Inorg. Chem. **2004**, *43*, 6067–6074

Synthesis, Characterization, and Dynamic Studies of 12-Vertex η^5-Ruthenium(II) *closo*-Phosphine Complexes with Monoanionic [10-L-*nido*-7-R-7,8-$C_2B_9H_9$]$^-$ Ligands

O. Tutusaus, R. Núñez, C. Viñas,* F. Teixidor,* I. Mata, and E. Molins

Institut de Ciència de Materials de Barcelona, CSIC, Campus UAB, 08193 Bellaterra, Spain

Received May 25, 2004

Ruthenacarborane complexes of formula [3-H-3,3-$(PPh_3)_2$-8-L-*closo*-3,1,2-$RuC_2B_9H_{10}$)] (L = SMe_2 (**2a**), SEt_2 (**2b**), $S(CH_2)_4$ (**2c**), SEtPh (**2d**)) and [1-Me-3-H-3,3-$(PPh_3)_2$-8-L-*closo*-3,1,2-$RuC_2B_9H_9$)] (L = SMe_2 (**2e**), SEt_2 (**2f**)) were prepared by reaction of the respective monoanionic charge-compensated ligands [10-L-*nido*-7,8-$C_2B_9H_{10}]^-$ and [7-Me-10-L-*nido*-7,8-$C_2B_9H_9]^-$ with $[RuCl_2(PPh_3)_3]$. Similary, complexes [3-H-3,3,8-$(PPh_3)_3$-*closo*-3,1,2-$RuC_2B_9H_{10}$)] (**4a**) and [3-H-3,3-$(PPh_3)_2$-8-PPh_2Me-*closo*-3,1,2-$RuC_2B_9H_{10}$)] (**4b**) were prepared from the corresponding phosphonium ligands. The reaction is done in one pot by reacting the ligand with the Ru(II) complex in a 1.5:1 ratio. All compounds have been fully characterized by multinuclear NMR spectroscopy, and the molecular structures for **2a** and **4a** have been elucidated by single-crystal X-ray diffraction analysis. The Ru(II) atom in this complex is on the open face of the monoanionic charge-compensated ligand adopting a pseudooctahedral coordination. Formally, three positions are supplied by the C_2B_3 open face, two PPh_3 groups occupy two other positions, and a hydride fulfills the remaining one. The hydride complexes were generated with no special reagent. They result from a dehalogenation in the presence of ethanol.

Introduction

First examples of metallacarboranes were prepared about 35 years ago by Hawthorne et al., using the dicarbollide, $[C_2B_9H_{11}]^{2-}$, as ligand to form *closo*-MC_2B_9 icosahedral clusters.[1] This ligand has been compared to $[C_5H_5]^-$, as both behave as formal 6-electron donors[2] to metal atoms via η^5-face bonding. Thus, a great number of researchers from a variety of scientific backgrounds have developed this field.[3] However, both type of ligands differ in their charges. To establish detailed comparisons between analogous cyclopentadienyl−metal and carborane−metal compounds, charge-compensated monoanionic carborane ligands of the type $[LC_2B_9H_{10}]^-$ (L = pyridine, THF, SR_2, PPh_3, etc) have been described.[4] Many transition metal (Rh, Fe, Pd, Mo, etc.) complexes of these monoanionic carboranes have been prepared and fully characterized.[3c,4−7] The majority of these charge-compensated complexes contain the carborane ligands with the substituent at the 9 position, [9-L-*nido*-7,8-$C_2B_9H_{10}]^-$ or [9-L-*nido*-7,8-R_2-$C_2B_9H_8]^-$. Ligands with the substituent at the 10 position, [10-L-*nido*-7,8-$C_2B_9H_{10}]^-$,[4c,5g] have been much less studied. The preparation of *closo* metalla complexes with monoanionic charge-compensated

* Author to whom correspondence should be addressed. E-mail: clara@icmab.es.

(1) (a) Hawthorne, M. F.; Young, D. C.; P. Wegner, A. *J. Am. Chem. Soc.* **1965**, *87*, 1818. (b) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879. (c) Hawthorne, M. F. *Pure Appl. Chem.* **1972**, *29*, 547. (d) Hawthorne, M. F. *Pure Appl. Chem.* **1973**, *33*, 475. (e) Callahan K. P.; Hawthorne, M. F. *Adv. Organomet. Chem.* **1976**, *14*, 145.

(2) Mingos, D. M. P. *J. Chem. Soc, Dalton Trans.* **1977**, 602.

(3) (*a*) *Contemporary Boron Chemistry*; Davidson, M., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000. (*b*) *Advances in Boron Chemistry*; Siebert, W. E., Ed.; Royal Society of Chemistry: Cambridge, U.K. 1997. (*c*) *Boron chemistry at the beginning of the 21st century published by the Russian*; Bubnov, Y. N., Ed.; Nauka (Science): Moscow, 2003. (d) *The Borane-Carborane-Carbocatiom Continuum*; Casanova, J., Ed.; Wiley-Interscience: New York, 1998. (e) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, England, 1995; Vol 1. (f) Housecroft, C. E. *Specialist Periodical Reports in Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Eds.; Royal Society of Chemistry: London, 1991. (g) Saxena, A. K.; Maguire J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, *97*, 2421.

(4) (a) Tebbe, F. N.; Garret P. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 869. (b) Young, D. C.; Howe D. V.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 859. (c) Plešek, J.; Zbyn_k, J.; He_mánek, S. *Collect. Czech. Chem. Commun.* **1978**, *43*, 2862. (d) Kang, H. C.; Lee, S. S.; Knobler C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2024. (e) Plešek, J.; Jelínek, T.; Mareš, F.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1993**, *58*, 1534. (f) Rosair, G. M.; Welch, A. J.; Weller A. S.; Zahn, S. K. *J. Organomet. Chem.* **1997**, *536*, 299. (g) Dunn, S.; Garrioch, R. M.; Rosair, G. M.; Smith, L.; Welch, A. J. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1013. (h) Tutusaus, O.; Teixidor, F.; Núñez, R.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *J. Organomet. Chem.* **2002**, *657*, 247.

10.1021/ic049322k CCC: $27.50
Published on Web 08/24/2004

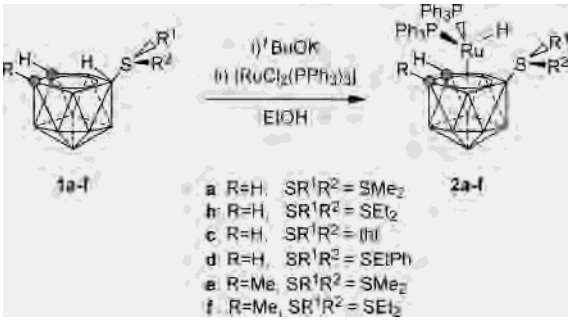
carborane ligands bearing an SR_2 or PR_3 group at the B(9) atom has been accomplished using two methods. The first one, generally used for [9-SMe_2-*nido*-7,8-R_2-7,8-$C_2B_9H_8$]$^-$ ligands, consists of the addition of the thallium salts of the ligand to a solution of the metalla complex in CH_2Cl_2.[6] The second method consists of the deprotonation of the charge-compensated carborane ligand with KOH or NaH in a solvent at reflux for several hours, followed by treatment with a convenient source of metal.[3c,5,7a−b] The latter has also been used to prepare the few known complexes of [10-L-*nido*-7,8-$C_2B_9H_{10}$]$^-$ ligands with Co, Mo, and Fe.[4c,g,5g]

We describe here the first systematic study of the preparation of a series of Ru(II) metallacarborane complexes incorporating the monoanionic charge-compensated ligands [10-L-*nido*-7-R-7,8-$C_2B_9H_9$]$^-$ (L = SMe_2, SEt_2, $S(CH_2)_4$, SEtPh, PPh_3, PPh_2Me; R = H, Me). A new and rapid method involving a one-pot reaction is described to synthesize the complexes in pure form. The aim in designing and preparing these complexes was their potential use as catalytic precursors for cyclopropanation, controlled radical polymerization, ATRP, and Kharasch addition reactions. Some results about their catalytic activity have already been published by us.[8] Crystal structures of [3-H-3,3-$(PPh_3)_2$-8-SMe_2-*closo*-3,1,2-$RuC_2B_9H_{10}$] and [3-H-3,3,8-$(PPh_3)_3$-*closo*-3,1,2-$RuC_2B_9H_{10}$] are also described.

Results

Synthesis and Characterization of [3-H-3,3-$(PPh_3)_2$-8-L-*closo*-3,1,2-$RuC_2B_9H_{10}$)] and [1-Me-3-H-3,3-$(PPh_3)_2$-8-L-*closo*-3,1,2-$RuC_2B_9H_9$)] (L = SMe_2, SEt_2, $S(CH_2)_4$, SEtPh). The reaction of 10-L-*nido*-7,8-$C_2B_9H_{11}$ (L = SMe_2 (**1a**), SEt_2 (**1b**), $S(CH_2)_4$ (**1c**), SEtPh (**1d**)) with K[*t*-BuO] and $[RuCl_2(PPh_3)_3]$ in 1.5/1.5/1 ratio in EtOH, at 50 °C for 1 h, resulted in the formation of yellow solids of general formula [3-H-3,3-$(PPh_3)_2$-8-L-*closo*-3,1,2-$RuC_2B_9H_{10}$)] (L = SMe_2 (**2a**), SEt_2 (**2b**), $S(CH_2)_4$ (**2c**), SEtPh (**2d**)), in yields ranging 85−95%. For the asymmetric ligands, 7-Me-10-L-*nido*-7,8-$C_2B_9H_{10}$ (L = SMe_2 (**1e**), SEt_2 (**1f**)), orange compounds of general formula [1-Me-3-H-3,3-$(PPh_3)_2$-8-L-*closo*-3,1,2-$RuC_2B_9H_9$)] (L = SMe_2 (**2e**), SEt_2 (**2f**)) were obtained. The reaction is depicted in Scheme 1.

Scheme 1. Formation of [1-R-3-H-3,3-$(PPh_3)_2$-8-SR^1R^2-*closo*-3,1,2-$RuC_2B_9H_{10}$]



The spectroscopic data and elemental analyses of **2a**−**f** were consistent with the proposed formula. The IR spectra of these complexes displayed a ν(B−H) absorption, between 2522 and 2576 cm^{-1}. Low-intensity bands were observed in the region 1960−2100 cm^{-1} attributable to ν(Ru−H).[5c] The absorptions at 1433, 1096, 744, and 695 cm^{-1} are typical of PPh_3-containing compounds. The ^{1}H NMR spectra for compounds **2a**−**f** showed no resonances attributable to B−H−B, near −1 ppm, indicating the formation of *closo* species.[4h] Resonances assigned to Ru−H were found ca. −10.30 ppm for compounds **2a**−**d** and near −12.10 ppm for **2e**,**f**. These Ru−H resonances present different coupling patterns as a function of the symmetry of the molecule (Figure 1). In the case of symmetric compounds **2a**−**c**, they appear as a triplet (^2J(P, H) = 33−34 Hz) (Figure 1a); however, for the asymmetric compounds **2d**−**f** the signal appears as a doublet of doublets with two different ^2J(P, H) (Figure 1b).[5c,e] Hydrogen atoms on the sulfonium groups are given in Table 1 for complexes **2a**−**f**. The $C_{cluster}$−H resonances for compounds **2a**−**c** appear as a singlet around 2.17 ppm, while the $C_{cluster}$−H proton of the **2e**,**f** ones is observed at 2.21 ppm. Compound **2d**, with nonequivalent substituents on sulfur, displays two $C_{cluster}$−H signals at 2.56 and 1.75 ppm whose average value is comparable to the $C_{cluster}$−H chemical shift for **2a**−**c**. The $^{13}C\{^1H\}$ NMR spectra for **2a**−**f** display resonances corresponding to the organic groups bonded to the sulfur and/or phosphorus atoms. The $^{11}B\{^1H\}$ spectra for **2a**−**f** was in agreement with the proposed symmetry; in all complexes the resonance at lower field was assigned to the sulfur-bearing atom B(8) by comparison with the ^{11}B NMR spectra. The $^{31}P\{^1H\}$ NMR spectra for **2a**−**c** display singlets in agreement with the

(5) (a) Wong E. H. S.; Hawthorne, M. F. *Inorg. Chem.* **1978**, *17*, 2863. (b) Teller, R. G.; Wilczynski J. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 472. (c) Marder, T. B.; Baker, R. T.; Long, J. A.; Doi, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 2988. (d) King, R. E., III; Miller, S. B.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3548. (e) Kang, H. C.; Do, Y.; Knobler C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 6530. (f) Kang, H. C.; Do, Y.; Knobler C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 1716. (g) Plesek, J.; Stibr, B.; Cooke, P. A.; Kennedy, J. D.; McGrath T. D.; Thorton, P. *Acta Crystallogr.* **1998**, *C54*, 36.

(6) (a) Hamilton E. J. M.; Welch, A. J. *Acta Crystallogr.* **1990**, *C46*, 1228. (b) Hamilton E. J. M.; Welch, A. J. *Polyhedron* **1991**, *10*, 471. (c) Douek, N. L.; Welch, A. J. *J. Chem. Soc, Dalton Trans.* **1993**, 1917. (d) Dunn, S.; Rosair, G. M.; Weller A. S.; Welch, A. J. *Chem. Commun.* **1998**, 1065. (e) Rosair, G. M.; Welch A. J.; Weller, A. S. *Organometallics* **1998**, *17*, 3227. (f) Boyd, A. S. F.; Rosair, G. M.; Tiarks, F. B. H.; Weller, A. S.; Zahn, S. K.; Welch, A. J. *Polyhedron* **1998**, *17* (16), 2627.

(7) (a) Yan, Y.-K.; Mingos, D. M. P.; Müller, T. E.; Williams, M.; Kurmoo, J. *J. Chem. Soc., Dalton Trans.* **1994**, 1735. (b) Yan, Y.-K.; Mingos, D. M. P.; Müller, T. E.; Williams, M.; Kurmoo, J. *J. Chem. Soc., Dalton Trans.* **1995**, 2509. (c) Kudinov, A. R.; Meshcheryakov, V. I.; Petrovskii, P. V.; Rybinskaya, M. I. *Izv. Akad. Nauk. Ser. Khim.* **1999**, 177 [*Russ. Chem. Bull.* **1999**, *48*, 176 (English translation)]. (d) Kudinov, A. R.; Petrovskii, P. V.; Meshcheryakov, V. I.; Rybinskaya, M. I. *Izv. Akad. Nauk. Ser. Khim.* **1999**, 1368 [*Russ. Chem. Bull.* **1999**, *48*, 1356 (English translation)]. (e) Kudinov, A. R.; Meshcheryakov, V. I.; Petrovskii, P. V.; Rybinskaya, M. I. *Izv. Akad. Nauk. Ser. Khim.* **1999**, 1817 [*Russ. Chem. Bull.* **1999**, *48*, 1794 (English translation)]. (f) Kudinov, A. R.; Perekalin, D. S.; Petrovskii, P. V.; Lyssenko, K. A.; Grintselev-Knyazev, G. V.; Starikova, Z. A. *J. Organomet. Chem.* **2002**, *657*, 115.

(8) (a) Tutusaus, O.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Núñez, R.; Viñas, C.; Teixidor, F. *Tetrahedron Lett.* **2002**, *43*, 983. (b) Tutusaus, O.; Delfosse, S.; Simal, F.; Demonceau, A.; Noels, A. F.; Núñez, R.; Viñas, C.; Teixidor, F. *Inorg. Chem. Commun.* **2002**, *5*, 941−945. (c) Tutusaus, O.; Viñas, C.; Núñez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Noels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, *125*, 11830. (d) Tutusaus, O.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Viñas, C.; Teixidor, F. *Tetrahedron Lett.* **2003**, *44*, 8421.

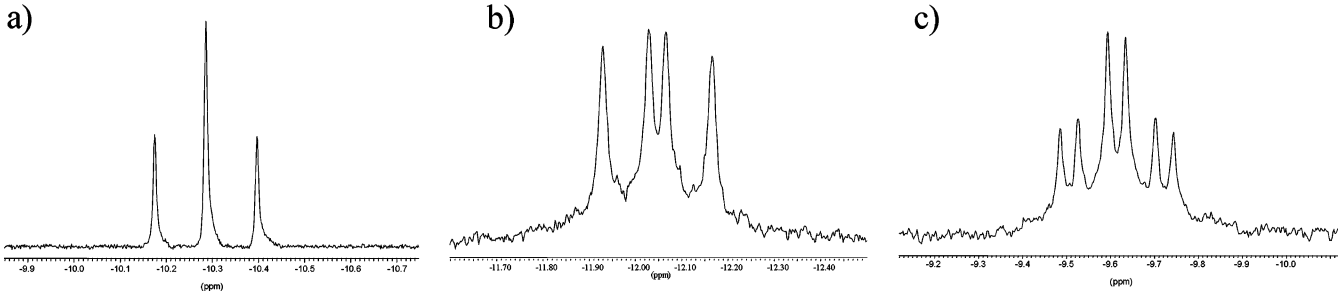


Figure 1. Selected ^{1}H NMR portion corresponding to the hydride region in (a) compound **2b**, (b) compound **2d**, and (c) compound **4a**.

Table 1. Chemical Shift of the Protons Corresponding to the Substituent on B(10) for Complexes **2a**−**f**

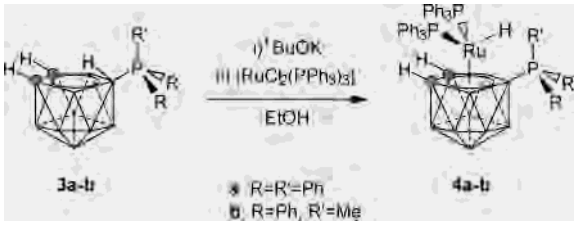
	$\delta(^1H)$ (ppm)[a]		
complexes	CH_3	SCH_2−	CH_2
2a	2.28 (6H)		
2b	1.21 (6H)	2.67 (2H), 3.09 (2H)	
2c		2.82 (2H), 3.31 (2H)	1.82 (2H), 2.18 (2H)
2d	0.84 (3H)	2.95 (2H)	
2e	1.79 (3H), 2.64 (3H)		
2f	0.91 (3H), 1.50 (3H)	2.35 (2H), 2.93 (1H), 3.77 (1H)	

[a] The number between parentheses corresponds to the protons area.

Table 2. ^{31}P Chemical Shifts Reported in ppm, ^2J(P, H) Values, and J(PP) Values Expressed in Hz for Compounds **2a**−**f**

complexes	$\delta(^{31}P)$	^2J(P, H)	^2J(P, P)
2a	55.88	33	
2b	55.77	33	
2c	55.80	34	
2d	58.19/53.01	30/30	31
2e	52.31/46.72	40/30	25
2f	51.98/46.71	40/31	26

Scheme 2. Formation of [3-H-3,3-$(PPh_3)_2$-8-PR_2R'-*closo*-3,1,2-$RuC_2B_9H_{10}$]



presence of a symmetry plane in the molecule, which were split into doublets in the ^{31}P NMR spectra with ^2J(P, H) ca. 30 Hz; a doublet of doublets is found for **2d**−**f** due to the nonequivalence of the two phosphorus atoms, as indicated by the ^2J(P, P), ranging 25−30 Hz (Table 2).

Synthesis and Characterization of [3-H-3,3,8-$(PPh_3)_3$-*closo*-3,1,2-$RuC_2B_9H_{10}$] and [3-H-3,3-$(PPh_3)_2$-8-PPh_2Me-*closo*-3,1,2-$RuC_2B_9H_{10}$]. Following a similar procedure as for the preparation of **2a**−**f**, the reaction of the potassium salts of [10-PPh_3-*nido*-7,8-$C_2B_9H_{10}$]$^-$ (**3a**) and [10-$PMePh_2$-*nido*-7,8-$C_2B_9H_{10}$]$^-$ (**3b**) with [$RuCl_2(PPh_3)_3$] led to the formation of complexes [3-H-3,3,8-$(PPh_3)_3$-*closo*-3,1,2-$RuC_2B_9H_{10}$] (**4a**) and [3-H-3,3-$(PPh_3)_2$-8-PPh_2Me-*closo*-3,1,2-$RuC_2B_9H_{10}$] (**4b**), respectively (see Scheme 2).

The IR spectra indicated the presence of the Ru−H bond through low-intensity bands in the region 2050−2100 cm^{-1}. The ^{1}H NMR spectra for **4a,b** confirmed the Ru−H bond by the resonance observed near −10 ppm, as a doublet of triplets (^2J(P, H) = 33 Hz, ^3J(P, H) = 11−12 Hz) (Figure 1c), the latter splitting being due to coupling to phosphorus of the phosphonium moiety, B−PPh_3. Resonances due to the two Cc−H protons are observed as a singlet around 3 ppm. The ^{31}P{^{1}H} NMR spectra of **4a**, at room temperature, has shown a singlet at 58.6 ppm, attributed to two equivalent PPh_3 ancillary ligands, and a nonbinominal quartet at 12.70 ppm due to the B−PPh_3 group (^1J(B, P) = 126 Hz). The equivalent resonances for **4b** are observed at 58.0 ppm, for PPh_3, and 2.2 ppm, for the B−PPh_2Me group (^1J(B, P) = 140 Hz). The resonances at 58.6 ppm for **4a** and 58.0 ppm for **4b** become a doublet with ^2J(P, H) = 33 Hz in the ^{31}P NMR spectra. A doublet is observed both in the ^{11}B{^{1}H} and ^{11}B NMR spectra at −5.3 ppm for **4a** and −7.6 ppm for **4b**, due to the B−P coupling.

X-ray Diffraction Studies of [3-H-3,3-$(PPh_3)_2$-8-SMe_2-*closo*-3,1,2-$RuC_2B_9H_{10}$)] (2a). Yellow crystals of **2a** crystallized from a CH_2Cl_2/hexane (1/1) solution, under nitrogen, to give yellow crystals adequate for X-ray diffraction analysis. The ORTEP[9] view of **2a**·CH_2Cl_2 is represented in Figure 2. Crystal data and selected interatomic dimensions are listed in Tables 3 and 4, respectively. The single-crystal structure analysis confirmed a Ru(II) complex in which the metal adopts a pseudooctahedral coordination, with three formal coordination sites occupied by the C_2B_3 open face, two by the PPh_3 ligands, and the remaining site by the hydride. The present coordination is similar to that observed in [3-H-3,3-$(PPh_3)_2$-*closo*-3,1,2-$RhC_2B_9H_{11}$].[10] The large P1−Ru3−P2 angle can be due to intramolecular crowding of the phosphine ligands, as is suggested by the short C···C distances observed between the C11 to C16 and the C41 to C46 rings (distance C11···C42 = 3.166(13) Å and distance C16···C42 = 3.236(16) Å). The distance from Ru3 to the open face of C_2B_9, defined as the mean plane of C1, C2, B4, B7, and B8, is 1.735(5) Å, with coordination distances

(9) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(10) Hardy, G. E.; Callahan, K. P.; Strouse C. E.; Hawthorne, M. F. *Acta Crystallogr.* **1976**, *B32*, 264.

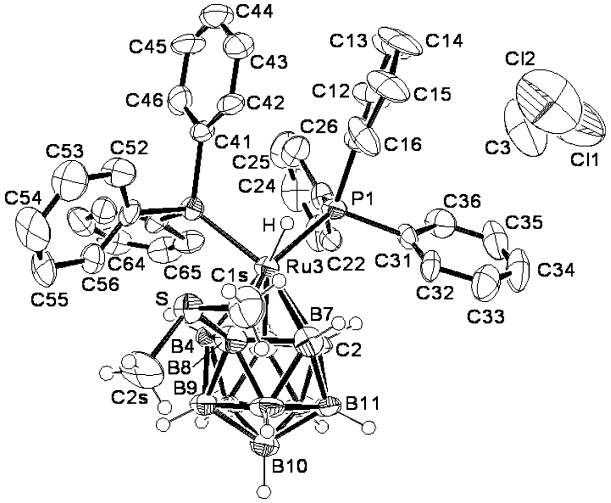


Figure 2. Simplified drawing for **2a**·CH_2Cl_2. Phenyl hydrogen atoms are omitted for clarity. Thermal displacement ellipsoids are drawn at the 50% probability level.

Table 3. Crystallographic Data for **2a**·CH_2Cl_2 and **4a**

	2a	4a
chem formula	$C_{41}H_{49}B_9Cl_2P_2RuS$	$C_{56}H_{56}B_9P_3Ru$
fw	905.06	1020.28
T (K)	293(2)	293(2)
λ(Mo Kα) (Å)	0.710 73	0.710 73
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	11.483(4)	11.632(2)
b (Å)	12.888(2)	11.523(3)
c (Å)	15.220(12)	38.514(4)
α (deg)	97.31(3)	90
β (deg)	97.65(4)	92.76(1)
γ (deg)	100.65(2)	90
V (Å^3)	2167(2)	5156.3
Z	2	4
cryst size (mm^3)	0.80 × 0.39 × 0.07	0.50 × 0.19 × 0.10
abs coeff (mm^{-1})	0.638	0.435
reflcns collcd	9123	15 413
indpndt reflcns	8721	15 209
R_{int}	0.066	0.0612
θ_{max} (deg)	26.24	30.41
GoF	0.96	0.978
R1 ($I > 2\sigma(I)$)	0.082	0.0852
wR2 (all data)	0.232	0.227
largest diff peak and hole (e Å^{-3})	1.542 and −1.588	2.073 and −2.434

Table 4. Selected Interatomic Distances (Å) and Angles (deg) (Esd's in Parentheses) for **2a**·CH_2Cl_2

C(1)−C(2)	1.587(14)	Ru(3)−P(1)	2.321(3)
Ru(3)−B(4)	2.203(11)	Ru(3)−P(2)	2.298(3)
Ru(3)-C(2)	2.234(9)	Ru(3)−S	3.435(3)
Ru(3)−B(8)	2.239(13)	C11···C42	3.166(13)
Ru(3)−B(7)	2.304(12)	C16···C42	3.236(16)
Ru(3)−C(1)	2.307(10)		
P(2)−Ru(3)−P(1)	96.12(10)	C(2)−Ru(3)−P(1)	91.5(3)
P(2)−Ru(3)−C(1)	111.3(3)	B(4)−B(8)−S	126.9(8)
C(2)−Ru(3)−P(2)	152.0(3)	B(7)−B(8)−S	119.4(8)
C(2)−Ru(3)−C(1)	40.9(4)	B4−B8−S−S(lone pair)	−36.8(1.5)
C(1)−Ru(3)−P(1)	106.2(2)		

to these atoms ranging from 2.203(11) to 2.307(10) Å. These distances are larger than those observed in rhutenium metallacarboranes with pentamethylcyclopentadienyl[7c] instead of phosphine ligands. The τ parameter,[3c] which, in this case, represents the torsion angle B4−B8−S−S(lone pair), is −36.8(1.5)°. This large value and the fact that the B4−B8−S angle is larger than B7−B8−S suggest that the

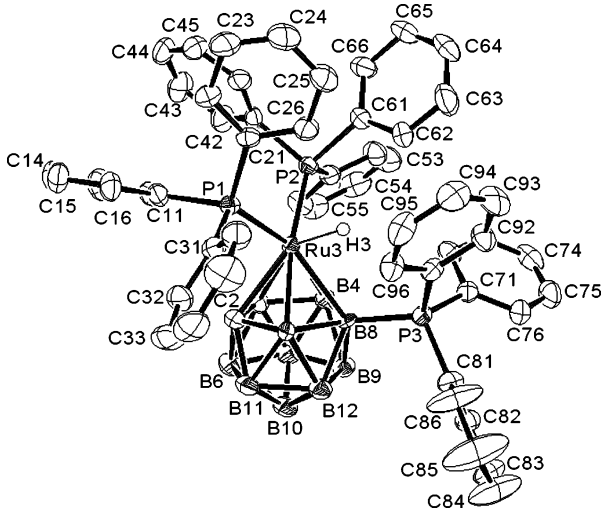


Figure 3. Simplified drawing for **4a**. Phenyl hydrogen atoms are omitted for clarity. Thermal displacement ellipsoids are drawn at the 50% probability level.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) (Esd's in Parentheses) for **4a**

C(1)−C(2)	1.570(7)	B(8)−P(3)	1.942(5)
C(1)−Ru(3)	2.318(4)	B(8)−Ru(3)	2.312(4)
C(2)−Ru(3)	2.285(4)	P(1)−Ru(3)	2.3146(12)
B(4)−Ru(3)	2.293(5)	P(2)−Ru(3)	2.3360(13)
B(7)−Ru(3)	2.288(5)		
C(2)−C(1)−Ru(3)	68.9(2)	C(2)−Ru(3)−P(2)	138.61(13)
B(6)−C(1)−Ru(3)	128.9(4)	P(1)−Ru(3)−P(2)	95.26(4)
B(7)−C(2)−Ru(3)	67.9(2)	C(1)−Ru(3)−P(2)	105.01(14)
C(2)−Ru(3)−P(1)	90.25(14)	B(7)−B(8)−P(3)	124.7(3)
C(2)−Ru(3)−C(1)	39.87(19)	B(4)−B(8)−P(3)	126.6(3)
P(1)−Ru(3)−C(1)	119.59(14)	B(9)−B(8)−P(3)	111.2(3)

interaction S(lone pair)···H4 is not dominating of the sulfonium group conformation. Like in the case of [3-(Cp*)-4-SMe_2-*closo*-3,1,2-$RuC_2B_9H_{10}$] and similar compounds,[7c] this conformation can be explained by steric repulsion between the SMe_2 hydrogen and the phosphine groups of the neighbor molecule, as there are two short H···H distances observed between the hydrogens of these groups: distance H1C···H25(1 + x, y, z) of 2.423 Å and distance H2A···H64(1+ x, y, z) of 2.424 Å.

X-ray Diffraction Studies of [3-H-3,3,8-(PPh_3)$_3$-*closo*-3,1,2-$RuC_2B_9H_{10}$)] (4a). Crystals of **4a** suitable for a single-crystal X-ray study were obtained by slow evaporation of a CH_2Cl_2/hexane/PPh_3 solution of the complex. A drawing of the compound may be seen in Figure 3, with crystal data and selected interatomic dimensions being listed in Tables 3 and 5, respectively. Compound **4a** is revealed to be a *closo*-ruthenacarborane in which a PPh_3 group is bonded to the B(8) atom of the upper face and the other two PPh_3 ligands are coordinated to Ru(II) placed on the C_2B_3 open face, in a way similar to that observed in complex **2a**. However, in complex **4a** the distance from Ru3 to the open face of C_2B_9, 1.777(2) Å, is longer to that found in **2a** (1.735(5) Å); in the same way the distances of Ru3 to the open face atoms C1, C2, B4, B7, and B8 are found in the ranging between 2.285(4) and 2.318(4) Å and are slightly longer than those observed in complex **2a**. In the latter, the distance Ru3−B8 is 2.239(13) Å, shorter than that for **4a** (2.312(4) Å), probably due to the presence of a less crowded sulfonium substituent,

instead of the phosphonium one. In both complexes, **2a** and **4a**, the large P1−Ru(3)−P2 angle, 96.12(10) and 95.26(4)°, respectively, and the short C···C distances between different rings have been found (C21···C46 = 3.157(7), C22···C16 = 3.266(8), C52···C66 = 3.157(9), C46···C46 = 3.182(9) Å) which evidence again the intramolecular crowding of the phenyl groups in the PPh_3 ligands. In complex **4a** the angles B4−B8−P3 and B7−B8−P3 are very close, while the angle Ru3−B8−P3 is longer than Ru3−B8−S in **2a**, suggesting a larger steric repulsion between the phosphonium group and the PPh_3 ligands. This repulsion may be clearly observed in the crystal structure, because the orientation of PPh_3 groups coordinated to the metal with respect to the substituent on the B(8) is different for both complexes; in **4a** the PPh_3 groups are situated as far as possible from the phosphonium group.

Discussion

To synthesize Ru(II) complexes of [10-L-*nido*-7-R-7,8-$C_2B_9H_{10}]^-$ ligands, preliminary studies of the reaction of $[RuCl_2(PPh_3)_3]$ with **1a** were done using a 1/1/1 ratio of **1a**/K[*t*-BuO]/Ru(II). The K[*t*-BuO] in EtOH removes the open face proton forming the partially charge-compensated monoanionic carborane ligand [10-SMe_2-*nido*-7,8-$C_2B_9H_{10}]^-$ that reacts with $[RuCl_2(PPh_3)_3]$. Pure **2a** is obtained in 70% yield by extraction with ethyl acetate. An improved procedure consists of increasing the ratio ligand/K[*t*-BuO]/$[RuCl_2(PPh_3)_3]$ to 1.5/1.5/1. In this way, complexes **2a**−**f** were obtained as pure solids after 30 min of reaction, in very good yield (≅90%). The excess of ligand might be recovered from the filtered solution in the neutral form, by protonation and extraction in organic solvents.

The room-temperature $^{31}P\{^1H\}$ NMR of all symmetric complexes (**2a**−**c** and **4a**,**b**) has shown the equivalency of both ancillary PPh_3 ligands, which is in agreement with the existence of a mirror plane in the molecule. A $^{31}P\{^1H\}$ NMR dynamic study for **2a**−**c** and **4a**,**b** was carried out so as to investigate the rotational behavior of these complexes. Interestingly, the $^{31}P\{^1H\}$ NMR spectra for compounds **2a**−**c** were invariant from 25 to −95 °C indicating very low rotational barriers. A similar behavior was observed in [3-H-3,3-$(PPh_3)_2$-*closo*-3,1,2-$MC_2B_9H_{11}$)] (M = Rh, Ir).[5c] The equivalence of the two phosphine ligands was removed for compounds **4a**,**b** in lowering temperature (see Figure 4). A transition from an A_2 spin system to an AB spin system was observed. If the $^{31}P\{^1H\}$ NMR spectra of **4a** at room temperature is considered, only a singlet at 58.6 ppm is found. Near −60 °C the decoalescence of this resonance takes place and two different phosphorus resonances (two doublets with a $^2J(P, P) = 38$ Hz) were clearly observed at −95 ± 2 °C. Complexes **4a**,**b** showed a dynamic behavior at low temperature, from which the activation energies was calculated. The $\Delta G^{\ddagger}$ values obtained for complexes **4a**,**b** were 8.9 ± 0.2 and 8.3 ± 0.2 kcal/mol, respectively. These values are in the range of $\Delta G^{\ddagger}$ values calculated for reported phosphinometallacarboranes.[5c] This dynamic process is due to a rotation of the metal fragment {HP_2Ru} upon the open C_2B_3 face of the cage, which breaks down at low temperature.

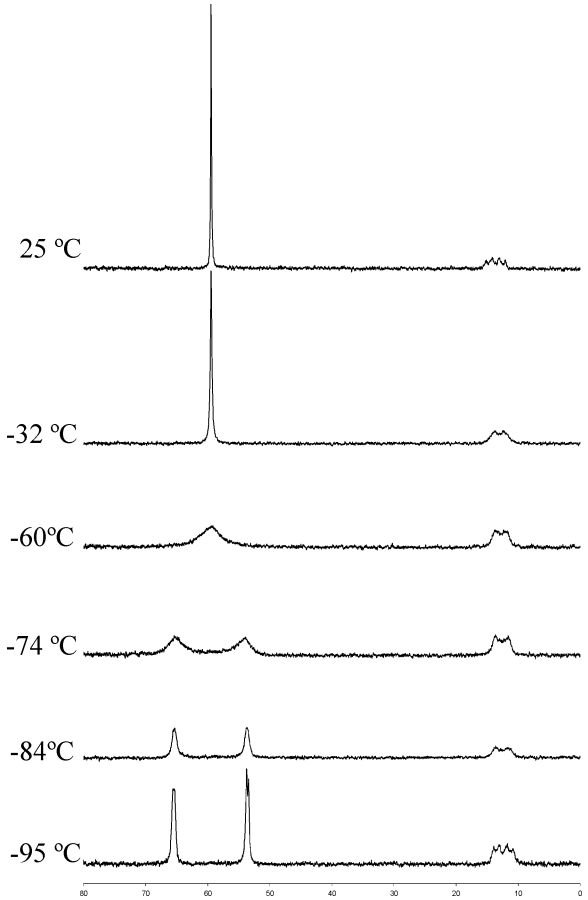


Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex **4a**.

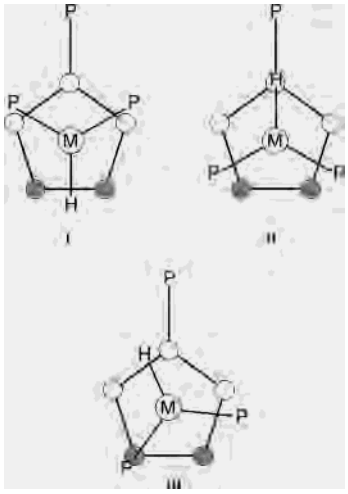


Figure 5. Possible conformational isomers I−III for **4a,b**, depending on the temperature.

Therefore, it is important to remark that even though both complexes **4a**,**b** are symmetrical molecules, the AB spin system at low temperature implies the absence of a mirror plane bisecting both the carborane ligand and the metal fragment. This unusual feature can be rationalized in terms of conformational isomers (see Figure 5). The NMR data could indicate that (i) all three conformations coexist at room temperature due to the continuous fast rotation of the {HP_2Ru} fragment, which gives an average signal in the ^{31}P spectrum, or (ii) rotamer I is disfavored due to the steric

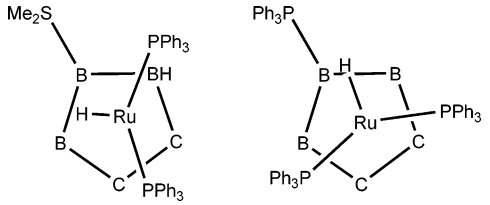


Figure 6. Conformational disposition of $\{HP_2Ru\}$ moieties with respect to pentagonal η^5-π-bonding C_2B_3 face in **2a** and **4a**, respectively, from X-ray data.

hindrance between PRR'_2 group and $\{HP_2Ru\}$ fragment that librates between mirror images of III passing through II. However, rotamer III, for which two phosphorus resonances have to be observed, is favored at low temperature for complexes **4a**,**b**.[5c] The fact that the two phosphine groups nonequivalence is not observed for complexes **2a**−**c** with sulfonium group is a clear consequence of the larger steric hindrance for the moiety PRR'_2 versus SR^1R^2. Figure 6 shows the actual disposition of $\{HP_2Ru\}$ moieties in solid state, according to X-ray diffraction. The conformation of complex **2a** is reminiscent of rotamer III; however, complex **4a** is better described as rotamer II. The difference in solid state and solution may originate in the crystal packing forces.

The characterization of the ruthenacarborane complexes unambiguously indicated that a hydride ligand was present in the molecule. This was unexpected since the starting Ru(II) complex contained chloride ligands and the bridging B−H−B had been removed on purpose. However, it is known that some chloride Ru systems are converted into hydride or deuteride in alcoholic solutions in the presence of a base.[11,12] For instance, $[RuCpClL_2]$ and $[RuCp^*ClL_2]$ are easily converted into $[RuCp(D)L_2]$ and $[RuCp^*(D)L_2]$, in methanol-d_4/sodium methoxide-d_3 at reflux and at room temperature, respectively. The latter occurs at room temperature, apparently due to the better electron-donating properties of Cp* vs Cp.[11] The monoanionic charge-compensated carboranes are also electron-donating ligands, although less than the Cp* and Cp, as has been demonstrated by the CO stretching frequencies[4f] and $E_{1/2}$ values[13] of related complexes. Thus, tentatively, we propose the formation of an initial species containing a Cl^- ligand that quickly reacts under mild conditions to give the corresponding hydride complex. The reaction is fast, which prevented the isolation of the chloride species.

Attempts to prepare the chloride complex by reaction of $[10\text{-L-}nido\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and $[RuCl_2(PPh_3)_3]$ avoiding alcohol were unsuccessful. This proves that the latter is necessary for the complexation to occur although $[3\text{-H-}3,3\text{-}(PPh_3)_2\text{-}8\text{-L-}closo\text{-}3,1,2\text{-}RuC_2B_9H_{10}]$ is ultimately formed. Generation of $[3\text{-Cl-}3,3\text{-}(PPh_3)_2\text{-}8\text{-}SMe_2\text{-}closo\text{-}3,1,2\text{-}RuC_2B_9H_{10}]$ (**5**) was achieved by addition of CCl_4 to a $CDCl_3$ solution of $[3\text{-H-}3,3\text{-}(PPh_3)_2\text{-}8\text{-}SMe_2\text{-}closo\text{-}3,1,2\text{-}RuC_2B_9H_{10}]$ (**2a**). Formation of (**5**) was evidenced by the vanishing of the Ru−H resonance in the ^1H NMR spectrum and the formation of a broad new resonance at 26.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum instead of the earliest narrow resonance at 58.6 ppm for **2a**. The broadness of the signal at 26.3 ppm suggests a fast exchange between different rotamers. A dynamic $^{31}P\{^1H\}$ NMR study down to −20 °C has shown that the original resonance at 26.3 ppm splits into two doublets centered at $\delta = 28.9$ and 24.5 ppm with $^2J(P,P) = 45$ Hz (Figure 7). The resonance decoalesces at 18 ± 2 °C producing a calculated $\Delta G^{\ddagger} = 12.8 \pm 0.2$ kcal/mol. The nonequivalency of the two phosphorus in **5** at 18 °C implies that rotamer III in Figure 5 (Cl instead of H) is the most stable. This is also the most stable for **2a** in the solid state; however, the small volume of H does not prevent fast exchange even at −95 °C.

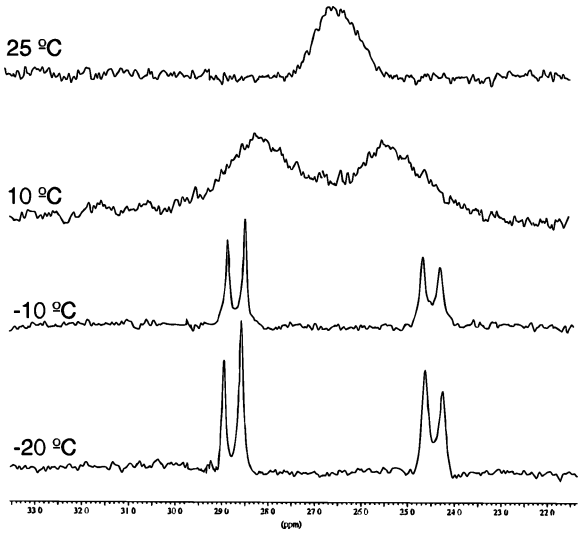


Figure 7. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex **5**.

All these ruthenium complexes have been already tested as catalytic precursors in radical reactions such as Kharasch addition of CCl_4 to olefins and cyclopropanation, where they have shown to be very efficient catalysts.[8]

Conclusion

These results demonstrate the preparation of ruthenacarborane complexes from $7\text{-R-}10\text{-L-}nido\text{-}7,8\text{-}C_2B_9H_{11}$ charge-compensated ligands, through a very simple one-pot reaction of the ligands with $[RuCl_2(PPh_3)_3]$ after deprotonation with K[*t*-BuO]. The new *closo* complexes were shown, after full characterization, to possess two PPh_3 groups and a hydride ligand in their molecule.

Experimental Section

General Comments. Unless otherwise noted, all manipulations were carried out under a dinitrogen atmosphere using standard vacuum line techniques. Solvents were purified by distillation from appropriate drying agents before use. Deuterated solvents for NMR (Fluorochem) were freeze−pump−thawed three times under N_2 and transferred to the NMR tube using standard vacuum line techniques.

(11) (a) Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1278. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

(12) (a) Aranyos, A.; Csjernyik, G.; Szabó, K. J.; Bäcjvall, J.-E. *Chem. Commun.* **1999**, 351 and references therein. (b) van der Schaaf, P. A.; Kolly, R.; Hafner, A. *Chem Commun*. **2000**, 1045.

(13) We have recently found that $E_{1/2}$ potential values of sandwich $[M(10\text{-}SMe_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10})_2]^{n+}$ complexes (M = Ru, Co, Fe, Ni; $n = 0$, 1) are more anodic than the respectively ones of Cp. Unpublished results.

The reagents **1a**−**c**,[4e] **1d**−**f**,[4c] **3a**,[5d] **3b**,[14] and $[RuCl_2(PPh_3)_3]$[15] were prepared according to literature methods. Microanalyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded with KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR (300.13 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz), ^{11}B and $^{11}B\{^1H\}$ NMR (96.29 MHz), ^{31}P and $^{31}P\{^1H\}$ NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories at room temperature. All NMR measurements were performed in deuterated solvents at 22 °C. Chemical shift data for ^{1}H and $^{13}C\{^1H\}$ NMR spectra were referenced to $SiMe_4$, those for $^{11}B\{^1H\}$ and ^{11}B NMR spectra were referenced to external $BF_3{\cdot}Et_2O$, and those for $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 (minus values upfield). Chemical shifts were reported in ppm, followed by a description of the multiplet (e.g. d = doublet), its relative intensity, and observed coupling constants (in Hz).

Synthesis of [3-H-3,3-(PPh$_3$)$_2$-8-SMe$_2$-*closo*-3,1,2-RuC$_2$B$_9$H$_{10}$] (2a). Method I. To a deoxygenated solution of ethanol (10 mL) containing **1a** (100 mg, 0.514 mmol) was added K[*t*-BuO] (58 mg, 0.514 mmol). The mixture was heated at 50 °C, and $[RuCl_2(PPh_3)_3]$ (493 mg, 0.514 mmol) was added. The mixture was stirred for 1 h at 50 °C, to observe a brown-yellow precipitant. At this point 50% more of K[*t*-BuO] was added to obtain a yellow solid after 30 min stirring. The solid was filtered off and washed with two 10 mL portions of water, 10 mL of cold ethanol, and two 10 mL portions of warm hexane. The resulted solid was treated with ethyl acetate to separate a white solid and a yellow solution. The solution was evaporated in vacuo to give a yellow solid (**2a**). Yield: 337 mg, 70% respect to the ligand.

Method II. The procedure was similar to that before using a 1.5/1 ligand/Ru(II) complex ratio: **1a** (100 mg, 0.514 mmol), K[*t*-BuO] (58 mg, 0.514 mmol), and $[RuCl_2(PPh_3)_3]$ (329 mg, 0.342 mmol). The mixture was stirred for 1 h at this temperature to form a yellow solid. The solid was filtered off and washed with two 10 mL portions of water, 10 mL of cold ethanol, and two 10 mL portions of warm hexane. Finally, the solid was dried in vacuo. Compound **2a** was obtained as a yellow solid (252 mg, 90% with respect to the metal). Anal. Calcd for $C_{40}H_{47}B_9P_2SRu$: C, 58.58; H, 5.77; S, 3.91. Found: C, 58.16; H, 5.50; S, 3. 70. IR (KBr): 2555 (B−H), 1963 cm^{-1} (Ru−H). ^{1}H NMR ($CDCl_3$): δ −10.37 [t, ^2J(P, H) = 33 Hz, 1H, Ru−H], 2.17 (s, 2H, C_c−H), 2.28 (s, 6H, S−CH_3), 6.98−7.92 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.9 (s). ^{31}P NMR ($CDCl_3$): δ 55.9 [d, ^2J(P, H) = 33 Hz]. ^{11}B NMR ($CDCl_3$): δ −2.3 (1B), −10.1 [d, ^1J(B,H) = 128 Hz, 1B], −14.2 (1B), −16.5 [d, ^1J(B, H) = 147 Hz, 3B,), −25.1(3B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.04 (s, S−CH_3), 127.25−138.67 (C_6H_5).

Synthesis of [3-H-3,3-(PPh$_3$)$_2$-8-SEt$_2$-*closo*-3,1,2-RuC$_2$B$_9$H$_{10}$] (2b). The process was the same as for compound **2a** using 100 mg (0.448 mmol) of **1b**, 50 mg (0.448 mmol) of K[*t*-BuO], and 286 mg (0.299 mmol) of $[RuCl_2(PPh_3)_3]$ in 10 mL of deoxygenated ethanol (method II). The mixture was stirred for 1 h at 50 °C obtaining yellow suspension. The solid was filtered out and washed as described above to give **2b** (238 mg, 94%). Anal. Calcd for $C_{42}H_{51}B_9P_2SRu$: C, 59.47; H, 6.06; S, 3.78. Found: C, 59.02; H, 5.84; S, 3.43. IR (KBr): 2536 (B−H), 2029 cm^{-1} (Ru−H). ^{1}H NMR ($CDCl_3$): δ −10.29 [t, ^2J(P, H) = 33 Hz, 1H, Ru−H], 1.21 [t, J(H, H) = 7.4 Hz, 6H, CH_3), 2.17 (br s, 2H, C_c−H), 2.67 [dq, ^2J(H, H) = 13.4 Hz, ^3J(H, H) = 7.4 Hz, 2H, S−CH_2], 3.09 [dq, ^2J(H, H) = 13.4 Hz, ^3J(H, H) = 7.4 Hz, 2H, S−CH_2], 7.73−7.00 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.8 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.8 [d, ^2J(P, H) 33 Hz]. ^{11}B NMR ($CDCl_3$): δ 0.5 (1B), −8.0 [d, ^1J(B, H) = 132 Hz, 1B,], −11.9 (1B), −14.4 [d, ^1J(B, H) = 134 Hz, 3B,], −23.0 (3B). ^{13}C NMR ($CDCl_3$): δ 13.30 (s, CH_3), 35.90 (s, S−CH_2), 127.16−138.74 (C_6H_5).

Synthesis of [3-H-3,3-(PPh$_3$)$_2$-8-S(CH$_2$)$_4$-*closo*-3,1,2-RuC$_2$B$_9$H$_{10}$] (2c). The process was the same as for compound **2a** using 100 mg (0.452 mmol) of **1c**, 61 mg (0.452 mmol) of K[*t*-BuO], and 289 mg (0.300 mmol) of $[RuCl_2(PPh_3)_3]$ in 10 mL of deoxygenated ethanol. The mixture was stirred for 1 h at 50 °C to form a yellow solid. The solid was filtered out and washed as described above to give **2c** (230 mg, 91%). Anal. Calcd for $C_{42}H_{49}B_9P_2SRu$: C, 59.61; H, 5.84; S, 3.79. Found: C, 58.83; H, 5.77; S, 3.61. IR (KBr): 2576, 2551, 2522 (B−H), 2052 cm^{-1} (Ru−H). ^{1}H NMR ($CDCl_3$): δ −10.29 [t, ^2J(P, H) = 34 Hz, 1H, Ru−H], 1.82 (m, 2H, CH_2), 2.18 (m, 2H, CH_2), 2.21 (br s, 2H, C_c−H), 2.82 (m, 2H, S−CH_2), 3.31 (m, 2H, S−CH_2), 7.00−7.73 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.8 (s). ^{31}P NMR ($CDCl_3$): δ 55.8 [d, ^2J(P, H) = 34 Hz]. ^{11}B NMR ($CDCl_3$): δ −1.5 (1B), −9.3 [d, ^1J(B, H) =129 Hz, 1B], −14.1 (1B), −16.1 [d, ^1J(B, H) = 126 Hz, 3B), −25.1 (3B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.30 (s, CH_2), 44.25 (s, S−CH_2), 127.16−138.72 (C_6H_5).

Synthesis of [3-H-3,3-(PPh$_3$)$_2$-8-SEtPh-*closo*-3,1,2-RuC$_2$B$_9$H$_{10}$] (2d). The process was the same as for compound **2a** using 100 mg (0.369 mmol) of **1d**, 41 mg (0.369 mmol) of K[*t*-BuO], and 236 mg (0.246 mmol) of $[RuCl_2(PPh_3)_3]$ in 10 mL of deoxygenated ethanol. The mixture was stirred for 1 h at 50 °C to obtain a yellow solid. The solid was filtered out and washed as described above to give **2d** (194 mg, 88%). Anal. Calcd for $C_{46}H_{51}B_9P_2SRu$: C, 61.66; H, 5.69; S, 3.57. Found: C, 61.12; H, 5.54; S, 3.60. IR (KBr): 2576, 2524 (B−H), 2064 cm^{-1} (Ru−H). ^{1}H NMR ($CDCl_3$): δ −10.38 [dd, ^2J(P, H) = 30.5 Hz, ^2J(P, H) = 30.4 Hz, 1H, Ru−H], 0.84 [t, ^3J(H, H) = 7.4 Hz, 3H, CH_3], 2.56 (s, 1H, C_c−H), 1.75 (s, 1H, C_c−H), 2.95 (m, 2H, S−CH_2), 6.98−7.77 (m, 35H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.2 [d, ^2J(P, P) 31 Hz], 53.0 [d, ^2J(P, P) 31 Hz]. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 0.02 (1B), −9.8 (1B), −12.2 (3B), −21.1(3B), −26.2 (1B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.93 (s, CH_3), 38.15 (s, S−CH_2), 127.70−139.90 (C_6H_5).

Synthesis of [1-Me-3-H-3,3-(PPh$_3$)$_2$-8-SMe$_2$-*closo*-3,1,2-RuC$_2$B$_9$H$_9$] (2e). The process was the same as for compound **2a** using 100 mg (0.479 mmol) of **1e**, 54 mg (0.479 mmol) of K[*t*-BuO], and 306 mg (0.320 mmol) of $[RuCl_2(PPh_3)_3]$ in 10 mL of deoxygenated ethanol. The mixture was stirred for 1 h at 50 °C to give orange solid. The solid was filtered out and washed as described above to give **2e** (227 mg, 85%). Anal. Calcd for $C_{41}H_{49}B_9P_2SRu$: C, 59.05; H, 5.88; S, 3.84. Found: C, 59.80; H, 5.54; S, 3.60. IR (KBr): 2551, 2517 (B−H), 2029 cm^{-1} (Ru−H). ^{1}H NMR ($CDCl_3$): δ −12.16 [dd, ^2J(P, H) = 40 Hz, ^2J(P, H) = 30 Hz, 1H, Ru−H], 1.79 (s, 3H, S−CH_3), 2.00 (br s, 1H, C_c-H), 2.21 (s, 3H, Cc-CH_3), 2.64 (s, 3H, S−CH_3), 7.00−7.73 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 52.3 [d, ^2J(P, P) = 25 Hz], 46.7 [d, ^2J(P, P) = 25 Hz]. ^{11}B NMR ($CDCl_3$): δ −1.5 (1B), −10.5 (2B), −13.2 [d, ^1J(B, H) = 141 Hz, 1B], −16.3 (3B), −19.7 [d, ^1J(B, H) = 126 Hz, 1B], −26.1 (1B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.86 (s, C_c−CH_3), 28.53 (s, S−CH_3), 127.86−140.03 (C_6H_5).

Synthesis of [1-Me-3-H-3,3-(PPh$_3$)$_2$-8-SEt$_2$-*closo*-3,1,2-RuC$_2$B$_9$H$_9$] (2f). The process was the same as for compound **2a** using 100 mg (0.423 mmol) of **1f**, 48 mg (0.423 mmol) of K[*t*-BuO], and 270 mg (0.282 mmol) of $[RuCl_2(PPh_3)_3]$ in 10 mL of

(14) Zakharkin, L. I.; Ol'shevskaya, V. A.; Zhigareva, G. G.; Antonovich, V. A.; Petrovskii, P. V.; Yanovskii, A. I.; Polyakov, A. V.; Struchkov, Yu. T. *Metalloorg. Khim.* **1989**, *2*, 1274.

(15) (a) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *XII*, 237. (*b*) Chappel, S. D.; Hamilton, D. J.; Galeas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1982**, 1867.

deoxygenated ethanol. The mixture was stirred for 1 h at 50 °C to obtain a orange solid. The solid was filtered out and washed as described above to give **2f** (214 mg, 88%). Anal. Calcd for $C_{43}H_{53}B_9SP_2Ru$: C, 59.91; H, 6.15; S, 3.72. Found: C, 60.11; H, 5.94; S, 3.77. IR (KBr): 2557, 2522 (B−H), 2042 cm^{-1} (Ru−H). ^1H NMR ($CDCl_3$): δ −12.04 [dd, ^2J(P, H) = 40 Hz, ^2J(P, H) = 31 Hz, 1H, Ru−H], 0.91 [t, ^3J(H, H) = 7.4 Hz, 3H, CH_3], 1.50 [t, ^3J(H, H) = 7.4 Hz, 3H, CH_3], 2.01 (br s, 1H, C_c−H), 2.23 (s, 3H, C_c−CH_3), 2.35 (m, 2H, S−CH_2), 2.93 [dq, ^2J(H, H) = 13.4 Hz, ^3J(H, H) = 7.4 Hz, 1H, S−CH_2], 3.77 [dq, ^2J(H, H) = 13.4 Hz, ^3J(H, H) = 7.4 Hz, 1H, S−CH_2], 7.00−7.73 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 52.0 [d, ^2J(P, P) = 26 Hz], 46.7 [d, ^2J(P, P) = 26 Hz]. ^{11}B NMR ($CDCl_3$): δ −1.5 (1B), −10.4(2B), −12.8 (1B), −16.7 (3B), −20.4 [d, ^1J(B, H) = 136 Hz, 1B], −26.1 (1B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.74 (s, CH_3), 22.42 (s, C_c−CH_3), 34.23 (s, S−CH_2), 127.85−139.72 (C_6H_5).

Synthesis of [3-H-3,3,8-(PPh_3)$_3$-*closo*-3,1,2-$RuC_2B_9H_{10}$] (4a). The process was the same as for compound **2a** using 204 mg (0.516 mmol) of **3a**, 64 mg (0.516 mmol) of K[*t*-BuO], and 330 mg (0.344 mmol) of [$RuCl_2(PPh_3)_3$] in 10 mL of deoxygenated ethanol (method II). The mixture was stirred for 2 days at 50 °C obtaining a yellow suspension. The solid was filtered out and washed as described above to give **4a** (333 mg, 95%). Anal. Calcd for $C_{56}H_{56}B_9P_3Ru$: C, 65.92; H, 5.53. Found: C, 65.78; H, 5.73. IR (KBr): 2543, 2575 (B−H), 2102 cm^{-1} (Ru−H). ^1H NMR ($CDCl_3$): δ −9.61 [dt, ^2J(P, H) = 33 Hz, ^3J(P, H) = 12 Hz, 1H, Ru−H], 3.17 (br, 2H, C_c−H), 6.91−7.36 (m, 45H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.6 (s), 12.7 [tp, ^1J(P, B) = 126 Hz]. ^{31}P NMR (CD_2Cl_2): δ 58.6 [d, ^2J(P, H) = 33 Hz], 12.7 [br tp, ^1J(P, B) = 126 Hz]. ^{11}B NMR (CD_2Cl_2): δ −5.3 [d, ^1J(P, B) = 126 Hz], −9.3, −14.9, −20.9, −25.5.

Synthesis of [3-H-3,3-(PPh_3)$_2$-8-PPh_2Me-*closo*-3,1,2-$RuC_2B_9H_{10}$] (4b). The process was the same as for compound **4a** using 50 mg (0.150 mmol) of **3b**, 18 mg (0.169 mmol) of K[*t*-BuO], and 96 mg (0.100 mmol) of [$RuCl_2(PPh_3)_3$] in 10 mL of deoxygenated ethanol. The mixture was stirred overnight at 50 °C to give a yellow solid which was filtered out and washed as described above to give **4b** (85 mg, 89%). Anal. Calcd for $C_{51}H_{54}B_9P_3Ru$: C, 63.92; H, 5.68. Found: C, 63.34; H, 5.66. IR (KBr): 2543 (B−H), 2056 cm^{-1} (Ru−H). ^1H NMR (CD_2Cl_2): δ −9.97 [dt, ^2J(P, H) = 33 Hz, ^3J(P, H) = 11 Hz, 1H, Ru−H], 1.39 [d, ^3J (P, H) = 11 Hz, 3H, CH_3], 3.14 (br, 2H, C_c−H), 6.98−7.48 (m, 40H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.0 (s), 2.2 [tp, ^1J(P, B) = 140 Hz]. ^{31}P NMR (CD_2Cl_2): δ 58.0 [d, ^2J(P, H) = 33 Hz], 2.2 [br tp, ^1J(P, B) = 140 Hz]. ^{11}B NMR (CD_2Cl_2): δ −7.6 [d, ^1J(P, B) = 140 Hz], −15.1, −21.7, −26.4.

X-ray Crystallography. Single-crystal data collection was performed on an Enraf-Nonius CAD4 diffractemeter using Mo Kα radiation. Cell parameters were from 16 reflections with $10° < \theta < 13°$ randomly searched for **2a**[8c] and 25 reflections with $11° < \theta < 13°$ for **4a**. Data were collected using $\omega/2\theta$ scans. The WinGX program[9] was used for applying Lorentz−polarization corrections. Absorption was corrected using ψ-scans[16] for **2a**. However, for **4a** this correction was not satisfactory and DIFABS[17] was finally used. For **4a** the structure was solved by direct methods using SIR2002[18] and refined by the full-matrix, least-squares method on F^2 using the SHELX97 programs.[19] All the hydrogen atoms were situated in calculated positions and refined riding on their bonded atom, except both hydride ligands, which were located in the Fourier difference maps. Non-hydrogen atoms were anisotropically refined. Isotropic thermal vibration for the hydrogen atoms was fixed to 1.2−1.5 times U_{iso} of the bonded atom. The final refinement statistics and crystallographic information are shown in Table 3. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference no. 211870.

Acknowledgment. We thank the MCyT (MAT01−1575) and Generalitat de Catalunya 2001/SGR/00337 for the partial support of this research. O.T. thanks the Ministerio de Educación, Cultura y Deporte for a grant (PN98 43734817).

IC049322K

(16) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.
(17) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(18) SIR2002: A new direct methods program for automatic solution and refinement of crystal structure. Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, C. Giocavazzo, G. L.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2003**, manuscript in preparation.
(19) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis (Release 97-2)*; University of Göttingen: Göttingen, Germany, 1997.