teracting metal centers. The oxo end of the $Ph_2P{=}O$ group has a significant effect on the π-acid ligands coordinated to the same metal atom, strengthening the bond to the trans CO group and increasing the cis metal–alkyne interaction. Such effects may presage a useful role for such ligands in modifying and directing reactivity at polynuclear sites. These results also suggest that the entire family of P(V)-derived anions, $[R_2P{=}X]^-$ (X = O, S, CR_2, NR),[15] may have an interesting organo coordination chemistry.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work.

Registry No. 1, 110096-54-3; 2, 110096-55-4; $Ph_2P(O)C{\equiv}C$-*t*-Bu, 110096-56-5; $Ru_3(CO)_{12}$, 15243-33-1; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Table S1, further details on X-day data, intensity collection, structure solution and refinement for 1 and 2, Tables S2 and S3, atomic positions (fractional $\times 10^4$), Tables S4 and S5, anisotropic thermal parameters ($\times 10^3$), Tables S6 and S7, bond lengths (Å) and angles (deg), Tables S8 and S9, hydrogen atom positions, thermal parameters, and C–H bond lengths, for 1 and 2 (13 pages); Tables S10 and S11, structure factors for 1 and 2 (40 pages). Ordering information is given on any current masthead page.

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[15] Examples of formally analogous bridging ylides μ-$R_2P{=}CR_2$ have been synthesized from μ-phosphido compounds. See, e.g.: Chau, C.-N.; Yu, Y.-F.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *Organometallics* **1987**, *6*, 308. (b) Werner, H.; Zolk, R. *Organometallics* **1985**, *4*, 601.

The Unexpected Open Cluster Structure of $[1\text{-}(\eta^6\text{-}MeC_6H_4\text{-}i\text{-}Pr)\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}RuC_2B_8H_8]$

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Summary: The structure of the title compound is found to contain a quadrilateral open face which casts some doubt on the previously assumed and generally accepted closo nature of this type of polyhedral metalladicarbaborane cluster.

Polyhedral metallaboranes that do not contain other cluster heteroatoms and that have the polar nine-,[1,2] ten-,[2-4] and eleven-vertex[4,5] configurations, I–III, respectively, are of interest[6] because they contravene the simple Williams–Wade[7,8] cluster geometry and electron-counting rules; consequently there is some discussion in the literature[6,9] concerning the nature of the cluster bonding in these so-called "isocloso" species.[10] In relation to this discussion, it has hitherto been assumed that the heteroatom-containing eleven-vertex metalladicarbaborane species such as $[(C_5H_5)CoC_2B_8H_{10}]$,[11] $[(PPh_3)_2HIrC_2B_8H_{10}]$,[12] $[(C_6H_6)RuC_2B_8H_{10}]$,[13a] etc. do *not* contravene the Williams–Wade rules because (i) they have the straightforward Wadian closo counts and (ii) they are presumed to have straightforward closo deltahedral geometries that are grossly similar to III.

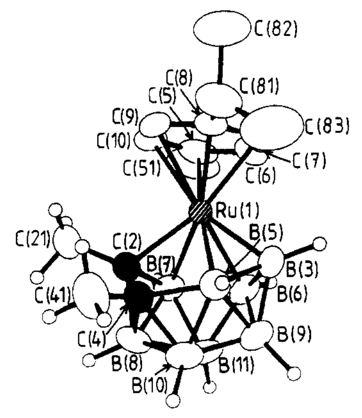
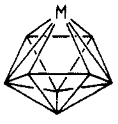
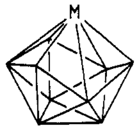


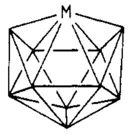
Figure 1. Crystallographically determined molecular structure of compound 1. Selected interatomic distances from Ru(1) are as follows: to C(2), 212.4 (6), to B(3), 206.5 (6), to C(4), 268.3 (7), to B(5), 236.3 (3), to B(6), 228.9 (6), and to B(7), 228.7 (6) pm. C(2)–C(4) is 148.5 (7) pm, and the dihedral angle between the aromatic $\{C_6\}$ plane and the B(5)B(6)B(7) plane is 7.35°. C(4) is 31.6 pm below the B(5)B(6)B(7) plane.



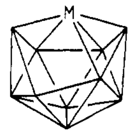
I



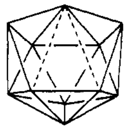
II



III



IV



V

We now report results of a single-crystal X-ray diffraction analysis on the eleven-vertex ruthenadicarbaundecaborane $[(MeC_6H_4\text{-}i\text{-}Pr)RuMe_2C_2B_8H_8]$ (compound 1) that cast serious doubt on the generality of the second of these two presumptions. This air-stable yellow compound

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[1] Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1982**, 346.

[2] Bould, J. *Metallaborane Clusters of some Platinum Metals*, Ph.D. Thesis, University of Leeds, 1983.

[3] Bould, J.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1982**, 465.

[4] Crook, J. E.; Elrington, M.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1985**, 2407.

[5] Elrington, M.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1398. Fowkes, H.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1985**, 517. Elrington, M.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1986**, 2277. Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; MacKinnon, P.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1987**, 442.

[6] Crook, J. E.; Elrington, M.; Greenwood, N. N.; Kennedy, J. D.; Woollins, J. D. *Polyhedron* **1984**, *3*, 901.

[7] Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210; *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67.

[8] Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792; *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[9] Nishimura, E. K. *J. Chem. Soc., Chem. Commun.* **1978**, 858. Greenwood, N. N.; Baker, R. T. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, D.C., 1983; p 346. Baker, R. T. *Inorg. Chem.* **1986**, *25*, 109. Kennedy, J. D. *Inorg. Chem.* **1986**, *25*, 111. Johnston, R. J.; Mingos, D. M. P. *Inorg. Chem.* **1986**, *25*, 3321. Greenwood, N. N. *Chem. Soc. Rev.* **1984**, *13*, 353. Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, *34*, 211.

[10] These "isocloso" geometries are generated by the capping of the open faces of adjacent-arachno geometries with a metal atom vertex (see ref 6).

[11] Evans, W. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 3063. Jones, C. J.; Francis, J. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1972**, *94*, 8391.

[12] Jung, C. W.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1980**, *102*, 3024.

[13] (a) Hanusa, T. P.; Huffman, J. C.; Curtis, T. L.; Todd, L. J. *Inorg. Chem.* **1985**, *24*, 787. (b) Hanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* **1982**, *1*, 77.

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1 is readily prepared in 30% yield by the reaction of $[(MeC_6H_4\text{-}i\text{-}Pr)RuCl_2]_2$ with the *nido*-dicarbaborane $Me_2C_2B_8H_{10}$ in the presence of tetramethylnaphthalenediamine, this route being essentially similar to that used to generate $R_2C_2B_9$ clusters from *nido*-C_2B_9 starting materials.[13b] The molecular structure of compound 1 is shown in Figure 1.[14] The η^6-C_6Me_6 analogue $[(\eta^6\text{-}C_6Me_6)RuMe_2C_2B_8H_8]$ (compound **2**) can be prepared similarly by using $[(C_6Me_6)RuCl_2]_2$,[15] but this has so far proved reluctant to crystallize in a crystallographically suitable habit. The extreme similarity to the NMR shielding parameters, however, show that compounds 1 and 2 have essentially identical geometrical and electronic structures,[16] and the reported NMR parameters for an η^6-C_6H_6 analogue (prepared by a degradative route from $[(C_6H_6)RuC_2B_9H_{11}]$)[13a] show that this last species also conforms to the same structural type.

It can be seen that there is considerable distortion of the molecular MC_2B_8 cluster structure (represented in IV) away from the idealized C_{2v} MB_{10} configuration III exhibited by "isocloso" eleven-vertex metallaboranes such as $[(\eta^5\text{-}C_5Me_5)RhB_{10}H_{10}]$.[17] The Ru(1)···C(4) distance is approaching nonbonding at 268.3 (7) pm [compared with 212.4 (6) pm for Ru(1)–C(2)], thereby generating an open quadrilateral face at Ru(1)–C(2)–C(4)–B(5), and there is also some lengthening of Ru(1)–B(5) [236.3 (6) pm] over that otherwise expected (ca. 229 pm). The anomalous open face together with the retention of the high metal-to-cluster connectivity is reminiscent of the structures about the metal in the isonido ten-vertex iridacarbaborane $[(PPh_3)(Ph_2P\overline{C_6H_4)Ir}B_8H_7C(OH)]$[18] and in the recently reported isoarachno-structured ten-vertex ruthenaborane $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}1\text{-}RuB_9H_{13}]$.[19]

It is of interest to speculate whether this eleven-vertex "isonido" configuration obtained for compound 1 arises from a localization of an electron pair in the intercarbon linkage [C(2)–C(4) = 148.5 (7) pm], and why this should be, or whether there are contributions from the higher metal valency state ruthenium(IV) which would engender contributions from a nido electron count that would be associated with four metal–borane cluster bonding orbitals. In this context it may be noted that the anomalous distortion toward nido observed for $[2,3\text{-}Me_2C_2B_8H_{10}\text{-}4,7\text{-}(OH)_2\text{-}10\text{-}Br]$ (structure V)[20] has also been attributed to additional electron density in the cluster but derived in this instance from oxygen atom π-donation into the cluster.

Acknowledgment. We thank the SERC (U.K.) for support.

Registry No. 1, 110173-48-3; 2, 110142-00-2; $[(MeC_6H_4\text{-}i\text{-}Pr)RuCl_2]_2$, 52462-29-0; *nido*-$Me_2C_2B_8H_{10}$, 31566-09-3; $[(C_6Me_6)RuCl_2]_2$, 67421-02-7.

Supplementary Material Available: Tables of crystal data, fractional atomic coordinates, thermal parameters, and interatomic distances and angles for 1 (9 pages); a listing of observed and calculated structure factors for 1 (11 pages). Ordering information is given on any current masthead page.

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(14) Crystal data: $C_{14}H_{28}B_8Ru$; M_r 393.93, orthorhombic, space group $P2_12_12_1$, a = 827.5 (1) pm b = 1066.0 (1) pm, c = 2154.4 (2) pm; U = 1.9004 nm^3; $Z = 4$; μ = 7.27 cm^{-1}; $F(000) = 784$; scan widths 2.0° + α-doublet splitting; scan speeds 2.0–29.3° min^{-1}; $4.0 < 2\theta < 50.0°$. All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the $\omega/2\theta$ scan mode by using graphite-monochromated Mo Kα radiation following a procedure described elsewhere.[21] The data set was corrected for absorption empirically.[22] The structure was solved by standard heavy-atom methods and refined by full-matrix least squares using SHELX76.[23] All non-hydrogen atoms were refined anisotropically with all carbon-attached hydrogen atoms included in calculated positions (C–H = 108 pm) and refined with an overall isotropic temperature factor. All borane hydrogen atoms were located in a Fourier map and were freely refined isotropically. The weighting scheme $w = [\sigma^2[F_0) + 0.0002(F_0)^2]^{-1}$ was used at the end of refinement. Final R and R_w values are 0.0232 and 0.0259, respectively (244 parameters, 1890 observed data).

(15) Bown, M.; Greenwood, N. N.; Kennedy, J. D. *J. Organomet. Chem.* **1986**, *309*, C67.

(16) NMR data {$\delta(^{11}B)$ [with $\delta(^1H)$ for directly attached H atoms in square brackets]}: compound 1 has BH(3) +58.4 [+7.61], BH(5) −37.2 [−2.07], BH(6) −5.2 [+1.20], BH(7) +3.5 [+2.47], BH(8) −11.9 [+1.73], BH(9) +9.6 [+3.79], BH(10) −10.8 [+1.07], and BH(11) −25.0 [+0.52]; compound 2 has BH(3) +61.5 [+7.07], BH(5) −37.3 [−2.23], BH(6) −2.1 [+1.07], BH(7) +2.8 [+2.19], BH(8) −9.9 [+1.85], BH(9) +9.1 [+3.67], BH(10) −11.0 [+0.96], and BH(11) −25.7 [+0.41] ($CDCl_3$ solution at 294 K); ^{11}B assignments by [^{11}B–^{11}B] COSY experiments together with the presumption that [$^{11}B(3)$] occurs at lowest field (ref 5 and 6) and that [^{11}B–^{11}B] COSY correlations between B atoms flanking B–C and C–C linkages are weaker. ^1H assigned to directly bound B atoms by $^1H\{^{11}B(\text{selective})\}$ experiments.

(17) Fontaine, X. L. R.; Fowkes, H.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.*, in press.

(18) Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc. Chem. Commun.* **1981**, 933.

(19) Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; MacKinnon, P. *J. Chem. Soc., Chem. Commun.* **1987**, 817.

(20) Leonowitcz, M. E.; Scholer, F. R. *Inorg. Chem.* **1980**, *19*, 122.

(21) Modinos, A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 1415.

(22) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1983**, *39*, 158.

(23) Sheldrick, G. M. SHELX 76, Program System for X-ray Structure Determination, University of Cambridge, 1976.

A Route to Heteronuclear μ-Methylene Complexes by Oxidative Addition

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Summary: A synthesis of heterobinuclear μ-methylene complexes involving oxidative addition of (chloromethyl)-metal derivatives is described, and it is shown that the metal substituent activates the carbon–chlorine bond to oxidative addition by a factor of $\geqslant 10^3$; for example, reaction of $[AuCH_2Cl(PPh_3)]$ with $[PtMe_2(2,2'\text{-}bpy)]$ (bpy = bipyridine) gave $[PtClMe_2(CH_2AuPPh_3)(bpy)]$.

We wish to report a new route to heteronuclear μ-methylene complexes and its application to the synthesis of the first such transition-metal complexes that do not contain either a metal–metal bond or an additional bridging ligand. μ-Methylene complexes are of general interest as models for catalytic intermediates,[1] and the labile homonuclear complex $[\{CpRu(CO)_2\}_2(\mu\text{-}CH_2)]$[2] appears to be the only previous example of a μ-methylene complex without a metal–metal bond or additional bridging ligand.[1,2]

Complexes **2a–c** (NN = 2,2′-bipyridine, Scheme I) were prepared in good yield by trans oxidative addition of $[Au(CH_2Cl)L]$[3] to $[PtMe_2(bpy)]$ (1)[4] and were unambiguously characterized by elemental analysis and by their ^1H

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(1) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

(2) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679.

(3) Nesmeyanov, A. N.; Perevalova, E. G.; Smyslova, E. I.; Dyadchenko, V. P.; Grandberg, K. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 2610.

(4) Chaudhury, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *84*, 105.

0276-7333/87/2306-2255$01.50/0