1 is readily prepared in 30% yield by the reaction of [(MeC$_6$H$_4$-*i*-Pr)RuCl$_2$]$_2$ with the *nido*-dicarbaborane Me$_2$C$_2$B$_8$H$_{10}$ in the presence of tetramethylnaphthalene-diamine, this route being essentially similar to that used to generate R$_2$C$_2$B$_9$ clusters from *nido*-C$_2$B$_9$ starting materials.[13b] The molecular structure of compound 1 is shown in Figure 1.[14]   The η^6-C$_6$Me$_6$ analogue [(η^6-C$_6$Me$_6$)-RuMe$_2$C$_2$B$_8$H$_8$] (compound 2) can be prepared similarly by using [(C$_6$Me$_6$)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$_6$H$_6$ analogue (prepared by a degradative route from [(C$_6$H$_6$)-RuC$_2$B$_9$H$_{11}$])[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$_2$B$_8$ cluster structure (represented in IV) away from the idealized C_{2v} MB$_{10}$ configuration III exhibited by "isocloso" eleven-vertex metallaboranes such as [(η^5-C$_5$Me$_5$)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$_2$P$\overline{C_6H_4}$)IrB$_8$H$_7$C(OH)][18] and in the recently reported isoarachno-structured ten-vertex ruthenaborane [1-(η^6-C$_6$Me$_6$)-1-RuB$_9$H$_{13}$].[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-Me$_2$C$_2$B$_8$H$_{10}$-4,7-(OH)$_2$-10-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.

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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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$_2$Cl(PPh$_3$)] with [PtMe$_2$(2,2'-bpy)] (bpy = bipyridine) gave [PtClMe$_2$(CH$_2$AuPPh$_3$)(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)$_2$}$_2$(μ-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$_2$Cl)L][3] to [PtMe$_2$(bpy)] (1)[4] and were unambiguously characterized by elemental analysis and by their ^{1}H

(14) Crystal data: C$_{14}$H$_{28}$B$_8$Ru; 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 < 2θ < 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).
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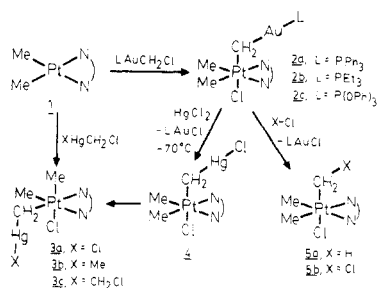
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Scheme I

and ^{31}P NMR spectra.[5] Complexes **2a** and **2b** are stable compounds, but **2c** has low thermal stability. Complex **2a** reacted rapidly and quantitatively with the electrophiles HCl, Cl$_2$, and HgCl$_2$ by selective cleavage of the Au–C bond to give [AuCl(PPh$_3$)] and **5a**, **5b**, and **3a**, respectively.[6] The reaction with HgCl$_2$ gave an intermediate (**4**) at –70 °C which was characterized by NMR and isomerized quantitatively at –10 °C to **3a**, both complexes containing the novel PtCH$_2$Hg linkage (Scheme I). In the isomer **3a**, the platinum centre is chiral and hence the μ-CH^{a}H^b protons are nonequivalent in the NMR spectrum.[5]

The PtCH$_2$Hg complexes **3a–c** could be prepared independently by oxidative addition of the appropriate (chloromethyl)mercury derivative, XHgCH$_2$Cl, to [PtMe$_2$(bpy)] (Scheme I), and in every case the CH$_2$HgX group was found only in the equatorial position.[5] It is possible that the initial oxidative addition is trans followed by rapid isomerization to **3**, but no intermediates were detected.

Oxidative addition of CH$_2$X$_2$ to bridged binuclear palladium, iridium, and gold complexes has given μ-methylene complexes, and these reactions involve intramolecular oxidative addition of MCH$_2$X units to the second metal center,[7] but complexes **2** and **3** are the first μ-methylene complexes to be formed by intermolecular oxidative addition of a (chloromethyl)metal complex. The metal has a strong activating effect on the C–Cl bond as shown by the second-order rate constants (k_2/L mol^{-1} s^{-1}) for reaction with [PtMe$_2$(bpy)] in acetone at 25 °C of 0.051 (PhCH$_2$Cl, 0.41 ([Au(CH$_2$Cl)(PPh$_3$)]), and 3.46 (Hg(CH$_2$Cl)$_2$). Since PhCH$_2$Cl reacts ~500 times faster than CH$_3$Cl in oxidative additions,[8] the activating effect is estimated to be ~4 × 10^3 for the AuPPh$_3$ substituent and ~2 × 10^4 for the HgCH$_2$Cl substituent. The kinetic order and the magnitudes of the activation parameters E_a (kJ mol^{-1}) = 32.0 and 26.5 and $\Delta S^\ddagger$ (J K^{-1} mol^{-1}) = –144 and –145, for reactions with [Au(CH$_2$Cl)(PPh$_3$)] and Hg(CH$_2$Cl)$_2$, respectively, strongly support the S$_N$2 mechanism of reaction. The observation of such a strong activating effect suggests that the synthesis of heterobinuclear μ-methylene complexes by the above method should have wider applicability.

(5) Typical NMR data (referenced to Me$_4$Si, (MeO)$_3$PO, or K$_2$PtCl$_4$, in CDCl$_3$ or CD$_2$Cl$_2$ solvent): **2a**, δ 1.25 [s, 6 H, ^2J(PtH) = 72 Hz *Me*Pt], 1.61 [d, 2 H, ^2J(PtH) = 65 Hz, ^3J(PH) = 4 Hz, μ-*CH*$_2$], 43.7 [s, ^3J(PtP) = 64 Hz, *P*Au]; **4** at –70 °C, δ 1.26 [s, 6 H, ^2J(PtH) = 68 Hz, *Me*Pt], 1.66 [s, 2 H, ^2J(PtH) = 56 Hz, ^2J(HgH) = 56 Hz, μ-*CH*$_2$], 1070 [s, ^2J(PtHg) = 2201 Hz, *Pt*]; **3c**, δ 0.48 [s, 3 H, ^2J(PtH) = 77 Hz, ^5J(HgH) = 4 Hz, *Me*Pt trans to Cl], 1.36 [s, 3 H, ^2J(PtH) = 70 Hz, *Me*Pt trans to N], 1.39 [m, ^2J(H^{a}H^b) = 11 Hz, ^2J(PtH) = 21.5 Hz, μ-*CH*^{a}H^b], 1.68 [m, ^2J(H^{a}H^b) = 11 Hz, ^2J(PtH) = 69.5 Hz, ^2J(HgH) = 48 Hz, μ-*CH*^{a}*H*^{b}], 3.14 and 3.15 [each m, ^2J(H^{a}H^b) = 11 Hz, ^4J(PtH) = 2 Hz, ^2J(HgH) = 51 Hz, HgC*H*^{a}*H*^{b}Cl], 1250 [s, ^2J(PtHg) = 1235 Hz, *Pt*].
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Ruthenium(II)-Promoted Site Selective Intramolecular Diels–Alder Syntheses of Rigid Chiral Bidentate Ligands from Phospholes

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Summary: Ruthenium(II)-promoted site selective intramolecular Diels–Alder cycloadditions of 1-phenyl-3,4-dimethylphosphole and vinylphenylphosphines or vinyl phenyl sulfoxide occur readily in high yield. These new compounds containing chiral bidentate ligands have been characterized by infrared and ^{31}P{^{1}H} NMR spectroscopy and in one case by X-ray crystallography.

Pursuing our interest[1] in the transition-metal-promoted intramolecular Diels–Alder [4 + 2] cycloadditions of phospholes, we sought to determine whether similar reactions would occur within the coordination sphere of ruthenium(II) complexes. The ruthenium(II) complexes were particularly attractive because they afford the possibility of controlling the site of reactivity and, hence, the overall stereochemistry of the products. This is possible because as we[2,3] and Mawby et al.[4] have independently shown ligand substitution reactions of *ttt*-(R$_3$P)$_2$Ru-(CO)$_2$Cl$_2$ occur regiospecifically to produce *trans-mer*-(R$_3$P)$_2$LRuCOCl$_2$ according to reaction 1.

$$(1)$$
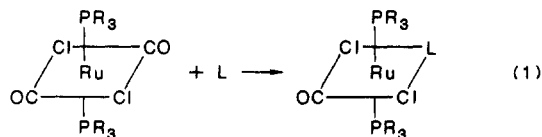
In these reactions, the entering ligand, L, occupies the site vacated by the departing carbon monoxide. It thus appeared that reaction 1 involving a ruthenium phosphole complex **1** with a vinylphosphine or a ruthenium vinylphosphine complex **2** with a phosphole should produce mixed phosphole–vinylphosphine complexes wherein these ligands would occupy mutually cis coordination positions. This appears[1] to be a necessary condition for transition-metal-promoted intramolecular [4 + 2] Diels–Alder cy-

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