 16-electron Os(IV) species **A** and/or **A′** (Scheme 2), in which the osmium-containing moiety interacts with the *nido*-carborane ligand via one labile B−H···Os bond and a σ-bond Os−B. Taking into account that these *exo-nido* precursors do not have *endo*-hydrogen atoms on their CBCBB open face, it is reasonable to assume that, upon warming, they would easily undergo the $\eta^1 \rightarrow \eta^5$ rearrangement with the shift of the osmium-containing moiety from the *exo* to *closo* position on the pentagonal face of the carborane cage, and simultaneous transfer of the terminal osmium hydride in **A**/**A′** to a cluster BH hydrogen position would be the most probable last step, completing the *exo-nido* to *closo* rearrangement of **9**.

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[15] Chizhevsky, I. T.; Petrovskii, P. V.; Sorokin, P. V.; Bregadze, V. I.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T. *Organometallics* **1996**, *15*, 2619.

[16] (a) Wong, E. H. S.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1976**, 257. (b) Wong, E. H. S.; Hawthorne, M. F. *Inorg. Chem.* **1978**, *17*, 2863. (c) Chizhevsky, I. T.; Lobanova, I. A.; Bregadze, V. I.; Petrovskii, P. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T. *Organomet. Chem. USSR (Engl. Transl.)* **1991**, *4*, 469. (d) Cheredilin, D. N.; Dolgushin, F. M.; Grishin, I. D.; Kolyakina, E. V.; Nikiforov, A. S.; Solodovnikov, S. P.; Il'in, M. M.; Davankov, V. A.; Chizhevsky, I. T.; Grishin, D. F. *Russ. Chem. Bull.* **2006**, *55*, 1163.

Table 2. Crystal Data, Data Collection, and Structure Refinement Parameters for **5**, **9**, and **13**

complex	**5**	**9**	**13**
formula	$C_{38}H_{42}B_9ClP_2Os$	$C_{38}H_{43}B_9P_2Os$	$C_{38}H_{43}B_9P_2Os$
molecular weight	883.60	849.15	849.15
crystal color, habit	purple prism	green prism	colorless plate
temperature, K	193(2)	295(2)	120(2)
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	11.216(4)	12.819(3)	9.5182(9)
b, Å	12.711(6)	12.963(3)	10.124(1)
c, Å	14.318(5)	13.787(3)	19.786(2)
α, deg	95.62(3)	75.405(16)	80.437(2)
β, deg	106.15(3)	62.997(15)	78.666(2)
γ, deg	91.10(3)	69.875(16)	80.784(2)
V, Å^3	1948.8(13)	1904.0(8)	1827.3(3)
Z	2	2	2
d(calcd), g cm^{-3}	1.506	1.481	1.543
diffractometer	Syntex P21	Siemens P3/PC	SMART 1000
scan mode	$\theta-2\theta$	$\theta-2\theta$	ω
θ_{max}, deg	25.0	28.0	28.0
μ(Mo Kα, λ=0.71073 Å), cm^{-1}	34.50	34.60	36.06
T_{min}/T_{max}	0.791/1.303	0.580/0.745	0.362/0.869
no. unique reflections (R_{int})	6780 (0.0000)	9178 (0.0654)	8712 (0.0653)
no. observed reflections ($I > 2\sigma(I)$)	5526	6695	6042
R_1 (on F for observed reflections)[a]	0.0391	0.0589	0.0585
wR_2 (on F^2 for all reflections)[b]	0.0908	0.0865	0.1194
GOF	1.020	1.065	0.887
largest diff peak and hole, e/Å^3	1.010/−1.313	1.059/−0.654	2.821/−2.576
	near Os(1)	near Os(1)	near Os(2)

[a] $R_1 = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$. [b] w$R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

Conclusion

In this paper, the syntheses of a short series of novel 16-electron *exo-nido*-osmacarboranes of the general formula [*exo-nido*-10,11-{$(Ph_3P)_2Os^{IV}HX$}-10,11-(μ-H)$_2$-7-R-7,9-$C_2B_9H_8$] (**5**: R = H, X = Cl; **6**: R = Ph, X = Cl; **9**: R = X = H) have been described. Structural studies carried out for two of these complexes, **5** and **9**, revealed that the carbons-apart [*nido*-7,9-$C_2B_9H_{10}$]$^{2-}$ dianion behaves in these species as a bidentate ligand and forms two 2e,3c B−H···Os bonds, both involving B−H vertices situated in the upper CBCBB belt of the cage ligand. In solution, complex **9** proved to be fluxional, showing H/H exchange between both terminal Os−H_2 and bridging {B−H}$_2$···Os hydrogen atoms, and this dynamic process can clearly be monitored via VT ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. It is important to note that this particular type of dynamic behavior (bridging-to-terminal hydrogen exchange) has not previously been observed within this category of *exo-nido*-metallacarborane complexes. We have also demonstrated that the *exo-nido* complex **9**, upon warming, undergoes irreversible rearrangement giving rise to the *closo* isomer [*closo*-2,2-(PPh$_3$)$_2$-2,2-H$_2$-2,1,7-OsC$_2$B$_9$H$_{11}$], **13**, whose structure was established by X-ray crystallography.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere using standard vacuum line techniques. THF was distilled from sodium/benzophenone under an argon atmosphere prior to use. All other solvents, including those used for column chromatography as eluents, were also distilled from appropriate drying agents prior to use. Starting reagents **3**[17] and both [K]$^+$ salts of anions **2**[18] and **4**[18] were prepared according to the published methods. Short chromatography columns packed with silica gel (Merck, 230−400 mesh) were used for separation and purification of the reaction products, and these were carried out under an argon atmosphere. The ^{1}H, ^{1}H{^{11}B}, ^{31}P{^{1}H}, and ^{11}B/^{11}B{^{1}H} NMR as well as VT NMR measurements were performed with a Bruker AMX-400 (^{1}H at 400.13 MHz; ^{31}P at 161.98 MHz; ^{11}B at 128.33 MHz) instrument using either TMS as an internal reference or 85% H_3PO_4 and BF_3·Et_2O as external references, respectively. IR spectra were obtained on a Carl−Zeiss M-82 spectrometer. Elemental analyses for all new compounds were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the Russian Academy of Sciences.

Preparation of [*exo-nido*-10,11-{(Ph$_3$P)$_2$OsHCl}-10,11-(μ-H)$_2$-7,9-C$_2$B$_9$H$_9$] (5). To a mixture of freshly prepared osmium reagent **3** (0.15 g, 0.143 mmol) and the [K]$^+$ salt of anion **2** (0.035 g, 0.2 mmol) flushed with argon was added 15 mL of the degassed C_6H_6, and the resulting solution was stirred at room temperature for 1.5 h until the color of solution became dark purple. The solvent was reduced under vacuum to approximately one-third, and the residue was treated by column chromatography on silica gel. The band that contained crude zwitterionic *nido*-carborane **7** and traces of green complex **9** was eluted first with C_6H_6. This material, after evaporation of solvent under vacuum and crystallization of the residue from CH_2Cl_2/*n*-hexane, afforded 0.019 g of NMR spectroscopically pure yellowish-white crystals of **7**. ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.72−7.57 (m + m, 15H, Ph), 1.88 (s br, 1H, CH$_{carb}$), 1.69 (s br, 1H, CH$_{carb}$), −1.1 (s v-br, 1H, B−H−B). ^{31}P{^{1}H} NMR (CD_2Cl_2, 22 °C): δ +5.54 (q-like m, ^1J(P,B) = 130 Hz). The second purple band containing complex **5** was eluted next with a mixture of C_6H_6/CH_2Cl_2 (4:1). Removal of solvent under vacuum followed by crystallization from CH_2Cl_2/*n*-hexane yielded 0.07 g (56% yield) of analytically pure complex **5** as a purple crystalline solid. IR (KBr, cm^{-1}): 2576 (ν_{B-H}). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.20−6.82 (m, 30H, PPh$_3$), 3.03 (s br, 2H, CH$_{carb}$), −5.85 (s v-br, 2H, (BH)$_2$···Os), −13.6 (t, 1H, ^2J(H,P) = 30 Hz, Os−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 22 °C): δ 2.36 (s, P(1,2)). ^{1}H{^{31}P} NMR (CD_2Cl_2, 22 °C, negative zone): δ −5.85 (s v-br, 2H, (BH)$_2$···Os), −13.6 (s, 1H, Os−H). ^{11}B NMR (CD_2Cl_2, 22 °C, J = J(B,H), Hz): δ 5.2 (s br, 2B, B(10,11)), −0.4 (d, 1B, J = 160 Hz), −7.4 (d, 3B, J = 151 Hz), −16.4 (d, 1B, J = 148 Hz), −20.3 (d, 2B, J = 157 Hz). Selective ^{1}H{^{11}B(10,11)} NMR (CD_2Cl_2, 22 °C, negative zone): δ −5.85 (d, 2H, ^2J(H,P) = 42.8 Hz, (BH)$_2$···Os), −13.6 (t, 1H, ^2J(H,P) = 30.0 Hz, Os−H). Anal. Calcd for $C_{38}H_{42}B_9ClP_2Os$: C, 51.66; H, 4.76; B, 11.01; Cl, 3.70. Found: C, 51.83; H, 4.75; B, 11.21; Cl, 3.82.

Preparation of [*exo-nido*-10,11-{(Ph$_3$P)$_2$OsHCl}-10,11-(μ-H)$_2$-7-Ph-7,9-C$_2$B$_9$H$_8$] (6). The complex was synthesized from **3** (0.15 g, 0.143 mmol) and the [K]$^+$ salt of anion **4** (0.05 g, 0.2 mmol) in 15 mL of C_6H_6 using similar reaction conditions and purification procedure as those for **5**; 0.085 g (62% yield) of complex **6** was thus obtained. IR (KBr, cm^{-1}): 2564 (ν_{B-H}). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.80−6.60 (m, 35H, PPh$_3$ + Ph), 2.26 (s br, 1H, CH$_{carb}$), −4.83 (s v-br, 1H, BH···Os), −7.37 (s v-br, 1H, BH···Os), −14.24 (dd, 1H, ^2J(H,P(1)) = 30.0 Hz, ^2J(H,P(2)) = 31.0 Hz, Os−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 22 °C): δ 5.88 (d, ^2J(P,P) = 12 Hz, P(1)), 0.04 (d, ^2J(P,P) = 12 Hz, P(2)). ^{11}B NMR (CD_2Cl_2, 22 °C, J = ^1J(B,H), Hz): δ 8.2 (s br, 1B),

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(17) Oudeman, A.; Van Rantwijk, F.; Van Bekkum, H. *J. Coord. Chem.* **1974**, *4*, 1.

(18) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Werner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862.

1.35 (d, 2B, $J = 128$ Hz), −5.2 (s br, 1B), −7.3 (d, 2B, $J = 150$ Hz), −14.2 (d, 1B, $J = 165$ Hz), −15.7 (d, 1B, $J = 165$ Hz), −20.7 (d, 1B, $J = 145$ Hz). Anal. Calcd for $C_{44}H_{46}B_9ClP_2Os$: C, 55.07; H, 4.80; B, 10.14; P, 6.47; Os, 19.81. Found: C, 54.89; H, 4.87; B, 10.32; P, 6.54; Os, 20.06. A small amount (0.016 g) of zwitterionic compound **8** was also obtained; its structure is deduced from analysis of its ^{1}H and $^{31}P\{^1H\}$ spectra. ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.72−7.58 (m + m, 15H, PPh_3), 7.43 (m, 2H, Ph−H(2,6)), 7.15 (m, 2H, Ph−H(3,5)), 7.06 (m, 1H, Ph−H(4)), 1.84 (s br, 1H, CH_{carb}), −0.47 (s v-br, 1H, B−H−B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 5.69 (q-like m, ^1J(P,B) = 122 Hz).

Preparation of [*exo-nido*-10,11-{$(Ph_3P)_2OsH_2$}-10,11-(μ-H)$_2$-7,9-$C_2B_9H_9$] (9). To a mixture of **3** (0.2 g, 0.19 mmol) and the $[K]^+$ salt of anion **2** (0.04 g, 0.23 mmol) flushed with argon was added 15 mL of absolute ethanol, and the resulting suspension was heated under stirring at 55−60 °C for 2.5 h and then for 15 min at 70 °C until the suspension became dark green. After cooling, the ethanol was evaporated under reduced pressure, and its traces were removed under high vacuum. The resulting residue was dissolved in 1.5 mL of the degassed CH_2Cl_2, and the solution was then treated by column chromatography on silica gel. The grayish-green band eluted from the column using benzene was found to contain crude **9**. This solution was repeatedly chromatographed on a smaller silica gel column using the same solvent as the eluent to afford **9** as solid (0.11 g, 68% yield), which after recrystallization from CH_2Cl_2/*n*-hexane at −5 °C, gave dark-green microcrystals of analytically pure sample. IR (KBr, cm^{-1}): 2565 (ν_{B-H}), 2066, 2037 (ν_{M-H}). ^{1}H NMR (−20 °C): δ 7.61−7.45 (m, 30H, PPh_3), 3.64 (s br (partially overlapped), 2H, CH_{carb}), −6.68 (s br, 2H, $(BH)_2\cdots$Os), −8.47 (dd, 2H, ^2J(H,P(1)) = 30.7 Hz, ^2J(H,P(2)) = 22.0 Hz, Os−H_2). $^{31}P\{^1H\}$ NMR (d_8-THF, $J = {}^2J$(P,P), Hz, −20 °C): δ 20.0 (d, $J = 213.6$ Hz, P(1)), 14.0 (d, $J = 213.6$ Hz, P(2)). $^{11}B\{^1H\}$ NMR (d_8-THF, 22 °C) [$^1H\{^{11}B\}$]: δ 10.9 (2B) [−6.68, s br], −7.4 (4B) [+0.75, +2.1, +2.35 (2H)], −15.4 (1B) [+1.2], −19.6(2B) [1.4]. Anal. Calcd for $C_{38}H_{43}B_9P_2Os$: C, 53.78; H, 5.07; B, 11.46; P, 7.31; Os, 22.30. Found: C, 53.92; H, 5.19; B, 11.58; P, 7.40; Os, 21.92.

Preparation of [*closo*-2,2-$(PPh_3)_2$-2,2-H_2-2,1,7-$OsC_2B_9H_{11}$] (13). Complex **9** (0.12 g, 0.142 mmol) was dissolved in 10 mL of THF and then heated in oil bath at 64−65 °C with stirring. For monitoring of the occurring process by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy, a parallel experiment with a sample of **9** in 0.7 mL of d_8-THF in the sealed NMR tube was carried out. The reaction was monitored by both ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopic methods every hour over the time of heating. After ca. 3.5 h, an initially dark-green solution turned colorless, and resonances of the starting compound **9** were no longer observed. After this time, the reaction mixture was evacuated to dryness. The residue was purified by chromatography using a small silica gel column (1,2 × 10 cm) and eluting a colorless fraction with benzene. Evaporation of the solvent and crystallization of the residue from C_6H_6/*n*-hexane (3:1) under conditions where slow evaporation of *n*-hexane at room temperature occurs afforded 0.088 g (62%) of analytically pure grayish-white crystals of **13**. IR (KBr, cm^{-1}): 2549 (ν_{B-H}), 2166, 2096 (ν_{M-H}). ^{1}H NMR (d_8-THF, 22 °C): δ 7.50 (t-like m, 12H, Ph−H(3,5)), (q-like m, 18H, Ph−H(2,4,6)), 3.01 (s br, H_2O (small solv. imp.)), 1.34 (s br, 2H, CH_{carb}), −9.33 (t, 2H, ^2J(H,P) = 32.0 Hz, Os−H_2). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.48 (t-like, 12H, J(H,H) = 8.5 Hz, Ph−H(3,5)), 7.27 (q, 6H, ^3J(H,P) = 14 Hz, J(H,H) = 7 Hz, Ph−H(4)), 7.22 (q, 12H, ^3J(H,P) = 13 Hz, J(H,H) = 6.5 Hz, Ph−H(2,6)), 1.23 (s br, 2H, CH_{carb}), −9.51 (t, 2H, ^2J(H,P) = 31.8 Hz, Os−H_2). $^{31}P\{^1H\}$ NMR (d_8-THF, 22 °C): δ 17.90 (s, P(1,2)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 17.65 (s, P(1,2)). $^{11}B\{^1H\}$ NMR (d_8-THF, 22 °C): δ 3.5 (s v-br, 1B), −10.5 (s v-br, 2B), −13.4 (s v-br, 2B), −14.4(s v-br, 2B), −17.7 (s v-br, 1B), −18.7 (s v-br, 1B). Anal. Calcd for $C_{38}H_{43}B_9P_2Os$: C, 53.76; H, 5.07; B, 11.01; P, 7.31. Found: C, 54.01; H, 4.97; B, 10.89; P, 7.28.

X-ray Structure Determination of Complexes 5, 9, and 13. Details of the crystal data, data collection, and structure refinement parameters for compounds **5**, **9**, and **13** are given in Table 2. The data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms at the carborane cages, including all hydride ligands, were located from the Fourier synthesis; the remaining hydrogen atoms were placed geometrically. All hydrogen atoms in **5**, **9**, and **13** were included in the structure factor calculations in the riding motion approximation. SHELXTL-97 program packages[19] were used throughout the calculations.

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Supporting Information Available: CIF files giving X-ray crystallographic data for complexes **5**, **6**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Sheldrick, G. M. *SHELXTL-97*, version 5.10; Bruker AXS Inc.: Madison, WI, 1997.